Theoret. Chim. Acta (Berl.) 54, 53–58 (1979)

THEORETICA CHIMICA ACTA

Theoretical Study of the Ethane Ionization Spectra within the Correlation Hole Model

Federico Moscardó, Miguel Paniagua and Emilio San-Fabián

Departamento de Química Física y Química Cuántica, Centro Coordinado UAM-CSIC, Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, Madrid 34, Spain

This work is an extension of a previous study on the assignment of the peaks of the photoionization spectrum of C_2H_6 [1].

The model of the correlation hole is reconsidered in order to carry out a new study of the states $^2A_{1g}$, ^2E_g, ^2E_u and $^2A_{2u}$ of the $C_2H_6^+$.

The qualitative relations which the average mass of the electrons in the Coulomb hole must have for the four states of the $C_2H_6^+$, lead to a new criterion for the assignation of the peaks of the spectrum. The arrangement obtained for the two lower peaks is in agreement with those obtained previously [1].

Key words: Ethane ionization spectrum

1. Introduction

We have recently reported the results of a study on the relative stability of the states $^2A_{1g}$ and ^2E_g of $C_2H_6^+$ [1]. The results obtained in [1] suggest that the lowest peak of the photoelectronic spectrum [2–9] should be assigned to the state $^2A_{1g}$.

There exist two other valence states for the $C_2H_6^+$, identified in the experimental spectrum [2, 4, 9, 10] as ^2E_u and $^2A_{2u}$ which present the maxima at 15–15.8 eV and 20.5 eV. The two first of these maxima are assigned to the two components of the Jahn–Teller splitting undergone by the state ^2E_u.

In this paper we report the results of a more elaborate study than [1] where the states ^2E_u and $^2A_{2u}$ are considered in addition to the $^2A_{1g}$, ^2E_g and $^1A_{1g}$. Also, the treatment of the electronic correlation is improved here.

In Sect. 2, the results of an open shell RHF (OSRHF) calculation for the states $^2A_{2u}$ and ^2E_u are given.

0040-5744/79/0054/0053/$01.20

A calculation of correlation energy, following the same approach as in [1], is performed and the results are discussed in Sect. 3.

The parametrization of the previously used equation, (18) of [12] established by optimizing the energy of the ground state of the He atom appears to be somewhat limited in the treatment of open-shell systems. Thus, in Sect. 4 we have recalculated the correlation energy of the $^2A_{1g}$, ^2E_g, ^2E_u, $^2A_{2u}$ states by using a modified form of Eq. (15) of [12] which does not have any parameters and only functional dependencies.

Taking into account the relations which exist between the average mass of the electrons inside the Coulomb hole ($\bar{m}$) for the states considered, we propose an assignment of the experimental peaks.

2. RHF Calculations

The wavefunctions used as starting points in the correlation energy calculation, have been obtained by solving the respective OSRHF equations.

In this section, we present the results made for the ^2E_u and $^2A_{2u}$ states of the $C_2H_6^+$. The calculations have been made taking the same Gaussian basis and the same geometry as in [1] for $^1A_{1g}$, $^2A_{1g}$ and ^2E_g.

In the first three columns in Table 1 we give the energies and ionization potentials (IP) RHF for the ^2E_u and $^2A_{2u}$ states, together with previously obtained results for the $^1A_{1g}$, $^2A_{1g}$ and ^2E_g states [1], included here in order to complete the data. The second column of this table corresponds to the IP obtained by applying the Koopmans' theorem to the $^1A_{1g}$ state.

The third column of Table 1 gives the IP obtained as difference between the RHF energy calculated for every state of the ion and the RHF energy corresponding to the $^1A_{1g}$ state. These ionization potentials suppose a theoretical improvement upon those found via Koopmans' theorem, since they have been obtained as differences between variationally optimized energies. The value 15.48 eV for the ^2E_u state is in good agreement with the peaks at 15 and 15.8 eV in the experimental spectra. These peaks must correspond to the Jahn–Teller splitting undergone by this state. The value 22.26 eV obtained for the $^2A_{2u}$ overestimates the corresponding experimental peak at 20.5 eV, and the results of recent CI calculations, 20.83 eV [11].

