THEORETICAL STUDY OF ACETYLENE IN THE EXTERNAL ELECTRICAL FIELD

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In this paper the stable configuration of an acetylene molecule exposed to the external homogeneous electrical field $\mathbf{F} = (0-10) \cdot 10^{10}\ \mathrm{Vm}^{-1}$ was searched. With all starting configurations considered the only minimum which was found on the energy hypersurface corresponds to the stable orientation of the $D_{\infty h}$ symmetry. Calculated eigenvalues of the Hessian matrix showed that this orientation is stable either rotationally or vibrationally. Calculations were performed on the semiempirical level using the ZDO approximation.

At this time several experimental data are available which describe the molecular behaviour in strong electrical fields. By field ion microscopy and field ionization mass spectroscopy methods the properties of molecules and ions were studied in fields up to $10^{10}-10^{11}\ \mathrm{Vm}^{-1}$ (see[1,2]). High fields of the order up to $5 \cdot 10^{9}\ \mathrm{Vm}^{-1}$ are characteristic at the metalelectrolyte interphase[3]. The role of external electrical field for a molecular adsorption in chanels of molecular sieves[4] as well as the influence of electrical double layers of solid surfaces on chemisorption and catalytic properties[5] is generally accepted.

Several theoretical papers can be found in the literature which deal with the study of a molecular behaviour in the homogeneous external electrical field. The influence of electrical field was treated in refs[6,7] using the perturbation method and polarizability and hyperpolarizability tensors were calculated by the MINDO/3 procedure. In papers[8-10] the electrical field operator was explicitly included in the molecular hamiltonian. Calculations were performed on both semiempirical[8-14] and nonempirical[15-16] levels. With the exception of paper[13] all studies dealt with molecules with permanent dipole moments. Molecules without permanent dipole moment are of some interest for such a study as the existence of several stable orientations cannot be excluded (*vide infra*).

In the paper[13] locations of stationary points of ethylene in the external electrical field were searched. It was shown that all orientations on the respective energetical hypersurface are stationary for which the field vector direction is parallel to any symmetry axis in. However, only one orientation is stable with respect to an arbitrary infinitesimal change of nuclear coordinates; it is the one where the field intensity vector is parallel to a C=C bond direction. In this paper the study was extended to the search of a stable acetylene configuration in an external electrical field. Calculations were performed on the semiempirical level in the ZDO approximation which enabled us to perform a complete analysis of energy hypersurfaces namely the geometry optimization and the analysis of stationary points obtained by means of the force constant matrices.

METHOD

The INDO method[17] (intermediate neglect of differential overlap) was used in the original parametrization throughout this work. The electrical field operator was directly incorporated into the hamiltonian using the formula[13]

$$\boldsymbol{H} = \boldsymbol{H}_0 - e\,\mathbf{F}\mathbf{z}\,, \qquad (1)$$

where $\boldsymbol{H}_0$ stands for the hamiltonian of the unperturbed system, $\mathbf{F}$ is the intensity of the electrical field and $\mathbf{z}$ is the component of the dipole moment operator in the direction of the field. (Conventionally, only the z-component of the field was chosen to bear a nonzero value.) Explicit formulas were used for the evaluation of an energy gradient the force constant matrix being calculated numerically and the geometry being optimized by the variable metric method[18,19].

Before the presentation of results a comment should be made about sources of molecular instability. By the interaction of a permanent or induced dipole moment of a molecule with the external electrical field the free rotation of a molecule with regard to the arbitrary axis perpendicular to the field intensity vector is "lost". It is convenient, therefore, to define two sources of a molecular instability – the rotational and structural ones[13]. If the gradient is vanishing and one or two nonzero eigenvalues of the force constant matrix corresponding to the rotation of a molecule as a whole are negative the system is then considered to be rotationally unstable. The stable configuration can be achieved by the rotation of a molecule around the respective axis[13]. The structural instability is connected with the existence of one or more negative vibrational eigenvalues of the force constant matrix. The stable configuration is achieved in this case by the coordinate displacement along the respective eigenvector(s).

