

The excited states of pyrazine: A basis set study

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Summary. Multiconfigurational second order perturbation theory (CASSCF/CASPT2) has been used to investigate the dependence of computed valence excitation energies and transition moments on the basis sets. Pyrazine has been selected as the test molecule. Atomic normal orbital (ANO) type basis sets are used throughout. Contractions of the structure ($4s3p1d/2s$) are found to be an optimal compromise between the quality and the size of the calculations and are capable of yielding results virtually identical to more extended basis sets.

Key words: Pyrazine – Valence excitation energies – Transition moments – CASSCF – CASPT2

1 Introduction

The electronic spectrum of pyrazine has been the subject of extensive experimental and theoretical work [1]. In spite of all this effort, the assignments of the excited states in the low and high energy range remain incomplete and controversial. The three lowest π - π^* excited states, located at (vertical excitation energies) 4.8, 6.5, and 7.7 eV [1], are of B_{2u} , B_{1u} and ($B_{1u} + B_{2u}$) symmetry and correlate with the corresponding ${}^1B_{2u}$, ${}^1B_{1u}$ and ${}^1E_{1u}$ states in benzene. The ${}^1B_{3g}$ and 1A_g states, corresponding to the ${}^1E_{2g}$ states in benzene have not been assigned yet. Four low-lying n - π^* states can be expected of which the lowest is located at 3.8 eV (0–0 transition of B_{3u} symmetry). Bolovinos et al. [2] reported an excitation energy of 6.1 eV for the lowest state of ${}^1B_{1g}$ symmetry, and Okuzawa et al. [3] located the ${}^1B_{2g}$ state at 5.2 eV.

Recently we reported vertical excitation energies for the azabenzene [4] including pyrazine, some small polyenes [5] and other aromatic system [6–7] using a novel scheme for *ab initio* calculations of electronic spectra. The results are surprisingly accurate: The computed excitation energies of pyrazine, 4.77, 6.68, 7.57 and 7.75 eV for the states of B_{2u} and B_{1u} symmetry are within 0.17 eV of experimental data. We also confirmed the location of the ${}^1B_{1g}$ and ${}^1B_{2g}$ bands with calculated excitation energies at 6.13 and 5.17 eV, respectively. Our calculations are in fairly good agreement with the results reported by Walker and Palmer [8]. On the one hand, these authors applied electron energy loss spectroscopy, and, on the other hand, they computed the excitation energies using the MRDCI technique.

The novel approach is based on the Complete Active Space Self-Consistent Field (CASSCF) method [9], which has proven to properly describe the electronic structure of the excited state, independent of its complexity, and accounts for all near degeneracy effects. The remaining dynamic correlation effects are in a subsequent step added using second-order perturbation theory [10, 11], called the CASPT2 method, with as CASSCF wavefunction as the reference state. The CASPT2 equations are formulated exclusively in terms of one-, two- and three-body density matrices and are therefore independent on the actual number of configuration state function included in the reference space. The limiting factor is the number of active orbitals which determine the size of the density matrices. On the one hand, the CASPT2 method thus allows to use basis sets big enough to avoid contamination of the results due to basis set deficiencies. On the other hand, provided reasonable small basis sets can be applied, the range of the applicability of the CASPT2 method is much larger than for any method of comparable accuracy.

The aim of the present calculations is to study the dependence of the computed valence excitation energies and transition moments on the basis sets. In particular, we are seeking for the smallest basis sets to be used in studies on more extended molecular systems. Generally contracted basis sets of atomic natural orbital (ANO) type [12] are used throughout and are contracted to various levels of approximation. These basis sets are constructed to optimally treat correlation and polarization effects and should thus describe the valence states with good accuracy. Diffuse functions are, however, missing and we cannot expect to be able to treat Rydberg states with high precision. Therefore, we preferred to neglect interactions with Rydberg states by modifying the molecular orbital set. Rydberg states have been successfully included in some of the earlier applications by adding diffuse functions to the ANO basis sets [5, 7]. A general technique to describe Rydberg states in CASPT2 calculations will be discussed in a forthcoming paper [13].