Table 1. Energies and vertical ionization potentials for the states considered

	E_{RHF} (a.u.)	I.P. (eV) Koopmans	I.P. (eV) Δ RHF	E_c (a.u.)	I.P. (eV)
$^1A_{1g}$	-79.1975	0.00	0.00	-0.4724	0.00
$^2A_{1g}$	-78.7550	13.68	12.04	-0.4431	12.84
^2E_g	-78.7372	13.24	12.53	-0.4427	13.33
^2E_u	-78.6285	16.29	15.48	-0.4414	16.33
$^2A_{2u}$	-78.3797	23.04	22.25	-0.4433	23.04

3. Correlation Energy Calculation

The electronic correlation energy has been calculated within the correlation hole model as in the preceding work [1]. For the sake of clarity of Sect. 4 we will describe here the basic features of the method [12]:

a) The correlated wavefunction is written as

$$\Psi(\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_N) = \Psi_{\text{P.I.}}(\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_N) \prod_{i>j} M(\bar{r}_i, \bar{r}_j) \tag{1}$$

where $\Psi_{\text{P.I.}}$ is a wavefunction defined on the independent particle model and $M(\bar{r}_i, \bar{r}_j)$ is a correlation factor for an electron pair.

b) The function $M(\bar{r}_i, \bar{r}_j)$ must satisfy the cusp condition and must have a good asymptotic behavior [14]. A function with these characteristics is

$$M(\bar{r}_i, \bar{r}_j) = 1 - \varphi(\bar{r}_i, \bar{r}_j) \tag{2}$$

with

$$\varphi(\bar{r}_i, \bar{r}_j) = \exp(-\beta^2 r^2)\left[1 - \phi(\bar{R})\left(1 + \frac{\bar{r}}{2}\right)\right] \tag{3}$$

where $\bar{r} = |\bar{r}_i - \bar{r}_j|$ and $\bar{R} = (\bar{r}_i + \bar{r}_j)/2$.

c) The first order density matrix is well represented by the first order density matrix obtained of the function $\Psi_{\text{P.I.}}\ (\bar{x}_1, \bar{x}_2, \ldots, \bar{x}_N)$

$$\rho_1(\bar{x}_1, \bar{x}_1') \simeq P_{1\text{HF}}(\bar{x}_1; \bar{x}_1'). \tag{4}$$

d) The volume for which $\varphi(\bar{r}_i, \bar{r}_j)$ has values sensibly different from zero must be proportional to the Wigner's exclusion volume [15], this involves the relation

$$\beta = q P_{1\text{HF}}(\bar{r}_1, \bar{r}_1')^{1/3} \tag{5}$$

where q is related to the average electronic mass in the Coulomb's hole by the expression

$$\bar{m} = \left(\frac{\pi^2}{q}\right)^3. \tag{6}$$

Using these assumptions, Colle and Salvetti [12] give the following expression for the correlation energy:

$$E_c = -2\pi \int \frac{P_{2\text{HF}}(\bar{R}; \bar{R})}{\beta^3} G(\beta, W)\, d\bar{R} \tag{7}$$

with

$$G(\beta, W) = \frac{0.121 - 0.0167W + 0.0458/\beta - 0.005W/\beta}{1 + 1.1289/\beta + 0.3183/\beta^2} \tag{8}$$

where

$$W = \frac{\left[\nabla_r^2 P_{2\text{HF}}\left(\bar{R} + \frac{\bar{r}}{2}; \bar{R} - \frac{\bar{r}}{2}\right)\right]_{r=0}}{\beta^2 P_{2\text{HF}}(\bar{R}; \bar{R})}. \tag{9}$$

$P_{2\mathrm{HF}}(\bar{r}_1, \bar{r}_2; \bar{r}_1', \bar{r}_2')$ is the second-order density matrix, without spin, for the independent particle model.

An alternative expression to (8), proposed by Colle and Salvetti, is:

$$G(\beta, W) = a\,\frac{1 + bW\exp(-c/\beta)}{1 + d/\beta} \tag{10}$$

with $a = 0.01565$, $b = 0.173$, $c = 0.58$, $d = 0.8$ and $q = 2.29$, obtained in the calculation of He by optimization.

