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Short Communication

An ab initio Calculation of the Dissociation $C_2H_2(^1\Sigma^+) \rightarrow C_2H(^2\Sigma^+) + H(^2S)$

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The collinear dissociation of acetylene to C_2H and H is studied by a generalized self-consistent procedure. The dissociation energy, the C—H force constant and stretching frequency are computed.

Key words: Geminals – Valence bond – Acetylene dissociation.

1. Introduction

The main concern of this note is to investigate the dissociation reaction of acetylene

$$C_2H_2(^1\Sigma^+) \rightarrow C_2H(^2\Sigma^+) + H(^2S),$$

employing our previously proposed method consisting in a generalized self-consistent valence bond procedure.

This dissociation is important both in its own right and for a planned study on the behaviour of acetylene absorbed on solid surfaces.

The possibility of interpreting the wave function in terms of valence bond (VB) structures is important also in the present case of a dissociation involving only the ground state and it will be even more useful for the study of other reaction paths and of the excited states [1].

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2. Theory

The theoretical framework is that described in our previous paper [2]. Since some improvements have been introduced, it is worth recalling the main steps in order to show the new points.

The orbitals at the end of the SCF optimization (step 1) are obtained diagonalizing an effective hamiltonian as defined in [3]. The next step 2 for the generation of the GVB-PP orbitals along the separated electron pair approximation (SEP) is unaltered. Then it has been found possible to perform directly the VB calculation without passing through the determination of the approximate spin coupled orbitals. This speeds up the overall procedure and entails a noticeable simplification.

3. Calculations and Conclusions

The basis set used consists of 22 orbitals expressed as standard 6-31G functions. The assumed equilibrium distances (experimental) are $R^0_{CH} = 2.0031$ and $R^0_{CC} =$

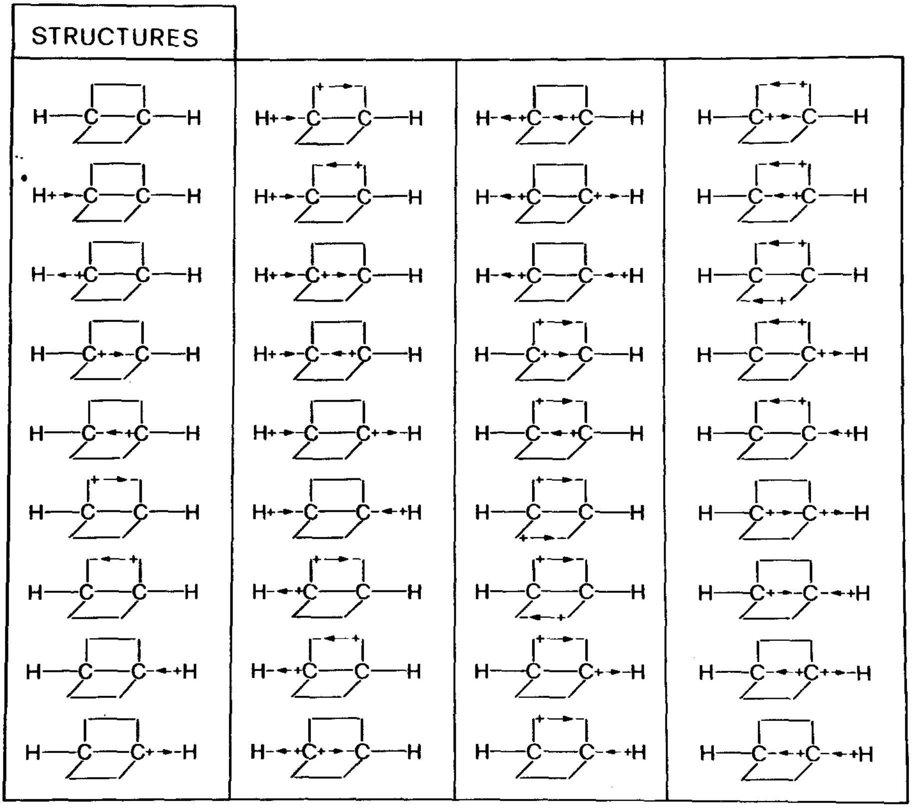

Fig. 1. Valence bond structures included in the final calculation. A line connecting two atoms means a covalent bond; an arrow with charges means an ionic bond

Table 1. Energies at different values of the C—H distance with respect to the equilibrium distance (a.u.)

