3. Automatic Geometry Optimization and Vibrational Analysis in External Electric Field: Ethylene

by **Jiří Pancíř** and **Rudolf Zahradník**

J. Heyrovský Institute of Physical Chemistry and Electrochemistry,
Czechoslovak Academy of Sciences, 121 38 Prague 2, Czechoslovakia

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Summary

Stationary points of the INDO energy hypersurface for various orientations of ethylene in external electric fields of the strength $F = 0, 2, 4, 6, 8$ and 10×10^{10} V m^{-1} were found and their characteristics studied by the force constant matrix analysis. Energies, structural parameters, charges, *Wiberg* indices and dipole moments are presented. The only stable orientation of the ethylene molecule is that for which the C–C bond is parallel to the field direction up to $F = 6 \times 10^{10}$ V m^{-1} (orientation (a) in *Fig. 1*). Above this value the molecule is structurally unstable and it decomposes to the hydride anion and the $C_2H_3^+$ cation. Rotational instability was found for two perpendicular orientations of the C–C bond with respect to the field vector, in which the field vector was parallel and perpendicular to the molecular plane. Pseudorotations with negative eigenvalues of force constant matrices lead to the stable orientation (a). No stationary points were found when the angle between the C–C bond and the field vector was between 0 and 90°. The five longest wavelength vibrational bands are presented for selected orientations and field strengths.

It is a well established fact that physical characteristics of molecules and ions in free-space approximation differ dramatically from those which characterize these systems under the influence of an external electric field. It is true that large changes are associated only with fields which could be until recently hardly generated by means of external sources. However, introduction of field ionization spectroscopy by *Müller* and of field ionization mass spectrometry (for a comprehensive account see [1]) made it possible to investigate properties of molecules and ions (including decomposition paths) in electric fields of the order 10^9-10^{11} V m^{-1}.

Previously special cells were developed [2] [3] for electro-optic studies which permitted to assign directions of polarization to electronic spectral bands (for theoretical treatment see [4]) and also to measure dipole moment changes when passing from electronic ground states to excited states. External fields used amounted to 10^6-10^7 V m^{-1} (*e.g.* in the case of acenaphthylene 5×10^6 V m^{-1} [5]). A significant progress has been made by *Jones* [6-8] who has been able to reach fields up to 5×10^7 V m^{-1} in a specially constructed infrared cell. (Recent literature concerning molecular electrostatics is reviewed in [7].)

Very high fields (up 5×10^9 V m^{-1}) can be applied not only at a metal-vacuum tip but also on a metal-electrolyte interphase [9].

Essentially each molecular or ionic species represents a source of a strong electric field. This might be of importance in quite a few connections. For example, electric fields associated *e.g.* with surface of cells in living systems may modify properties of adsorbed systems to a nonnegligible extent.

Changes in infrared spectra of nerve preparations during conduction have been interpreted in terms of high local electric fields [10] (see also [11]). In the field of physisorption, chemisorption and catalysis, the electric field inherent to the system under study may affect properties of substances and processes occurring in the system [12]. It seems that rather strong fields operate on surfaces of heterogenous catalysts regardless if the latter are metals or oxides. Species located in channels of molecular sieves are, according to rough estimates [13], exposed to fields of about 5×10^{10} V m^{-1}. Accordingly, we think that in any application of quantum chemical calculations to the behaviour of reacting molecules under common conditions of the heterogeneous catalysis, the effect of the electric field of the surface should be considered.