For a doublet system, the density matrices of first and second order, without spin, associated to an OSRHF problem are

$$P_{1\mathrm{HF}}(\bar{r}_1; \bar{r}_1') = 2P^{c}_{1\mathrm{HF}}(\bar{r}_1; \bar{r}_1') + P^{o}_{1\mathrm{HF}}(\bar{r}_1; \bar{r}_1') \tag{11}$$

$$P_{2\mathrm{HF}}(\bar{r}_1, \bar{r}_2; \bar{r}_1', \bar{r}_2') = 4P^{c}_{1\mathrm{HF}}(\bar{r}_1; \bar{r}_1')[P^{c}_{1\mathrm{HF}}(\bar{r}_1; \bar{r}_1') + P^{o}_{1\mathrm{HF}}(\bar{r}_2; \bar{r}_2')] \tag{12}$$

where P^{c}_{1} and P^{o}_{1} are the density matrices for the closed and open shells respectively.

As in [1], we calculate the correlation energy for the ^2E_u and $^2A_{2u}$ states by integrating numerically Eq. (7) using Eqs. (9, 10), and the accuracy in the results is of four decimal digits, which is sufficient for our purposes.

In the fourth and fifth columns of Table 1 we give the results of the calculations described here, together with those obtained previously for the $^1A_{1g}$, $^2A_{1g}$ and ^2E_g states [1]. The vertical ionization energies to the states ^2E_u and $^2A_{2u}$ are higher than the experimental [2, 4, 9, 10] and other *ab initio* results [11].

4. Change in Correlation Energy with the Average Electron Mass

In our problem, the system has an odd number of electrons, and, consequently, the use of the optimized parameters for the He atom (closed shell with the electrons coupled strongly by pairs) would not be suitable for the representation of the electronic states of the $C_2H_6^+$. This is apparent in the data reported in the fourth column of Table 1 since for different states there is practically no difference in the values of the correlation energy.

Table 2. Correlation energy (a.u.), for the states considered, versus the q value

q	$^1A_{1g}$	$^2A_{1g}$	^2E_g	^2E_u	$^2A_{2u}$
2.17	−0.4916	−0.4653	−0.4661	—	—
2.19	−0.4785	−0.4528	−0.4536	—	—
2.21	−0.4658	−0.4408	−0.4415	−0.4411	−0.4433
2.23	−0.4536	−0.4292	−0.4299	−0.4295	−0.4316
2.25	−0.4418	−0.4180	−0.4187	−0.4183	−0.4203
2.27	−0.4304	−0.4072	−0.4079	−0.4075	−0.4095
2.29	−0.4195	−0.3968	−0.3970	−0.3971	−0.3990
2.31	−0.4088	−0.3867	−0.3873	−0.3870	−0.3889
2.33	−0.3986	−0.3770	−0.3776	−0.3772	−0.3791
2.35	−0.3888	−0.3676	−0.3682	−0.3678	−0.3697
2.37	—	—	—	−0.3587	−0.3605
2.39	—	—	—	−0.3500	−0.3517

Here, we present the results obtained using Eqs. (5–9). The only unknown is q, but this variable has a clear physical interpretation, because it is directly related with the average electron mass ($\bar{m}$) in the Coulomb's hole, through Eq. (6).

In Table 2 we give the correlation energy, for the four states considered, versus the q value. At first sight this table shows how the correlation energy depends sensibly upon the q value (two hundredths in q implies, approximately, a variation of 0.3 eV in the correlation energy).

As our reference state is the closed-shell one $^1A_{1g}$, we will select the q which reproduces for this state the value obtained for the correlation energy in our previous calculation [1]. The resulting q value is 2.20.

Let us assume that our N electrons are moving in a central field, we can define a $\bar{m}_1$. If we eliminate one electron, the remaining $N-1$ electrons would have a new average mass in the Coulomb's hole, $\bar{m}_2$, with the condition that the relation $\bar{m}_2 > \bar{m}_1$ must be obeyed.

Now, if we assume that the N electrons were distributed in shells, the elimination of one electron in the ith shell, would lead to an average mass $\bar{m}_i$ with a greater value if the depopulated shell is the electronic deeper one.

For the states studied the following relation must be satisfied

$$\bar{m}(^2A_{2u}) > \bar{m}(^2E_u) > \bar{m}(^2A_{1g}), \qquad \bar{m}(^2E_g) > \bar{m}(^1A_{1g})$$

or

$$q(^2A_{2u}) < q(^2E_u) < q(^2A_{1g}), \qquad q(^2E_g) < q(^1A_{1g}).$$

Here we have not differentiated between the $^2A_{1g}$ and the ^2E_g states because of the proximity in the RHF $3a_{1g}$ and $1e_g$ levels obtained for the $^1A_{1g}$ state (-0.5028 a.u. and -0.4864 a.u. respectively). However, it is reasonable to suppose that $\bar{m}(^2A_{1g}) > \bar{m}(^2E_g)$.

