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Short Communication

Relative Stability of the $^2A_{1g}$ and ^2E_g States of the $C_2H_6^+$ Ion

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An *ab initio* study of the relative stability for the states $^2A_{1g}$ and ^2E_g of $C_2H_6^+$ has been carried out. The results of the Open Shell Restricted Hartree–Fock calculations lead to assign the $^2A_{1g}$ as the ground state of the molecule in agreement with previous SCF calculations.

The correlation energy associated to both states has been calculated within the correlation hole model and the results, contrary to those obtained from Configuration Interaction calculations, do not alter qualitatively the conclusions from SCF.

Key words: $C_2H_6^+$ ion, relative stability of the $^2A_{1g}$ and ^2E_g states of ~

1. Introduction

The study of the electronic states of $C_2H_6^+$ has been the subject of attention both from the experimental [1–8] and theoretical [9–14] viewpoints. This interest is wholly justified by the importance of ethane in the series of aliphatic hydrocarbons.

Experimentally, the existence of three well defined bands between 11 eV and 22 eV has been clearly established. The first of these bands extends itself from around 11.5 eV with a progressive increase in intensity up to 12 eV. At that point begins a zone of maximum intensity up to 13 eV decreasing in intensity and disappearing at 14.5 eV, where the second band approximately starts, with the maximum intensity centered around 15 eV. The third band starts around 20 eV, presenting a maximum at 20.6 eV.

It is experimentally accepted that the first band is due to the overlap of the $^2A_{1g}$ and ^2E_g states whilst the other two are associated to ^2E_u and $^2A_{2u}$ respectively. Nevertheless it is highly complex to interpret the first band due to the proximity that must

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exist between the energies of the maxima for the states $^2A_{1g}$ and ^2E_g as well as the Jahn–Teller effect in the ^2E_g. As a consequence it is difficult to assign a relative stability to both states. While the PE spectra show a well defined maximum around 12 eV [1], the (*e*, 2*e*) spectroscopy [2] indicates a maximum for the Frank–Condon factor between 11.5 and 12.2 eV, but with such a dispersion that no vibrational structure can be assigned.

The high resolution PE spectra, carried out by Baker *et al.* [4], shows a clear vibrational structure with an average spacing of 0.14 eV (similar to that of the third spectral band).

To the complexity introduced by the Jahn–Teller effect in the ^2E_g state, one has to add the loss of the adiabaticity that seems to exist according to the threshold electronic photoelectroionization spectra, since a slow progression in intensity at the beginning of the band can be observed [3]. Finally it must be remembered that the existence of an autoionizing process in the PE spectra might complicate the interpretation of the data obtained through this technique.

Theoretical calculations could therefore be of help in interpreting the ionization spectra of the ethane. *Ab initio* RHF calculations assign the following electronic configuration for the ground state of the ethane:

$$1a_{1g}^2 1a_{2u}^2 2a_{1g}^2 2a_{2u}^2 1e_u^4 3a_{1g}^2 1e_g^4 \ldots {}^1A_{1g}.$$

According to that configuration, and accepting the predictions given by the Koopmans theorem, the relative stability for the states of $C_2H_6^+$ must correspond to

$$^2E_g > {}^2A_{1g} > {}^2E_u > {}^2A_{2u}$$

which coincides with the interpretation given by several authors, based on experimental data [2, 4, 6].

Direct Hartree-Fock calculations on the two states considered here, with a theoretical improvement over the frozen orbitals approximation, predict the $^2A_{1g}$ as the more stable state [12, 13].

As it is well known, the correlation energy associated to a Hartree–Fock calculation depends basically on the average electronic density in the state considered and, therefore, in a molecule the correlation energy can vary significantly with each electronic state. In the cases of the ^2E_g and $^2A_{1g}$ states for $C_2H_6^+$, with little difference between energies (independently of their relative stability), the conclusions from a Hartree–Fock calculation must be treated with great care, and it is then particularly interesting a precise calculation of the correlation energy. Extensive configuration interaction calculations have been carried out for the vertical ionization of C_2H_6 [13]. Their findings yield ionization potentials similar for both $^2A_{1g}$ and ^2E_g.

Other theoretical approaches have been made by studying the potential curves for the $^2A_{1g}$ state and the components associated to the ^2E_g as a consequence of the Jahn–Teller effect. Again the findings are not in agreement, since some conclude that the first peak of the first band corresponds to the vertical ionization to the $^2A_{1g}$ [12], whilst others using the configuration interaction technique, already employed in [13], assign the ^2B_g component from the ^2E_g state [14].

