

On the $n_+ \pi^* (B_{3u}) - n_- \pi^* (B_{2g})$ Splitting in Pyrazine

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Abstract Ab Initio Restricted Hartree-Fock calculations of the $n_+ \pi^* (B_{3u})$ and $n_- \pi^* (B_{2g})$ singlet-singlet and triplet-triplet splittings in pyrazine are presented. Insofar as the splittings are concerned the results are in excellent agreement with recent experimental results. However it is pointed out that one should not take the mistaken impression that RHF wavefunctions correctly describe the excited states.

In a recent communication Inoue, Webster and Lim (IWL)¹ have reported experimental triplet-triplet absorption in pyrazine in the region of 230-1900 m and attributed the absorption at 830 m to the origin band of the ${}^3B_{3u} (n_+ \pi^*) \rightarrow {}^3B_{2g} (n_- \pi^*)$ absorption. The separation between these states is therefore ~ 1.5 ev¹. As ML pointed out this splitting is in a remarkable agreement with ab initio CI calculations. Hackmeyer and Whitten (HW)², Wadt and Goddard (WG)³ and Wadt, Goddard and Dunning (WGD)⁴ have calculated this separation to be 1.43 ev, 1.31 ev and 1.28 ev. respectively. The above mentioned splitting is of great importance as the separation and ordering of $n\pi^*$ states in diazines provide useful information regarding the interaction between the two nonbonding orbitals. As such it has been the subject of many investigations⁵. It is our opinion that one has left undiscussed some interesting theoretical questions particularly those related to the existence of broken symmetry solutions to the Hartree-Fock equations. With this in mind we shall present ab initio calculations within the Restricted Hartree-Fock (RHF) level for both triplet states in order to obtain this triplet-triplet splitting. For completeness the corresponding singlet-singlet splitting will also be reported. At the end we briefly comment on the broken symmetry solutions.

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The pyrazine molecular structure is taken from Sutton⁶. The contracted Gaussian basis set is the $\langle 4s2p|2s \rangle$ suggested by Dunning⁷. The program package MOLECULAR-ALCHEMY⁸ has been used and a D_{2h} symmetry constraint has been imposed. The calculated total energy for the ${}^3B_{3u}(n_+\pi^*)$ is -262.41337 hartrees. The result for the triplet-triplet splitting is shown in the table along with the previous theoretical calculations as well as the experimental value reported by IWL. The ΔE (RHF) triplet-triplet splitting calculated as 1.562 eV (800 nm) is in a very good agreement with the result of IWL. Actually the agreement is as close as those obtained from the best CI calculations. Therefore one may conclude that the RHF scheme is able to give the $n_+\pi^*({}^3B_{3u}) - n_-\pi^*({}^3B_{2g})$ splitting of pyrazine within the experimental accuracy. Reversely, one may also say that the present calculation reinforces that the near infrared absorption observed by IWL is due to the above triplet-triplet absorption.

The corresponding singlet-singlet splitting has been calculated as 1.679 eV (740 nm). This transition has never been observed. In due agreement with previous CI calculations we predict this splitting to be almost equal to the triplet one^{2-4,9}.

In conclusion the $n_+\pi^*(B_{3u}) - n_-\pi^*(B_{2g})$ splitting in pyrazine has been calculated within the RHF level with fully symmetrized molecular orbitals and the result is in excellent agreement with experiment. However, it is known¹⁰ that in order to represent the excited states of pyrazine a broken symmetry solution is required if one remains within the confines of ab initio SCF level. Indeed, our previous studies¹⁰⁻¹² indicate that the RHF wavefunctions does not correctly represent these states. Nevertheless, insofar as the splitting is concerned the RHF scheme may give reasonable results. In the better case of the localized broken symmetry description, on the other hand, one obtains artificially degenerate $n\pi^*$ states. It becomes necessary a proper projection to restore the symmetry and obtain the splitting. In the case when the splitting is sizable, however, the procedure may be questionable¹² as the final states are hence not properly optimized. Striving for consistent accuracy either scheme has its own drawbacks. The localized broken symmetry approach with projection seems

less risky. At this stage a conventional CI representation may give a far better description but will hidden interesting effects.

Table: Comparison of calculated and experimental $n_4\pi^*(B_{3u})-n_-\pi^*(B_{2g})$ splitting in pyrazine (ev).

	This Work	HW (a) Ref.2	WG (a) Ref.3	WGD (a)(b) Ref.4	RZ (c) Ref.9	IWL (exp.) Ref.1
triplet-triplet splitting	1.562	1.43	1.31	1.28	1.22	1.5
singlet-singlet splitting	1.679	1.43	1.21	1.30	1.15	-

(a) CI calculations. (b) Results from "best estimates". (c) INDO-CI calculations.

REFERENCES

1. A. Inoue, D. Webster and E. C. Lim, *J. Chem. Phys.* 72, 1419 (1980).
2. M. Hackmeyer and J. L. Whitten, *J. Chem. Phys.* 54, 3739 (1971).
3. W. R. Wadt and W. A. Goddard III, *J. Am. Chem. Soc.* 97, 2034 (1975).
4. W. R. Wadt, W. A. Goddard III and T. H. Dunning Jr., *J. Chem. Phys.* 65, 438 (1976).
5. I. G. Ross, *Photochemistry of Heterocyclic Compounds*, edited by O. Buchard, Wiley, New York, (1976) p.1; K. K. Innes, A. H. Kalantar, A. Y. Khan and T. J. Durnick, *J. Mol. Spectrosc.* 11, 477 (1972); W. R. Moomaw, M. R. DeCamp and P. C. Podore, *Chem. Phys. Lett.* , 255 (1972); H. K. Kong and G. W. Robinson, *J. Mol. Spectrosc.* 52, 1 (1974). I. Suzuki, N. Mikami and M. Ito, *J. Mol. Spectrosc.* 52, 21 (1974); S. N. Thakur and K. K. Innes, *J. Mol. Spectrosc.* 52, 130 (1974). E. F. Zalewski, D. S. McClure and D. L. Narva, *J. Chem. Phys.* 61, 2964 (1974), P. Esherick, R. Zinsli and M. A. El-Sayed, *Chem. Phys.* 10, 415 (1975).
6. G. L. E. Sutton, Ed., *Tables of Interatomic Distances and Configurations in Molecules and Ions*, Special Publication No 18 (Chem. Soc. London, 1965).

7. T.H.Dunning Jr. J. Chem. Phys. 53, 2823 (1970).
8. J.S.Aimlőf, P.S.Bagus, B. Liu, D.McLean, U. I. Wahlgren and M. Yoshimine, IBM Research Laboratory, San José, California.
9. J.E.Ridley and M.C.Zerner, Theor. Chim. Acta 42, 223 (1976).
10. S.Canuto, O.Goscinski and M.Zerner, Chem. Phys. Lett. 68, 232 (1979).
11. R.L.Martín, J.Chem.Phys. 74, 1852 (1981).
12. S.Canuto, Rev. Brasil. Física 12, 459 (1982).

RESUMO

Cálculos ab initio a nível de Hartree-Fock restrito da separação singleto-singleto e tripleto-tripletto entre os estados $n \pi^*(B_{3u})$ e $n \pi^*(B_{2g})$ da pirazina são apresentados. Os resultados estão em excelente concordância com recentes resultados experimentais. Enfatiza-se entretanto que as funções de onda de Hartree-Fock restrita não são adequadas para descrever estes estados excitados.