Being interested in changes of the electronic structure of polyatomic molecules and, in particular, in their decomposition paths under the influence of very strong fields, we have to use semiempirical types of calculations because of the following reasons: (1) to investigate the field influence it is inevitable to optimize the molecular (ionic) geometry with respect to all internal degrees of freedom. Such calculations on the *ab initio* level would be of prohibitive cost with molecules containing 6-15 atoms; (2) non-empirical *Hartree-Fock* SCF calculations alone are in principle not capable of describing correctly the decomposition paths even when performed in extensive AO-basis sets. Few interesting attempts based on semiempirical methods appeared during the last years. *Lorquet & Hall* [14] have interpreted some dissociation processes of aliphatic hydrocarbons in field ionization mass spectra by means of the equivalent orbital method [15]. An INDO study on the effect of an external electric field on methanol was published [16]. *Aleksankin et al.* studied fragmentation of positive molecular ions [17-19] behaviour of acetaldehyde [20], dioxan [21] and methylamine [22] in external electric fields. The conformational path "boat-bath" was studied for dioxan and the mechanism of rearrangement of the CH_3NH_2 positive ion was investigated. The CNDO/2 method has been used throughout. Important nonempirical studies appeared recently [23] [24]. Also the perturbation calculations in the electric field were attempted. These were the MINDO/3 calculations of elements of the polarizability and hyperpolarizability tensor [25] [26].

Method. In the presence of an external electric field, the H-core and *Hartree-Fock* matrix elements can be written as follows:

$$H_{\mu\nu} = H^0_{\mu\nu} - eF\langle\chi_\mu | z | \chi_\nu\rangle \qquad (1)$$

$$F_{\mu\nu} = F^0_{\mu\nu} - eF\langle\chi_\mu | z | \chi_\nu\rangle \qquad (2)$$

$H^0_{\mu\nu}$ and $F^0_{\mu\nu}$ are the respective terms in the absence of an external field, e is the electron charge, F is the field strength and $\langle\chi_\mu|z|\chi_\nu\rangle$ are matrix elements of the projections of the electronic radius vector on to the vector of the electric field. In our calculation, this vector was directed along the z-axis. In the CNDO/2 or INDO calculations only diagonal elements and nondiagonal elements with the basis functions s and p_z, centered on the same atom, are nonvanishing for the z operator. Hence

$$\langle\chi_{\mu,\mathrm{A}}|z|\chi_{\mu,\mathrm{A}}\rangle = z_\mathrm{A} \tag{3}$$

$$\langle\chi_{\mathrm{s,A}}|z|\chi_{2\mathrm{p_z,A}}\rangle = 0.76379/\vartheta_\mathrm{A} \tag{4}$$

otherwise

$$\langle\chi_\mu|z|\chi_\nu\rangle = 0 \tag{5}$$

z_A is the z coordinate of the atom A, ϑ_A is the *Slater* exponent. The total energy can be written as

$$E = E^0 - \mathrm{e}F\Big(\sum_\mu P^\mathrm{A}_{\mu\mu} z_\mathrm{A} + 1.52758 \sum_\mathrm{A} P^\mathrm{A}_{2\mathrm{s},2\mathrm{p_z}}/\vartheta_\mathrm{A} - \sum_\mathrm{A} Z_\mathrm{A} z_\mathrm{A}\Big) \tag{6}$$

where E^0 is the total energy in the absence of an electric field, $P^\mathrm{A}_{\mu\mu}$ are the electron densities of the electrons centered on the atom A, $P^\mathrm{A}_{\mathrm{s},2\mathrm{p_z}}$ and Z_A are bond orders for s and p_z atomic orbitals and core charges. Elements of the energy gradient in the z coordinate are

$$\frac{\partial E}{\partial z_\mathrm{A}} = \frac{\partial E^0}{\partial z_\mathrm{A}} - \mathrm{e}F\Big(\sum_{\mu\varepsilon\mathrm{A}} P_{\mu\mu} - Z_\mathrm{A}\Big) \tag{7}$$

The stationary point is achieved, when all these gradient elements vanish. Relations (1)–(7) were incorporated into our program for the automatic molecular geometry optimization and for the *Wilson* vibrational analysis [27]. The INDO method was used throughout.