In the following, details concerning the approach and the basis sets are given. In Sect. 3 the results are presented and discussed. Finally Sect. 4 contains a summary and some concluding remarks.

2 Methods and computational details

2.1 Geometries and basis sets

The geometry used in the present calculations are taken from experiment [14]. The molecule is placed in the yz -plane with the z -axis passing through the N atoms. Generally contracted basis sets of ANO type are used. The primitive sets, (14s, 9p, 4d) and (8s, 4p) for the first row atoms and hydrogen, respectively, are contracted to the following final structure: (C, N; 3s2p) and (H; 2s). Larger basis set are build by progressively increasing the number of contracted functions. Although the primitive sets are rather large we abandoned from selecting smaller sets for reasons of comparison with our previous results.

The basis sets used are constructed to optimally treat correlation and polarization effects and should be large enough to describe the electronic structure of the valence excited states. Diffuse functions are, however, missing in the basis set and we cannot expect to be able to treat Rydberg states with high precision. Since we are seeking for basis sets to describe valence excited states of extended molecular systems, the calculation have been simplified by deleting the corresponding diffuse orbital from the molecular orbital (MO) space. A possible real interaction between

Rydberg and valence excited states has, as a consequence, been neglected. This procedure has been tested previously [4, 7, 13] and it has been shown that interaction of Rydberg states and the valences excited states are generally of minor importance.

2.2 The CASSCF and the CASSI methods

Initially, multiconfigurational wavefunctions are determined at the CASSCF level of approximation. In the study of the benzene molecule [6] it was found that it is preferable to use large active spaces to avoid contamination of the CASPT2 results due to interference with nearby Rydberg states. Therefore, to compute the π - π^* singly excited states 12 π -orbitals ($4b_{3u}$, $2b_{1g}$, $4b_{2g}$, $2a_u$) are included in the active space. To determine the n - π^* singly excited states the lone pair orbitals are also included in the active space. Interference with Rydberg states was less common for the n - π^* excited states and the corresponding active space for the π -orbitals could be kept smaller. Our final choice is ($2a_g$, $2b_{1u}$, $2b_{3u}$, $1b_{1g}$, $2b_{2g}$, $1a_u$). The wavefunctions have been optimized for each state individually and the 1s core orbitals have been kept frozen at the HF-SCF level of approximation.

The wavefunctions obtained by optimizing individual state functions are, unless restricted by symmetry, not mutually orthogonal. The CASSCF state interaction (CASSI) method [15] has been developed to compute transition properties from non-orthogonal state functions and is used here to compute the oscillator strength. In the formula for the oscillator strength we used energy differences corrected for by the second order perturbation method.

2.3 The CASPT2 method

The CASPT2 method computes the first order wavefunction and the second order energy in the full CI space without any further approximation, with a CASSCF wavefunction 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 are possible: one which utilizes only the diagonal part of the Fock matrix (PT2D) and one which includes also the off-diagonal elements (PT2F). The first choice is computationally simpler and leads in most cases to results not very different from the PT2F method. It should be emphasized, however, that it is only the nondiagonal approach, which is invariant to rotations of the molecular orbitals. Here we shall only present the results obtained with the PT2F approach.

The CASPT2 program also calculates the weight, ω , of the CASSCF reference in the first-order wavefunction. This weight is a measure of how large a fraction of the wavefunction is treated variationally. The relative weight of ω in different states then 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. In some cases, however, interference with nearby Rydberg states not included in the reference CI space, deteriorates this balance for some of the excited states. However, such a situation can be tolerated in cases where the interaction is very weak, and consequently the effect on the second order energy small. A large coefficient for

the interfering Rydberg state may then appear in the first order wavefunction with only a very small effect on the energy. A typical example will be discussed in the next section.

All calculations have been performed on IBM RS/6000 workstations (models 530H and 550) using the MOLCAS-2 quantum chemistry software [16], which includes as one module the CASPT2 program.