ΔR_{CH}	SCF	SEP	VB
−0.75	−76.4990	−76.5521	−76.5783
−0.25	−76.7760	−76.8218	−76.8471
0.0	−76.7925	−76.8420	−76.8687
1.0	−76.6917	−76.7698	−76.7945
2.0	−76.5766	−76.7018	−76.7292
3.5	−76.4647	−76.6669	−76.6939
4.5	−76.4211	−76.6638	−76.6909
6.0	−76.3838	−76.6637	−76.6913
15.0	−76.3369	−76.6629	−76.6901

2.2734 a.u. During the collinear detachment of the H atom the C_2H geometry is kept fixed at its equilibrium value.

The final VB wave function consists of a linear combination of 36 structures belonging to the A_1 representation of the C_{4v} point group, built up from the set of localized, non orthogonal GVB-PP orbitals generated in step 2. In this way

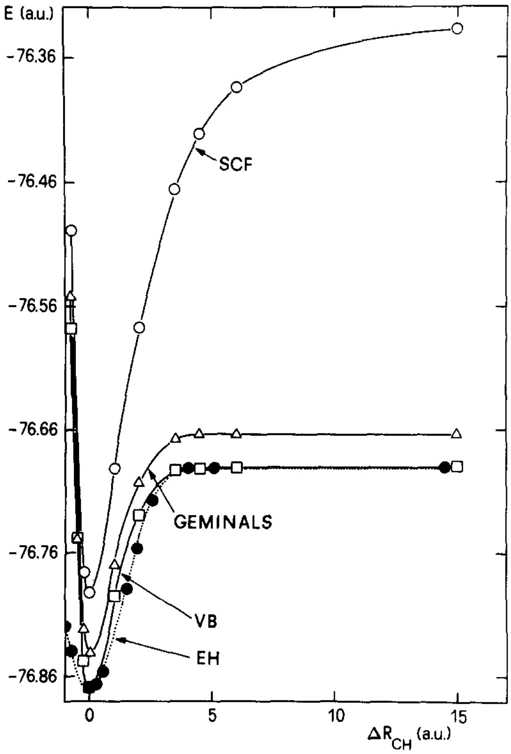

Fig. 2. Potential energy curves for the C—H distance computed at different stages: SCF, geminal, valence bond and extended Hückel

Table 2. Vibrational analysis for C—H potential energy curves

	SCF	SEP	VB	Exp
R^0_{CH} (a.u.)	1.9960	2.0040	2.0480	2.0031
D_e (a.u.)	0.448	0.171	0.172	0.180
F_{CH} (md/Å)	6.07	7.10	5.10	6.4
$\tilde{\nu}_{CH}$ (cm^{-1})	3259	3132	3026	3250

all the covalent, singly and doubly ionic structures (see Fig. 1) have been introduced, allowing for the relaxation of the strong orthogonality constraint and the inclusion of the interpair correlation energy.

Table 1 shows the energy values at the three stages of the calculation for the various C---H distances and the Fig. 2 displays the corresponding curves. The dissociation energy (zero point energy apart) turns out to be of 0.179 a.u. for both geminal and valence bond calculation. The analysis of the final geminal orbitals and the VB structures confirms the dissociation in the C_2H and H neutral fragments, while the SCF calculation gives rise to C_2H^- and H^+ ionic fragments.

A vibrational analysis has been performed [4] for all the three curves in order to get the dissociation energy corrected for the zero point energy and other quantities like the equilibrium distance (R^0_{CH}), the force constant (F_{CH}) and the fundamental frequency of the C—H stretching ($\tilde{\nu}_{CH}$). This analysis has been made treating the HC_2—H system like a diatomic molecule. The results are shown in Table 2 together with the experimental data [5, 6]. Albeit of approximate nature, these results compare well with the experimental data, giving thus reliability to our potential curves and allowing also a more complete comparison of the geminal and valence bond curves.

On the computational side the SCF and SEP iterative procedures have shown a satisfactory rate of convergence and a good numerical stability.

On the overall the proposed method has proven to be suitable for the problem at hand. As said in the introduction, the importance of the VB treatment in calculations of this type will be fully apparent in a future study of the excited state curves of acetylene.

Finally, a standard extended Hückel (EH) calculation has been performed in order to test the applicability of this semiempirical method to reaction paths of the present type. The curve obtained after a simple scaling to fit the dissociation energy, is reported as dotted line in Fig. 2. Its shape turns out to be quite similar to the valence bond (or geminal) one. This encourages the use of the EH method to the study of the dissociation reaction on a metal surface, when a cluster of metal atoms is introduced in the calculations.

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