Results. Before presenting specific results a few general remarks are worth mentioning. A nonlinear molecule looses two rotational degrees of freedom in the external electric field, only a free rotation around the z-axis is retained. The *Hessian* matrix will then contain four zero eigenvalues corresponding to translations and the rotation around the z-axis, two nonzero eigenvalues corresponding to hindered rotations around the x- and y-axes and 3N-6 vibrational eigenvalues. It is thus possible to consider two sources of molecular instability, rotational and structural. If the gradient is zero and one or both nonzero rotational eigenvalues are negative, the molecule is rotationally unstable. It is possible to achieve the stable configuration by rotation of the molecule around the corresponding axis. Structural instability is associated with one or more nonzero vibrational eigenvalues. The passage to the stable configuration must be accompanied by structural changes. With strong fields, two new bands in vibrational spectra can be observed which can be assigned to the above mentioned pseudorotations.

In the previous studies, except for molecular hydrogen only molecules with a permanent dipole moment were calculated. As the elements $\langle\chi_\mu|z|\chi_\nu\rangle$ are virtually the elements of the dipole moment, it is not surprising that for the stable configuration the dipole moment must lie in the direction of the electric field. Particularly interesting are then molecules without a permanent dipole moment. In such cases the question arises whether the dipole moment induced by the electric field can stabilize the molecule in several orientations. Ethylene seemed to be a proper molecule for such a study.

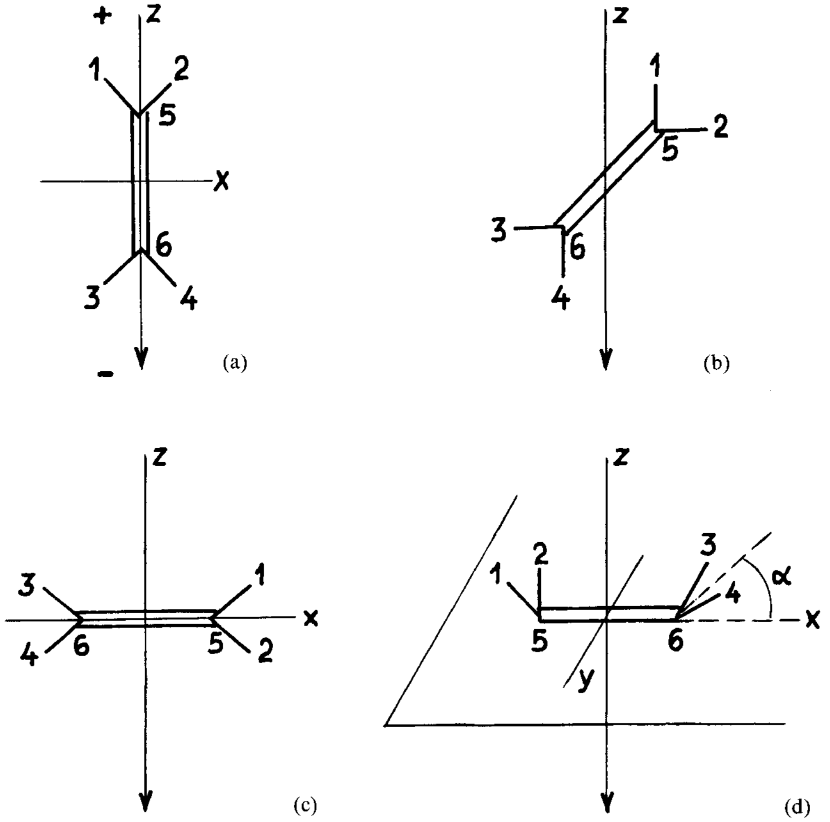

Fig. 1. *Orientations of ethylene in the electric field*

By means of the method described the following characteristics for the stationary points on the energy hypersurface of ethylene, exposed to an external electric field, have been obtained: total energies, geometry, electron distribution, dipole moments, force constant matrix and energies of normal vibrational modes. Calculations have been performed for four ethylene orientations labelled (a) to (d) in *Figure 1*. Six external field gradients have been considered, namely 0, 2, 4, 6, 8 and 10×10^{10} V m^{-1}. Results associated with the (b)-orientation *(Fig. 1)* are not considered in the further text because when $F \leqq 6 \times 10^{10}$ V m^{-1} this orientation passes into the (a) orientation; for $F = 8 \times 10^{10}$ V m^{-1} one of the C-, H-bonds undergoes polar splitting and the hydride anion (H^-) and the $C_2H_3^+$ cation are formed. If F equals 2 or 4×10^{10} V m^{-1} the convergence of the optimization procedure is very poor and reaching a stationary point requires up to one thousand variable metric iterations. This effect can be ascribed to an extremely low eigenvalue of the rotation around the y-axis with the structure (a) (0.4 J m^{-2} for $F = 2 \times 10^{10}$ V m^{-1}).