3 Results and discussion

The calculated CASSCF and PT2F energies for the different basis sets are collected in Tables 1–8 and given in the Appendix. The tables are organised such that the results for the π - π^* states are given first followed by the n - π^* states. They also include the excitation energies, the CASSCF reference weight, ω , and the oscillator strength.

3.1 Total energies

At the CASSCF level of approximation the ground- and excited state total energies differ by only ≈ 5 mH (Hartree) for the two smallest basis sets. Upon adding an additional p -type function to the basis sets of the first row atoms the energy decreases further by ≈ 30 mH. However, a dramatic energy lowering, ≈ 0.15 H, is observed when polarization functions are included in these basis sets. This effect is much less pronounced, ≈ 15 mH, for the improvement of the hydrogen atom basis functions. Further extensions of the basis sets lead to an additional correction of the CASSCF energies by ≈ 10 mH. In total, our best state energies are ≈ 0.2 H lower in energy as compared to the smallest basis sets.

A similar pattern is observed for the ground and excited state energies computed at the PT2F level of approximation. Since in this method all, except the atomic core-, electrons are correlated, the effects are larger in magnitude. The total lowering of the state energies when proceeding from the smallest to the most extended basis sets is ≈ 0.6 H. The major contributions, ≈ 0.5 and ≈ 0.1 H, are due to the addition of one set of polarization functions and an extra, correlating valence orbital to the basis sets of the first row atoms, respectively.

3.2 Excitation energies

In Fig. 1 we plotted the excitation energies computed at the CASSCF and PT2F level of approximation for the 1^1B_{2u} , 2^1B_{2u} and 1^1B_{3u} states as a function of the basis sets. From these curves it can be seen that the dependency of the computed excitation energies on the basis sets in use closely resembles the behaviour discussed above for the total state energies. The basis sets of the structure $(4s3p1d/2s)$ yield results that are virtually identical to the most extended basis sets, i.e., the excitation energies differ, in general, by less than 0.1 eV at the PT2F level of calculation. The deviations are somewhat bigger, ≈ 0.15 eV, for the ionic states 2^1B_{2u} and 2^1B_{1u} corresponding to the E_{1u} state in benzene. Considering, however, that the positioning of these absorption lines are strongly affected by dynamic correlation effects – the correction amounts to ≈ 2 eV – this result has to be regarded as highly satisfactory.

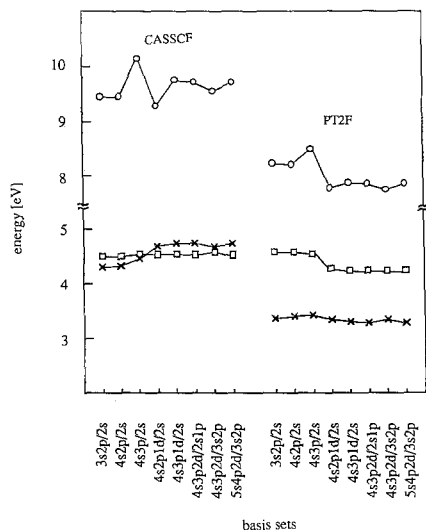


Fig. 1. Excitation energies computed at the CASSCF, PT2F level of approximation for the 1^1B_{2u} (boxes), 2^1B_{2u} (circles) and 1^1B_{3u} (crosses) states as a function of the basis sets

Another way to validate the results is to compare the absorption line positions relative to one another. A glimpse at Tables 1–8 shows that the state ordering is the same for all basis sets. As pointed out previously, the 2^1B_{2u} and 2^1B_{1u} states are of strong ionic character. They are highest in energy at the CASSCF level of approximation and become lower in energy than the 2^1A_g and 1^1B_{3g} states (these correspond to the E_{2g} state of benzene) at the PT2F level. It is gratifying to note that the energy splitting of these near degenerate pairs is virtually constant for all basis sets better than (4s3p1d/2s). These results strongly favour the present state ordering which differ from the ordering suggested earlier [8, 17, 18].