RESULTS

In this work the stable configurations of the acetylene molecule were searched in external fields of $F = 0, 2, 4, 6, 8$, and $10 \,.\, 10^{10}\ \mathrm{V\,m^{-1}}$. Calculations were performed for several starting orientations of a molecule with respect to the field intensity vector (Fig. 1).

To achieve the true energy minimum starting geometries were purposely chosen unsymmetrical. This unsymmetry was evoked by displacements of hydrogen atoms from their equilibrium positions. For all energy minima found on the energy hypersurface total energies, force constant matrices, geometrical parameters, and density

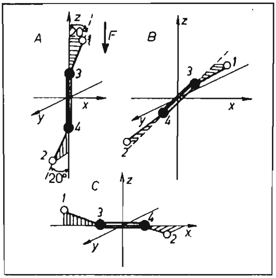


FIG. 1

Starting Orientations of the Acetylene Molecule in the External Electrical Field **F** the Intensity of which is Parallel to the *z* Axis

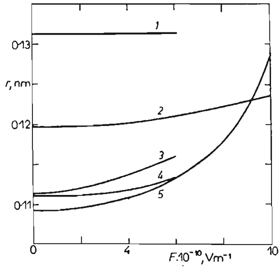


FIG. 2

Interatomic Distances *r* for Stable Orientations of Acetylene and Ethylene Molecules as Functions of the External Electrical Field Intensity **F** (curves *1* and *2* stand for C—C bond lengths of ethylene and acetylene, resp., curves *3* and *4* express the C—H bond lengths of ethylene in the negative and positive direction of the field vector, resp., curve *5* stands for a C—H bond length in acetylene)

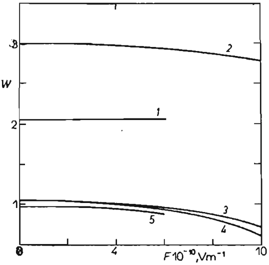


FIG. 3

Wiberg Indices for Stable Orientations of Acetylene and Ethylene Orientation as Functions of the External Electrical Field Intensity **F**.

For further explanation see the caption to Fig. 2.

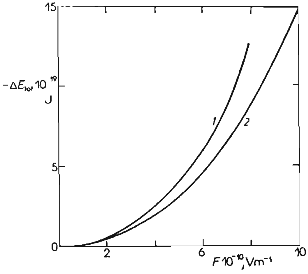
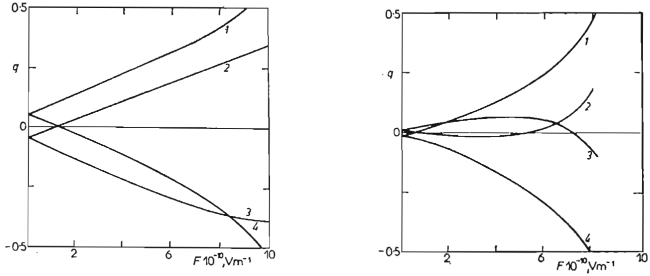


FIG. 4

Dependence of the Total Energy Changes E_{tot} for Stable Orientations of Acetylene (curve *2*) and Ethylene (curve *1*) Molecules on the External Electrical Field Intensity **F**



a *b*

FIG. 5

The Charge Distribution q Provoked by the External Electrical Field of the Intensity **F** with Stable Orientations of Acetylene (*a*) or Ethylene (*b*) (curves 1 and 2 stand for charges on atoms H and C, resp., in the negative direction of the field, curves 3 and 4 express charges on atoms C and H, resp. in the positive field direction)

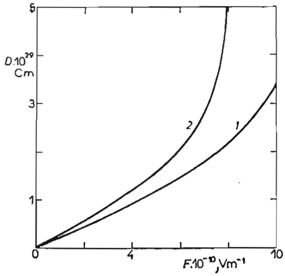


FIG. 6

Dependence of the Total Dipole Moment D on the External Electrical Field Intensity **F** for Stable Orientations of Acetylene (curve 1) and Ethylene (curve 2)