Optimized energy and geometry characteristics for the orientations (a), (c) and (d) are summarized in *Table 1;* charges, *Wiberg* bond indices and dipole moments in *Table 2.* For all these orientations stationary points were obtained with zero norm of gradient unless the structural instability arose with structure (a).

Table 1. *Energies and geometrical parameters for ethylene in the electric field*[a])

Structure[a])	F [b])	-E [c])	r_{15} [d])	r_{25} [d])	r_{36} [d])	r_{46} [d])	r_{56} [d])	ϑ_{156}	ϑ_{256}	ϑ_{365}	ϑ_{465}	α [e])
(a)	0	7.2223	0.1115	0.1115	0.1115	0.1115	0.1312	124.3	124.3	124.3	124.3	
	2	7.2282	0.1121	0.1121	0.1114	0.1114	0.1313	126.0	126.0	123.7	123.7	
	4	7.2468	0.1135	0.1135	0.1118	0.1118	0.1314	128.9	128.9	124.6	124.6	
	6	7.2807	0.1162	0.1162	0.1130	0.1130	0.1311	133.2	133.2	128.2	128.2	
	8	7.3478	0.1294	0.1294	0.1236	0.1236	0.1255	143.6	143.6	152.6	152.6	
(c)	2	7.2260	0.1121	0.1113	0.1121	0.1113	0.1312	122.8	125.2	122.8	125.2	
	4	7.2374	0.1133	0.1116	0.1133	0.1116	0.1311	121.0	125.3	121.0	125.3	
	6	7.2572	0.1152	0.1124	0.1152	0.1124	0.1310	119.1	124.0	119.1	124.0	
	8	7.2874	0.1181	0.1140	0.1181	0.1140	0.1307	117.3	121.2	117.3	121.2	
	10	7.3303	0.1234	0.1173	0.1234	0.1173	0.1301	114.9	117.1	114.9	117.1	
(d)	2	7.2223	0.1115	0.1115	0.1115	0.1115	0.1312	124.3	124.3	124.3	124.3	0.33
	4	7.2223	0.1115	0.1115	0.1115	0.1115	0.1312	124.3	124.3	124.3	124.3	0.91
	6	7.2223	0.1115	0.1115	0.1115	0.1115	0.1312	124.3	124.3	124.3	124.3	1.15
	8	7.2223	0.1115	0.1115	0.1115	0.1115	0.1312	124.3	124.3	124.3	124.3	2.03
	10	7.2219	0.1115	0.1115	0.1115	0.1115	0.1311	124.3	124.3	124.3	124.3	4.22

[a]) For structure and numbering of atoms *cf. Fig. 1.* [b]) Electrical field strength in 10^{-10} V m^{-1}. [c]) Total energy in 10^{17} J. [d]) Bond lengths in nm. [e]) *Cf. Fig. 1.*

Table 2. *Charges* (q), Wiberg *bond indices* (p) *and dipole moments* (D) *for ethylene in electric field*[a])