The relative weight, ω , for the different states decreases slowly and monotonically with increasing basis sets size. In some cases, however, we observed that interference with nearby Rydberg states not included in the reference CI space deteriorates this balance for some excited states and basis sets. Such a situation can occur in cases where the active space is not large enough to include all those Rydberg states which are nearly degenerate with the valence excited states. The energy denominator in the perturbation expansion then becomes very small. As long as the interaction is small the effect on the second order energy is in most cases negligible. If the Rydberg orbital in question can be clearly defined, it can be removed from the MO basis set. As an illustration we plot in Fig. 2 the weight of the 2^1A_g state for the PT2D method as a function of the basis sets. A sharp drop in the weight of the reference function occurs for the basis sets (4s3p1d/2s) and (4s3p2d/2s1p). On the other hand, by inspection of Tables 1–8 it becomes evident that the excitation energy, are hardly affected. Thus the contribution from the intruder state to the correlation energy is small. This seems to be typical in most cases, where Rydberg type states come close to valence excited states. Only if the degeneracy is very close, will the energy be affected to a sizeable extent. In such situations it becomes necessary to either delete the corresponding Rydberg type orbital from the basis set (if it can be clearly defined) or to extend the basis set and include the orbital. It is obvious that the situation would be much more severe if important valence orbitals are left outside the active space, since in such cases the

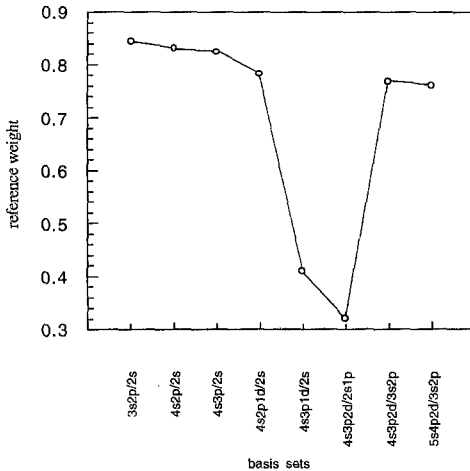


Fig. 2. Weight of the 2^1A_g state for the PT2D method as a function of the basis sets

corresponding intruder states would interact more strongly with the excited states under consideration.

3.3 Transition dipole moments

In Fig. 3 we plotted the transition dipole matrix elements, $\langle \Phi_0 | \mu | \Phi_1 \rangle$, for the 1^1B_{2u} , 2^1B_{2u} and 1^1B_{3u} states, respectively, as a function of the basis sets. The matrix elements are computed by the CASSI method with Φ_0 being the ground state. Comparing the figures obtained from the most extended basis sets and the next to best basis sets, the matrix elements differ by less than 0.5%, but change their values by as much as 30% relative to the smallest basis sets and for small matrix elements. Using basis sets of the structure (4s3p1d/2s) the relative errors are less than 5% compared to the results applying (5s4p2d/3s2p) basis sets. From Fig. 3 it is also seen that the absolute error for the three states is approximately equal in magnitude. Thus somewhat larger relative errors occur for the small transition moments.

It is well established that the transition dipole moments computed by the CASSI method and CASSCF reference functions are close to the full CI limit [19, 20]. However, to compute the oscillator strength both, the excitation energies and the transition dipole moments, are needed. The excitation energies are much more affected by the dynamic electron correlation energy. It is therefore a better approximation to use the PT2F excitation energies in the calculation of the oscillator strengths. The error in this quantity will depend on the error in the transition moment as well as the error in the excitation energy. Because of that we can expect sizeable errors of the computed oscillator strengths with the small basis sets, e.g., the computed oscillator strength for the weak transition from the ground state to the 1^1B_{3u} state decreases in magnitude by 60% and when going from the (3s2p/2s) to the (4s2p1d/2s) basis set. Further improvements of the basis set modifies the oscillator strength with less than 10%. For the strongest transition, 2^1B_{1u} , the largest and smallest values differ by about 20% and the value for the most extended basis sets is close to the experimental estimate, 0.72 [2].