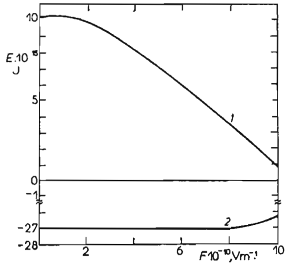


FIG. 7

Dependence of Frontier Orbital Energies on External Electrical Field Intensity **F** for Stable Orientations of Acetylene (curves 1 and 2 stand for E_{LUMO} and E_{HOMO}, resp.)

matrices were calculated. By the analysis of both the gradient and the force constant matrix it was estimated that molecular coordinates are accurate in 0·0001 nm withing the framework of the Born–Oppenheimer approximation used currently in this study.

The same energy minimum was found from all starting orientations. Similarly as in the case of ethylene[13], here also exists only one stable orientation which has $D_{\infty h}$ symmetry. All CH bond lengths are getting longer parallely with the increase of the field intensity by the similar way as with ethylene[13], the C≡C bond length is also lengthened whereas that of the C=C bond in ethylene[13] remains practically constant (Fig. 2.).

The bond strengths (Wiberg indices) of all CH bond in ethylene as well as acetylene decrease at the same time with the increase of the field intensity, the C≡C bond strength in acetylene falls down whereas that of the C=C bond remains constant. (Fig. 3).

The calculated eigenvalues of the Hessian matrix show that the A orientation of acetylene is stable either rotationally or structurally even at high fields where the similar ethylene orientation is no longer structurally stable. All eigenvalues of a Hessian matrix are non negative for this orientation (Table I) which supports the suggestion that these orientations are real minima and the molecule is therefore rotationally and structurally stable.

As for B and C orientations the geometry optimization evokes the molecular rotation with all field strengths studied and the A configuration results in all cases.

TABLE I

Selected Eigenvalues of the Hessian Matrix for Acetylene in the External Electrical Field (all values in Jm^{-2})[a]

F^b	$W_x{}^c$	$W_y{}^c$	k_1	k_2	k_3	k_4	k_5
0	0	0	151·0	155·1	373·8	378·3	1 078·2
2	4	7	150·0	152·9	367·4	387·1	1 055·8
4	13	20	162·7	168·6	391·6	401·4	986·3
6	24	21	175·4	178·0	396·9	432·5	860·1
8	40	47	198·5	203·2	461·0	468·8	469·5
10	58	55	103·8	207·4	210·0	422·2	447·0

[a] Values for a structure A presented in Fig. 1; [b] electrical field intensity in 10^{10} Vm^{-1}; [c] pseudorotation round x- and y-axes.

The dependence of total energies of acetylene and ethylene stable configurations on the electrical field intensity is presented in Fig. 4. It is seen that the geometry relaxation due to the interaction with the external field stabilises the energy of ethylene more than that of acetylene.

The polarization effect is also more pronounced with the ethylene molecule than with acetylene. This is supported by both the molecular charge redistribution and the dipole moment changes. The former property as a function of the external field is presented for acetylene and ethylene in Figs. 5*a*,*b*. It is seen that the larger energy stabilization in ethylene compared with acetylene is in the same line with the larger changes of ethylene charge densities. These changes bear a strongly parallel those of the dipole moment (Fig. 6).

The dependence of frontier orbitals E_{HOMO} and E_{LUMO} of acetylene on the field strength is presented in Fig. 7. It is seen that the ionization potential of acetylene is almost independent of the field strength unlike the distinct decrease of the electron affinity in strong fields. It follows that acetylene in electrical field becomes a stronger electron acceptor. The metal catalytic activity can be readily understood on this basis as the charge transfer from the metal to the substrate is accompanied with important molecular stabilization.

As the interaction between hydrocarbons and metal surfaces is not governed exclusively by the field effect it seems to be appropriate to extend this study in the search for configurations other than the stable ones. The corresponding calculations extended to the study of methane and ethane molecules will be presented in subsequent papers.

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