Here we present the results of calculations carried out for the $^1A_{1g}$ state of C_2H_6 and the ^2E_g and $^2A_{1g}$ of $C_2H_6^+$, in which the correlation energy is obtained within the correlation hole model, already applied with satisfactory results [15, 17]. This approach allows high precision in the evaluation of the correlation energy with errors of about the 5% [15], making it very suitable in the present problem.

2. SCF Calculations

SCF calculations have been carried out in the Open Shell Restricted Hartree–Fock (OS RHF) model. The pseudo-eigenvalue equations have been those proposed in a previous paper [16].

The geometry adopted for the present calculations has been that of the equilibrium configuration in the ground state of the neutral molecule [13] (point group D_{3d}). The basis used is the GTO 6-31G [18], being adequate in the present case since both states $^2A_{1g}$ and ^2E_g, are related to the depopulation of a doubly occupied orbital in the ground state of the neutral molecule.

The first two rows of Table 1 show the OS RHF energies and the ionization potentials for the case studied ($^1A_{1g}$, $^2A_{1g}$, ^2E_g). The present results assign the ion ground state to the $^2A_{1g}$ with the ^2E_g as the first excited state, separated by a gap of 0.47 eV (this ordering of stability is considered only for the vertical ionization). The present result is in good agreement with predictions derived from direct SCF calculations [12, 13]. The last row of Table 1 collects the three maxima appearing in the first band of the experimental spectra.

3. Calculation of the Correlation Energy

This calculation follows the method proposed by Colle and Salvetti [15], successfully used in previous papers [15, 17] and based on the correlation hole model.

Table 1. Results of this work

State	$^1A_{1g}$	$^2A_{1g}$	^2E_g
E_{RHF} (a.u.)	-79.1975	-78.7550	-78.7372
$I.P._{\text{RHF}}$ (eV)	0	12.0	12.5
E_c (a.u.)	-0.4726	-0.4435	-0.4439
$I.P._{\text{corr.}}$ (eV)	0	12.88	13.35
$I.P._{\text{Exp}}$[a] (eV)	0	12.0[b]	12.65 and 13.40[c]

[a] See for example Ref. [4].

[b] Assuming that the first peak of the spectra corresponds to this ionization.

[c] These two values are experimental maxima.

Apart from its simplicity this model does not require representation on a basis of Slater determinants avoiding the problem of slow convergence typical of any configuration interaction or perturbative method.

The physical meaning of the correlation energy obtained by this method depends basically on a good representation for the first-order density matrix. That requisite is, in general, well satisfied by the Hartree–Fock wavefunctions, as long as the bond distances are near those of equilibrium and as long as poor representations of the long range effects such as inadequate proportions between ionic and covalent structures do not appear [17].

Those types of difficulties are not present in the Hartree–Fock solutions associated to the cases studied here and, therefore, it is expected that the correlation hole method proposed by Colle and Salvetti is adequate to give a good estimation of the correlation energy associated to the solutions given in the previous section.

Since the $C_2H_6^+$ states present an open shell electronic structure with doublet multiplicity, the first and second order density matrices $\rho_1(\boldsymbol{r}_1;\boldsymbol{r}_1')$ and $\rho_2(\boldsymbol{r}_1\boldsymbol{r}_2;\boldsymbol{r}_1'\boldsymbol{r}_2')$ will be given by

$$\rho_1(\boldsymbol{r}_1;\boldsymbol{r}_1') = 2P^{c}_{\mathrm{HF}}(\boldsymbol{r}_1;\boldsymbol{r}_1') + P^{o}_{\mathrm{HF}}(\boldsymbol{r}_1;\boldsymbol{r}_1'), \tag{1}$$

$$\rho_2(\boldsymbol{r}_1\boldsymbol{r}_2;\boldsymbol{r}_1'\boldsymbol{r}_2') = 4P^{c}_{\mathrm{HF}}(\boldsymbol{r}_1;\boldsymbol{r}_1')[P^{c}_{\mathrm{HF}}(\boldsymbol{r}_2;\boldsymbol{r}_2') + P^{o}_{\mathrm{HF}}(\boldsymbol{r}_2;\boldsymbol{r}_2')], \tag{2}$$

where $P^{c}_{\mathrm{HF}}(\boldsymbol{r}_1;\boldsymbol{r}_1')$ and $P^{o}_{\mathrm{HF}}(\boldsymbol{r}_1;\boldsymbol{r}_1')$ are the OS RHF first order density matrices for closed and open shells, respectively.