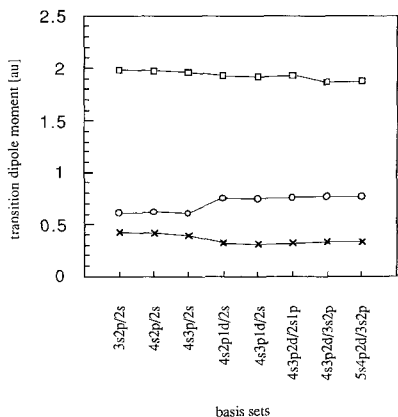


Fig. 3. CASSCF Transition dipole moments for the 1^1B_{2u} (boxes), 2^1B_{2u} (circle) and 1^1B_{3u} (crosses) states as a function of the basis sets

4 Conclusions

We computed vertical excitation energies, transition dipole moments and oscillator strengths for some of the singlet excited states in pyrazine using ANO-type basis sets. The latter were contracted to split valence level and then systematically improved by adding more contracted functions. The present results fully support our previous results for pyrazine [4] which made use of the PT2D method only. For all properties we concentrated on rather large changes are observed for the smallest basis sets. The presence of an extra valence orbital optimized for correlation and a set of polarization functions for the first row atoms is essential. The results appear not to be sensitive to the number and type of contracted functions used for the hydrogen atoms. Hence, basis sets of the structure (4s3p1d/2s) are capable of yielding results virtually identical to more extended basis' sets and represent a reasonable compromise to investigate more extended molecular systems. This basis set gives 18 ANOs for each first row atom. With a basis set limit of about 300 functions it should consequently be possible to perform the present type of calculations on molecules comprising up to 16 first row atoms. Excitation energies obtained with such a basis set should be within 0.2 eV of the basis set limit results. For larger molecules one would preferably reduce the *s*- and *p*-type functions before removing the *d*-type ANO. This would result in a basis set of the type (3s2p1d/2s), which has 14 ANOs per first row atom. Systems with up to 21 first row atoms can then be handled. In addition, one might use basis sets constructed from a smaller primitive set. The accuracy will, however, decrease somewhat the smaller the basis set are. For 'very large' molecules the (3s2p/2s) can be used, but errors larger than 0.5 eV for the excitation energies are expected. For pyrazine all the errors were positive and this seems to be rather general, indicating that excited states are more sensitive to the basis sets quality than the ground state.

Appendix

Tables 1–8 include the calculated total state energies calculated using the CASSCF and PT2F methods (the PT2D results are virtually identical to PT2F). The tables are organized such that the results for the $\pi-\pi^*$ states are given first followed by the $n-\pi^*$ states. They also include the excitation energies, δE , the CASSCF reference weight, ω , and the oscillator strength, f .

Table 1. Total energies in Hartrees, weights (ω), excitation energies (δE) in eV, and oscillator strengths (f) of pyrazine for the (3s2p/2s) basis sets

	E(CASSCF)	δE	f	E(PT2F)	ω	δE	f
<i>π-π^* states</i>							
1^1A_g	-262.681681			-263.109226	.856		
2^1A_g	-262.369662	8.49	-	-262.782268	.844	8.90	-
1^1B_{2u}	-262.497493	5.01	.046	-262.921793	.849	5.10	.046
2^1B_{2u}	-262.334807	9.44	.908	-262.806652	.814	8.23	.792
1^1B_{1u}	-262.365537	8.60	.113	-262.835131	.827	7.46	.098
2^1B_{1u}	-262.305631	10.23	1.146	-262.807076	.784	8.22	.921
1^1B_{3g}	-262.365313	8.61	-	-262.782678	.849	8.89	-
<i>n-π^* states</i>							
1^1A_g	-262.711586			-263.108839	.865		
1^1B_{3u}	-262.534826	4.81	.022	-262.966331	.843	3.88	.017
1^1A_u	-262.498484	5.80	-	-262.939247	.835	4.61	-

Table 2. Total energies in Hartrees, weights (ω) excitation energies (δE) in eV, and oscillator strengths (f) of pyrazine for the (4s2p/2s) basis sets