Structure[a])	*F* [b])	q_1	q_2	q_3	q_4	q_5	q_6	p_{15}	p_{25}	p_{36}	p_{46}	p_{56}	D [c])
(a)	0	−0.008	−0.008	−0.008	−0.008	0.015	0.015	0.956	0.956	0.956	0.956	2.073	0.00
	2	−0.083	−0.083	0.064	0.064	−0.008	0.044	0.945	0.945	0.952	0.952	2.065	5.40
	4	−0.168	−0.168	0.141	0.141	−0.012	0.067	0.915	0.915	0.931	0.931	2.048	11.47
	6	−0.276	−0.276	0.237	0.237	0.021	0.057	0.848	0.848	0.879	0.879	2.057	19.75
	8	−0.525	−0.525	0.479	0.479	0.170	−0.077	0.570	0.571	0.576	0.576	2.643	48.93
(c)	2	−0.083	0.065	−0.083	0.065	0.017	0.017	0.945	0.954	0.945	0.954	2.074	3.04
	4	−0.161	0.138	−0.161	0.138	0.023	0.023	0.922	0.941	0.922	0.941	2.079	6.34
	6	−0.243	0.213	−0.243	0.213	0.030	0.030	0.884	0.915	0.884	0.915	2.087	10.21
	8	−0.332	0.297	−0.332	0.297	0.035	0.035	0.828	0.871	0.828	0.871	2.104	15.18
	10	−0.438	0.398	−0.438	0.398	0.040	0.040	0.737	0.795	0.737	0.795	2.141	22.55
(d)	2	−0.008	−0.008	−0.008	−0.008	0.016	0.016	0.956	0.956	0.956	0.956	2.073	0.00
	4	−0.008	−0.008	−0.008	−0.008	0.017	0.017	0.956	0.956	0.956	0.956	2.073	0.02
	6	−0.010	−0.010	−0.010	−0.010	0.020	0.020	0.956	0.956	0.956	0.956	2.073	0.03
	8	−0.013	−0.013	−0.013	−0.013	0.027	0.027	0.955	0.955	0.955	0.955	2.073	0.07
	10	−0.022	−0.022	−0.022	−0.022	0.045	0.045	0.954	0.954	0.954	0.954	2.074	0.13

[a]) For structure and numbering of atoms *cf. Fig. 1.* [b]) Electric field strength in 10^{-10} V m^{-1}. [c]) Dipole moment in 10^{30} cm.

As the field strength is increased, the energy decrease with the orientation (a) is steeper than it is with the orientation (c). The orientation (a) is therefore favoured on energy grounds. The calculated eigenvectors of the *Hessian* matrix do correspond to this finding. These values are presented in *Table 3.* For the sake of brevity only eigenvalues corresponding to pseudorotations and the five lowest vibrational eigenvalues are presented. All eigenvalues of the *Hessian* matrix for the orientation (a) are positive for the field up to 6×10^{10} V m^{-1}; this means that all the points are real minima.

Table 3. *Selected eigenvalues of* Hessian *matrix* (all values in J m^{-2})

Structure[a])	*F* [b])	W_x [c])	W_y [c])	k_1	k_2	k_3	k_4	k_5
(a)	0	0	0	46	96	152	233	256
	2	2	0.4	44	96	149	236	255
	6	16	4	30	97	111	253	259
	8	34	51	−69	48	115	122	268
(c)	2	2	−1	47	96	151	234	252
	10	62	−13	83	103	148	167	212
(d)	2	−2	−3	46	93	152	227	256
	10	−44	−64	30	46	81	113	153

[a]) See *Fig. 1.* [b]) Electronic field strength in 10^{-10} V m^{-1}. [c]) Pseudorotations around the x- and y-axes.

One of the eigenvalues becomes negative if $F = 8 \times 10^{10}$ V m^{-1}; accordingly this point represents a saddle point. The molecule then will be structurally unstable; the respective eigenvector informs us about the decomposition path of this saddle point. The corresponding motion is indicated in *Fig. 2.* Its main features are the hydride migration and shortening of the C–C bond. This shortening reflects the fact that the remaining atoms rearrange in such a way that protonized acetylene is formed. With a gradient of 10×10^{10} V m^{-1} the hydride ion is completely removed. The situation after four hundred variable metric iterations is visualized in *Figure 3.* The molecule is split into two ions and the separation between them increases in each variable metric step. Therefore, a complete geometry optimization cannot be accomplished.