The expression for the correlation energy is not in this case that of Eq. (19) in [15] for a closed shell, but that appropriate for a doublet open shell

$$E_c = -2\pi\int \frac{\rho_2(\boldsymbol{r}_1\boldsymbol{r}_2;\boldsymbol{r}_1\boldsymbol{r}_2)}{\beta^3}\, G(\beta,\omega)\, d\left(\frac{\boldsymbol{r}_1+\boldsymbol{r}_2}{2}\right), \tag{3}$$

where

$$G(\beta,\omega) = 0.01565\,\frac{1+0.173\omega\exp[-0.58/\beta]}{1+0.8/\beta}, \tag{4}$$

$$\omega = \frac{[\nabla^2_{(\boldsymbol{r}_1-\boldsymbol{r}_2)}\rho_2(\boldsymbol{r}_1\boldsymbol{r}_2;\boldsymbol{r}_1'\boldsymbol{r}_2')]_{\boldsymbol{r}_1=\boldsymbol{r}_2}}{\beta^2\rho_2(\boldsymbol{r}_1\boldsymbol{r}_2;\boldsymbol{r}_1\boldsymbol{r}_2)}, \tag{5}$$

with

$$\beta = 2.29\rho_1(\boldsymbol{r}_1;\boldsymbol{r}_1')^{1/3}. \tag{6}$$

Equation (3) has been solved by numerical quadrature, with four digits precision, considered adequate for the present problem. The third row of Table 1 shows the correlation energy obtained for the states considered whilst the fourth row shows the corrected ionization potentials.

According to Table 1, the results obtained in this section do not change the conclusions derived from SCF calculations in assigning the relative order in the vertical ionization. Indeed, we find that the ionization potentials associated to the two lower vertical ionizations of C_2H_6 occur at 12.88 and 13.35 eV corresponding to the two lower states of $C_2H_6^+$, i.e. $^2A_{1g}$ and ^2E_g. Accepting this ordering, the value of 12.88 eV associated to the $^2A_{1g}$ must be correlated to the first peak of the spectrum which appears at 12 eV, whilst the 13.35 eV obtained for ^2E_g must be correlated to the value of 13 eV equidistant from the two following peaks located at 12.65 eV and 13.40 eV approximately (assuming that the Jahn–Teller effect splits symmetrically the ^2E_g state).

References

1. Rabalais, J. W., Katrib, A.: Mol. Phys. **27**, 923 (1974)
2. Dey, S., Dixon, A. J., McArthy, I. E., Weigold, E.: J. Spectry. Related Phenomena **9**, 397 (1976)
3. Stockbauer, R., Inghram, M. G.: J. Chem. Phys. **54**, 2242 (1971); Stockbauer, R.: J. Chem. Phys. **58**, 3800 (1973)
4. Baker, A. D., Baker, C., Brundle, C. R., Turner, W.: Intern. J. Mass Spectry. Ion Phys. **1**, 285 (1968)
5. Chupka, W. A., Berkowitz, J.: Rev. Sci. Instrum. **43**, 1872 (1971)
6. Lasseter, E. N., Skerbele, A., Dillon, M. A.: J. Chem. Phys. **49**, 2382 (1968)
7. Weigold, E., Dey, S., Dixon, A., McArthy, I. E., Teubner, P. J. O.: Chem. Phys. Letters **41**, 21 (1976)
8. Narayan, B.: Mol. Phys. **23**, 281 (1972)
9. Fink, W., Allen, L. C.: J. Chem. Phys. **46**, 2261 (1967)
10. Veillard, A.: Chem. Phys. Letters **3**, 128 (1969)
11. Clementi, E., Popkie, H.: J. Chem. Phys. **57**, 4870 (1972)
12. Lathan, W. A., Curtiss, L. A., Pople, J. A.: Mol. Phys. **22**, 1081 (1971)
13. Buenker, R. J., Peyerimhoff, S.: Chem. Phys. **8**, 56 (1975)
14. Richartz, A., Buenker, R. J., Bruna, P. J., Peyerimhoff, S.: Mol. Phys. **33**, 1345 (1977)
15. Colle, R., Salvetti, O.: Theoret. Chim. Acta (Berl.) **37**, 329 (1975)
16. Moscardó, F., Fernandez-Alonso, J. I.: Theoret. Chim. Acta (Berl.) **47**, 305 (1978)
17. Colle, R., Moscardó, F., Riani, P. R., Salvetti, O.: Theoret. Chim. Acta (Berl.) **44**, 1 (1977)
18. Hehre, W. J., Ditchfield, R., Pople, J. A.: J. Chem. Phys. **56**, 2257 (1972)

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