	E(CASSCF)	δE	f	E(PT2F)	ω	δE	f
<i>π-π^* states</i>							
1^1A_g	-262.686092			-263.123883	.854		
2^1A_g	-262.374222	8.49	-	-262.797336	.831	8.89	-
1^1B_{2u}	-262.502138	5.01	.047	-262.936812	.847	5.09	.048
2^1B_{2u}	-262.339252	9.44	.905	-262.822211	.812	8.21	.787
1^1B_{1u}	-262.370108	8.60	.113	-262.850495	.825	7.44	.098
2^1B_{1u}	-262.310259	10.23	1.146	-262.823804	.778	8.17	.915
1^1B_{3g}	-262.369999	8.60	-	-262.797532	.848	8.88	-
<i>n-π^* states</i>							
1^1A_g	-262.716725			-263.123560	.863		
1^1B_{3u}	-262.539000	4.84	.020	-262.980035	.841	3.91	.017
1^1A_u	-262.502391	5.83	-	-262.952756	.833	4.65	-

Table 3. Total energies in Hartrees, weights (ω) excitation energies (δE) in eV, and oscillator strengths (f) of pyrazine for the (4s3p/2s) basis sets

	E(CASSCF)	δE	f	E(PT2F)	ω	δE	f
<i>π-π^* states</i>							
1^1A_g	-262.716035			-263.204017	.849		
2^1A_g	-262.402030	8.54	-	-262.878910	.828	8.85	-
1^1B_{2u}	-262.530567	5.05	.045	-263.018530	.834	5.05	.045
2^1B_{2u}	-262.343713	10.13	.958	-262.891747	.793	8.50	.803
1^1B_{1u}	-262.400100	8.60	.118	-262.932493	.819	7.39	.101
2^1B_{1u}	-262.341408	10.19	.985	-262.894959	.783	8.41	.813
1^1B_{3g}	-262.398355	8.64	-	-262.880085	.842	8.81	-
<i>n-π^* states</i>							
1^1A_g	-262.748035			-263.203718	.858		
1^1B_{3u}	-262.565499	4.97	.018	-263.059434	.836	3.93	.015
1^1A_u	-262.528951	5.96	-	-263.032134	.828	4.67	-

Table 4. Total energies in Hartrees, weights (ω) excitation energies (δE) in eV, and oscillator strengths (f) of pyrazine for the (4s2p1d/2s) basis sets

	E(CASSCF)	δE	f	E(PT2F)	ω	δE	f
<i>π-π^* states</i>							
1^1A_g	-262.828708			-263.538827	.803		
2^1A_g	-262.520201	8.39	-	-263.234946	.783	8.27	-
1^1B_{2u}	-262.643498	5.04	.070	-263.362677	.792	4.79	.066
2^1B_{2u}	-262.487705	9.28	.850	-263.253267	.762	7.77	.711
1^1B_{1u}	-262.528611	8.17	.085	-263.290611	.775	6.75	.070
2^1B_{1u}	-262.468681	9.80	1.065	-263.260657	.736	7.57	.823
1^1B_{3g}	-262.515061	8.53	-	-263.230440	.793	8.39	-
<i>n-π^* states</i>							
1^1A_g	-262.856702			-263.538710	.810		
1^1B_{3u}	-262.665901	5.19	.013	-263.397048	.786	3.85	.010
1^1A_u	-262.625640	6.29	-	-263.368431	.777	4.63	-

Table 5. Total energies in Hartrees, weights (ω) excitation energies (δE) in eV, and oscillator strengths (f) of pyrazine for the (4s3p1p/2s) basis sets

	E(CASSCF)	δE	f	E(PT2F)	ω	δE	f
<i>π-π^* states</i>							
1^1A_g	-262.844045			-263.597176	.800		
2^1A_g	-262.534694	8.42	-	-263.294955	.339	8.22	-
1^1B_{2u}	-262.658396	5.05	.069	-263.422071	.788	4.76	.065
2^1B_{2u}	-262.485818	9.75	.882	-263.307793	.748	7.87	.712
1^1B_{1u}	-262.544647	8.15	.087	-263.349537	.772	6.74	.072
2^1B_{1u}	-262.486116	9.74	1.018	-263.314379	.722	7.69	.802
1^1B_{3g}	-262.529589	8.56	-	-263.289818	.788	8.36	-
<i>n-π^* states</i>							
1^1A_g	-262.873096			-263.596865	.807		
1^1B_{3u}	-262.680015	5.25	.013	-263.457013	.782	3.81	.009
1^1A_u	-262.639670	6.35	-	-263.427866	.773	4.60	-