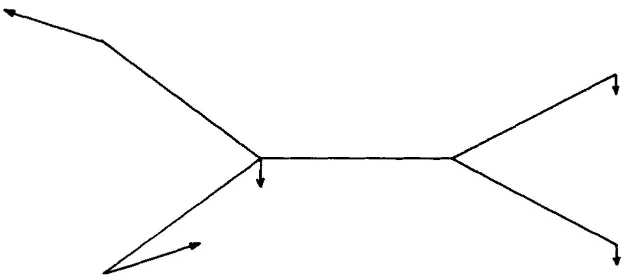

Fig. 2. *The eigenvector of the force constant matrix with negative eigenvalue for the orientation (a)* (cf. Fig. 1) *and the field strength* 8×10^{10} V m^{-1}

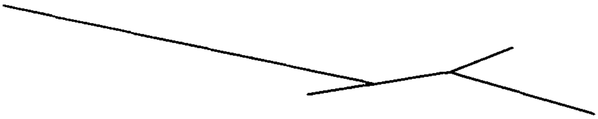

Fig. 3. *The decomposition path for the orientation (a)* (cf. Fig. 1) *and the field strength 10^{11} V m^{-1}.* Situation after 400 variable metric iterations (see also the text).

With the orientation (c), similarly as with (a), the total energy decreases with increasing field strength but the decrease is less pronounced. In this case the *Hessian* matrix has a single negative eigenvalue; its eigenvector suggests that the orientation (c) passes into the energetically most convenient orientation (c) by a single pseudorotation around the x-axis *(Fig. 1)*. This configuration is thus rotationally unstable. The bonds do not dissociate even when $F = 10 \times 10^{10}$ V m^{-1}. The C–H bonds somewhat increase and the C–C bond decreases in length with increasing F. The overall effects of the field are less pronounced than with the orientation (a). As far as the (d)-orientation is concerned, the angle a somewhat increases with increasing F while the other energy and geometry characteristics are only little influenced. The change of a is entirely due to the polarization terms of the $\langle\chi_{s,A}|z|\chi_{2p_z,A}\rangle$ elements in Eq. (4). However, in spite of the lack of sensitivity of the total energy and geometry with respect to the external field, the force constants are changed to a large extent as with the other studied orientations. The *Hessian* matrix possesses two negative eigenvalues. Their eigenvectors correspond to the molecular pseudorotations with respect to two axes which are perpendicular to the electric field vector. Due to these rotations the orientations (d) would pass into the orientations (a) and (c), respectively. Orientation (d) is thus rotationally unstable.

Finally, the bond length changes are correctly reflected in the values of the *Wiberg* indices (*cf. Table 2*).

Table 4. *Lowest frequencies of normal vibration modes for ethylene in the electric field* (all values are in cm^{-1})[a])

Structure[b])	F[c])	W_x[d])	W_y[d])	k_1	k_2	k_3	k_4	k_5
Type of vibration mode				CH_2 sym. rock	CH_2 wag	CH_2 wag	CH_2 twist	CH_2 asym. rock
experimental	0	0	0	826	943	949	1023	1236
(a)	0	0	0	797	1236	1238	1269	1254
	2	113	62	771	1223	1262	1271	1255
	6	341	206	594	1264	1323	1277	1270
(c)	2	202	[e])	807	1218	1239	1295	1248
	10	1020	[e])	1106	1181	1316	1474	919
(d)	2	[e])	[e])	797	1211	1220	1230[f])	1276[f])
	10	[e])	[e])	794	462	730	700	1284

[a]) Frequencies are arranged in order of experimental values. [b]) See *Fig. 1*. [c]) Electric field strength in 10^{-10} V m^{-1}. [d]) Pseudorotations around the x- and y-axes. [e]) Imaginary value results. [f]) Strong coupling between rock and twist character.