With these ideas in mind, we studied the two possible ways to assign the peaks in the experimental spectra, assuming that the larger intensities correspond to the vertical ionization processes, and that the Jahn–Teller effect splits a degenerate state symmetrically.

In Tables 3 and 4 we give the q values and the correlation energies in terms of the assignments considered. These values have been obtained by application of Newton's interpolation method to data given in Table 2.

Table 3. Correlation energies and q values as function of peaks assignment. First option

State	I.P. (eV)[a]	q	E_c (a.u.)
$^2A_{2u}$	20.50	2.066	-0.5368
^2E_u	15.40	2.151	-0.4754
$^2A_{1g}$	12.05	2.159	-0.4720
^2E_g	13.10	2.194	-0.4513
$^1A_{1g}$	0.00	2.200	-0.4724

[a] See Ref. [4].

Table 4. Correlation energies and q values as function of peaks assignment. Second option

State	I.P. (eV)[a]	q	E_c (a.u.)
$^2A_{2u}$	20.50	2.066	-0.5368
^2E_u	15.40	2.151	-0.4754
$^2A_{1g}$	13.50	2.249	-0.4188
^2E_g	12.40	2.153	-0.4770
$^1A_{1g}$	0.00	2.200	-0.4724

[a] See Ref. [4].

While the q values in Table 3 are in agreement with the relation given above, those appearing in Table 4 are inconsistent as they imply an arrangement without justification from theoretical considerations.

The results of this section suggest that the $^2A_{1g}$ is the ion ground state in the geometry associated to the vertical ionization, while the ^2E_g would be the first excited state. These results are qualitatively in agreement with the conclusions of the direct RHF calculations [16, 17], as well as with the conclusions obtained by introducing the short range correlation energy through Eq. (10).

The approach used here in order to analyze the photoionization spectrum of the C_2H_6, within the correlation hole model, is the most satisfying one given the present state of development of this model. In spite of its simplicity, this treatment shows that an explicit consideration of the concept of Coulomb's hole enlarges the possibilities of the method in their application to open shell systems.

References

1. Moscardó, F., Paniagua, M., San-Fabián, E.: Theoret. Chim. Acta (Berl.), in press
2. Baker, A. D., Baker, C., Brundle, C. R., Turner, D. W.: Intern. J. Mass Spectry. Ion Phys. **1**, 285 (1968)
3. Narayan, B.: Mol. Phys. **23**, 281 (1972)
4. Rabalais, J. W., Katrib, A.: Mol. Phys. **27**, 923 (1974)
5. Chupka, W. A., Berkowitz, J.: J. Chem. Phys. **47**, 2921 (1967)
6. Nicholson, A. J. C.: J. Chem. Phys. **43**, 1171 (1965)
7. Watanabe, K.: J. Chem. Phys. **26**, 542 (1957)
8. Steiner, B., Giese, C. F., Inghram, M. G.: J. Chem. Phys. **34**, 189 (1961)
9. Stockbauer, R.: J. Chem. Phys. **58**, 3800 (1973)
10. Dey, S., Dixon, A. J., McCarthy, I. E., Weigold, E.: J. Electron Spectry. Rel. Phenom. **9**, 397 (1976)
11. Richartz, A., Buenker, R. J., Peyerimhoff, S. D.: Chem. Phys. **28**, 305 (1978)
12. Colle, R. and Salvetti, O.: Theoret. Chim. Acta (Berl.) **37**, 329 (1975)
13. McWeeny, R., in: The new world of quantum chemistry, pp. 3–31. Pullman, B., Parr, R., Eds. Amsterdam: North Holland 1977
14. Bingel, W. A.: Theoret. Chim. Acta (Berl.) **8**, 54 (1967)
15. Wigner, E. P.: Phys. Rev. **46**, 1002 (1934)
16. Lathan, W. A., Curtiss, L. A., Pople, J. A.: Mol. Phys. **22**, 1081 (1971)
17. Buenker, R. J., Peyerimhoff, S. D.: Chem. Phys. **8**, 56 (1975)

Received April 9, 1979