Table 6. Total energies in Hartrees, weights (ω) excitation energies (δE) in eV, and oscillator strengths (f) of pyrazine for the (4s3p1d/2s1p) basis sets

	E(CASSCF)	δE	f	E(PT2F)	ω	δE	f
<i>π-π^* states</i>							
1^1A_g	-262.859143			-263.636861	.796		
2^1A_g	-262.550177	8.41	-	-263.336544	.255	8.17	-
1^1B_{2u}	-262.673844	5.04	.071	-263.461987	.784	4.76	.067
2^1B_{2u}	-262.502244	9.71	.891	-263.348439	.745	7.85	.720
1^1B_{1u}	-262.560772	8.12	.093	-263.389933	.768	6.72	.077
2^1B_{1u}	-262.501970	9.72	1.018	-263.354674	.718	7.68	.804
1^1B_{3g}	-262.545285	8.54	-	-263.330273	.783	8.34	-
<i>n-π^* states</i>							
1^1A_g	-262.888238			-263.636551	.803		
1^1B_{3u}	-262.695733	5.25	.013	-263.497091	.778	3.79	.010
1^1A_u	-262.655861	6.32	-	-263.468632	.770	4.57	-

Table 7. Total energies in Hartrees, weights (ω) excitation energies (δE) in eV, and oscillator strengths (f) of pyrazine for the (4s3p2d/3s2p) basis sets

	E(CASSCF)	δE	f	E(PT2F)	ω	δE	f
<i>π-π^* states</i>							
1^1A_g	-262.869332			-263.681587	.792		
2^1A_g	-262.560611	8.40	-	-263.379538	.771	8.22	-
1^1B_{2u}	-262.683947	5.10	.073	-263.506815	.780	4.76	.068
2^1B_{2u}	-262.518349	9.55	.817	-263.397155	.708	7.74	.662
1^1B_{1u}	-262.572057	8.51	.103	-263.435740	.764	6.69	.081
2^1B_{1u}	-262.514524	9.65	0.966	-263.404937	.694	7.53	.754
1^1B_{3g}	-262.555862	8.53	-	-263.376184	.779	8.31	-
<i>n-π^* states</i>							
1^1A_g	-262.898205			-263.538710			
1^1B_{3u}	-262.705584	5.19	.014	-263.397048	.786	3.85	.010
1^1A_u	-262.665946	6.29	-	-263.368431	.777	4.63	-

Table 8. Total energies in Hartrees, weights (ω) excitation energies (δE) in eV, and oscillator strengths (f) of pyrazine for the (5s4p2d/3s2p) basis sets

	E(CASSCF)	δE	f	E(PT2F)	ω	δE	f
<i>π-π^* states</i>							
1^1A_g	-262.871620			-263.704309	.791		
2^1A_g	-262.563082	8.40	-	-263.403110	.764	8.19	-
1^1B_{2u}	-262.686299	5.04	.069	-263.529736	.665	4.75	.065
2^1B_{2u}	-262.523377	9.48	.818	-263.421248	.740	7.70	.665
1^1B_{1u}	-262.575456	8.06	.101	-263.458105	.764	6.70	.084
2^1B_{1u}	-262.518704	9.60	.916	-263.426149	.692	7.57	.722
1^1B_{3g}	-262.558797	8.51	-	-263.400777	.768	8.26	-
<i>n-π^* states</i>							
1^1A_g	-262.900502			-263.702986	.798		
1^1B_{3u}	-262.707640	5.25	.014	-263.569707	.034	3.63	.010
1^1A_u	-262.668034	6.33	-	-263.536733	.763	4.52	-

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