Chemically quite significant changes in the electron distribution and induced dipole moments occur already with the weakest field studied in this paper *(cf. Table 2)*. The most pronounced changes of electron distribution and dipole moments occur with the orientation (a) which is due to the high polarizability along the C=C bond. This orientation is also the only one stable at low fields and it is structurally unstable at higher fields. No stationary point corresponds to the nonsymmetric location of a molecule in the electrical field (structure (b)). Structures (c) and (d) are stationary points on the energy hypersurface but both are rotationally unstable. However, structures (c) and (d) may be stabilized on the catalytic surface *e.g.* due to specific interactions with metal atoms. The IR. spectrum can then be used to recognize among structures. The longest wavelength band (CH_2 sym. rocking mode) is shifted to lower frequencies with the structure (a), to higher frequencies with the structure (b) and very slightly with the structure (c). Large shift to lower frequencies can be observed with the structure (c) for two CH_2 wagging and CH_2 twisting modes. The changes are summarized in the *Table 4* for five longest wavelength bands along with two new bands which originate from the hindered rotation in the electric field.

REFERENCES

[1] *H.-D. Beckey*, 'Field Ionization Mass Spectrometry', Akademie-Verlag, Berlin 1971.
[2] *H. Labhart*, Chimia *15*, 20 (1961).
[3] *J. Czekalla*, Chimia *15*, 26 (1961).
[4] *W. Liptay*, Angew. Chem., Int. Ed. *8*, 177 (1969).
[5] *K. Seibold, R. Zahradník & H. Labhart*, Helv. *53*, 805 (1970).
[6] *D. E. H. Jones*, J. Chem. Soc. Chem. Commun. *1972*, 435.
[7] *D. E. H. Jones*, J. Chem. Soc. Faraday Trans. II *1976*, 1397.
[8] *D. E. H. Jones*, J. Chem. Soc. Faraday Trans. II *1976*, 1406.
[9] *J. D. E. McIntyre*, in 'Advances in Electrochemistry and Electrochemical Engineering', edited by R. H. Muller, Vol. 9, John Wiley & Sons, Inc., New York 1973.
[10] *M. H. Sherebrin, B. A. E. MacClement & A. J. Franko*, Biophys. J. *12*, 977 (1972).
[11] *F. H. Jonhson, H. Eyring & M. J. Polissar*, 'The Kinetic Basis of Molecular Biology', p. 556, Wiley & Sons, Inc., New York 1954.
[12] *A. J. Bennett*, Surface Sci. *50*, 77 (1975).
[13] *V. Bosáček*, personal communication (1976).
[14] *J. C. Lorquet*, Mol. Physics *9*, 101 (1965).
[15] *J. C. Lorquet & G. G. Hall*, Mol. Physics *9*, 29 (1965).
[16] *D. G. Bounds, A. Hinchliffe & M. Barber*, J. mol. Struct. *37*, 283 (1977).
[17] *M. M. Aleksankin & V. V. Lobanov*, Int. J. Mass Spectr. Ion Physics *15*, 1 (1974).
[18] *V. V. Lobanov, M. M. Aleksankin & Yu. A. Kruglyak*, Int. Mass Spectr. Ion Physics *18*, 275 (1975).
[19] *V. V. Lobanov, Yu. A. Kruglyak & M. M. Aleksankin*, Teor. eksper. Chimia *12*, 48 (1976).
[20] *V. V. Lobanov, M. M. Aleksankin & Yu. A. Kruglyak*, Preprint No. ITP-74-15E.
[21] *V. V. Lobanov, M. M. Aleksankin & Yu. A. Kruglyak*, Preprint No. ITP-76-141P.
[22] *V. V. Lobanov, M. M. Aleksankin & Yu. A. Kruglyak*, Preprint No. ITP-76-146P.
[23] *P. Drussbach & P. Schmittinger*, Z. Naturforsch. *25a*, 834 (1970) and papers cited therein.
[24] *G. B. Bacskay & N. S. Hush*, Theor. chim. Acta *32*, 311 (1974).
[25] *R. C. Bingham, M. J. S. Dewar & D. H. Lo*, J. Amer. chem. Soc. *97*, 1307 (1975).
[26] *M. J. S. Dewar, S. H. Suck, P. K. Weiner & J. G. Bergman, Jr.*, Chem. Physics Letters *38*, 226 (1976).
[27] *J. Pancíř*, Collect. Czechoslov. chem. Commun. *40*, 2726 (1975).