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BUDAPEST

THEORETICAL APPROACH TO CHARGE TRANSFER BETWEEN MOLECULES AND THEIR IONS

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ABSTRACT

   Fast charge transport due to electron transfer between positive or
negative ions and corresponding molecules has been observed in certain cases
the conjecture being that similarity in ionic and molecular structure is a
prerequisite of such processes. The aim of the present work is to prove this
suggestion made by Warman, Hummel et al. A series of CNDO/2 calculations
were carried out for *cyclo*-hexane, *cyclo*-pentane and methane molecule and
positive ion, and for hexafluorobenzene molecule and negative ion. The ionic
and molecular bond lengths were found to differ less then the RMS molecular
vibrational amplitudes in the cyclic compounds whereas a large difference
between the geometries of ion and molecule was obtained for methane. This
showns the structural similarity to be a sufficient condition for effective
electron transfer.
   The mobility of positive holes was estimated in terms of a modified
activated complex theory. The results are in reasonable agreement with the
experiments.

АННОТАЦИЯ

   Между положительными и отрицательными ионами и соответствующими им ней-
тральными молекулами при передаче электрона в отдельных случаях возможно явление
быстрого транспорта заряда. По мнению Вармана и Хаммеля необходимым условием
для данного процесса является подобие в структуре иона и молекулы. Целью ра-
боты являлось исследование данного предположения. Проведены серии вычислений
методом CNDO/2 для молекул циклогексана, циклопентана, метана и их соответ-
ствующих положительных ионов, а также молекулы гексафторбензола и её отрица-
тельного иона.
   Было найдено, что для циклических соединений отличие между соответству-
ющими ионными и молекулярными длинами связей меньше, чем средняя вибрацион-
ная амплитуда, изьеренная для нейтральных молекул, а в случае метана расчет-
ные данные для молекулы и положительного иона значительно отличаются. Полу-
ченные данные подтверждают, что подобность в структуре является достаточным
условием для эффективной передачи электрона.
   Проведена оценка подвижности положительных дырок, исходя из модифициро-
ванной теории "активированного комплекса".
   Полученные результаты находятся в разумном согласии с эксперименталь-
ными данными.

KIVONAT

   Semleges molekulák és pozitiv vagy negativ ionjaik között lejátszódó
elektronátadás bizonyos esetekben gyors töltésvándorlást eredményezhet.
Warman, Hummel és munkatársaik feltételezték, hogy ennek szükséges feltétele
az ion és a molekula szerkezetének hasonlósága. Munkánk célja e hipotézis
vizsgálata volt.
   CNDO/2 módszerrel meghatároztuk a c-hexán, c-pentán és metán molekula
és a megfelelő pozitiv ion, valamint a hexafluor-benzol molekula és a nega-
tiv ion egyensulyi geometriáját. A ciklikus vegyületekben a molekula és az
ion megfelelő kötéshosszainak eltérését kisebbnek találtuk az adott kötés -
semleges molekulán mért - közepes rezgési amplitudójánál. A metán molekula
és a pozitiv ion geometriája - az előző értelemben - lényegesen különbözik.
Eredményeink arra utalnak, hogy a geometriai hasonlóság a gyors elektronván-
dorlásnak valóban szükséges feltétele.
   Az "aktivált komplex"-elmélet módositásával megbecsültük a pozitiv lyu-
kak mozgékonyságát is: az eredmények a kisérleti adatokkal ésszerü egyezés-
ben állnak.

INTRODUCTION

The concept of electrical conductivity in liquids has been associated with the process of ion migration since Arrhenius's days. Electricity in aqueous solutions has been thought to be transported by the motion of charge carriers of atomic or molecular dimensions ever since. Only the exceptionally high mobility of protons and hydroxyl ions has cast some doubt on this picture recalling the old idea, conceived by Grotthuss, which assumes a series of ionic dissociations and recombinations as a possible mechanism of charge transfer. It happened only as late as the early sixties that excess electrons, known earlier to exsist in ammonia were discovered in water, and in other dipolar solutions and hence a third mechanism of conductance, the transport of excess /solvated/ electrons, had to be considered.

Non-polar insulating liquids do not contain charge carriers of any nature as stable species. Nevertheless, these substances can also be made to conduct electricity either by irradiating them with high energy particles or quanta or by injecting electrons from a suitable source. By virtue of analogy to aqueous systems this increased conductivity was also attributed to ion transport. It has become clear only fairly recently that, provided no electron capturing agent is present, the negative charge in liquids like liquified rare gases or saturated hydrocarbons is carried by excess electrons. The positive charge, however, was immutably thought to be bound to molecular ions. This picture rested on the early observations that a/ negative charge mobility is usually much higher than that attributable to molecular ions, b/ this high mobility decreases to that of molecular ions if an electron scavenger is present, and c/ positive charge mobility is as low as that of mulecular ions.

A series of experiments carried out at the Interuniversitair Reactor Institute, Delft, rendered the above statements to be of limited validity[1]. Determination of reaction rate constants and microwave conductivity have shown that the positive charge carrier in *cyclo*-hexane, *trans*-decaline and methyl-cyclohexane exhibits a mobility which is one or two orders of magnitude higher than that of a molecular ion in the same liquid.

It has also been demonstrated that the absence of any electron scavenger is not an absolute necessity for high mobility of the negative charge carriers.

Whereas it has been found true that an admixture of hexafluorobenzene, a well known electron scavenger, decreases drastically the negative charge mobility in saturated hydrocarbons, pure hexafluoreobenzene has been demonstrated to contain a negative charge carrier which moves much faster than a conventional negative ion [2].

This unorthodox behaviour of charge migration is attributed by the Delft group to resonance charge transfer [1]. Positive charges are thought to migrate as holes - the charge jumping from ion to neighbouring molecule, viz.

$$C_6H_{12}^+ + C_6H_{12} \rightarrow C_6H_{12} + C_6H_{12}^+ \quad .$$
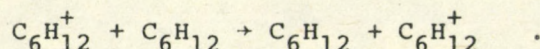
The negative charge motion in hexafluorobenzene is assumed to obey a similar scheme,

$$C_6F_6^- + C_6F_6 \rightarrow C_6F_6 + C_6F_6^- \quad .$$
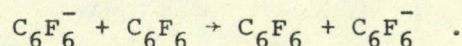
It was soon realized [1] that a prerequisite of such processes was the geometrical similarity of molecule and ion. The transformation of ion to molecule and _vice versa_ can proceed fast only when does not involve any rearrangement of the skeleton of the molecule or the ion. This can be regarded as a consequence of the Franck-Condon principle.

The aim of the present treatment is to attempt a quantitative description of the above idea. A series of quantum chemical calculations were carried out to determine the geometrical structures of certain molecules and corresponding molecular ions. Four molecules were selected, two of them were experimentally found to be prone to charge transfer, two others were not demonstrated as exhibiting this ability. Hexafluorobenzene and _cyclo_-hexane are the examples for electron and hole transport, respectively, whereas methane and _cyclo_-pentane are the liquids in which such a process has not been observed.

If the conjecture of the Delft group [1] is correct liquids in which charge transfer proceeds are made of molecules which are similar to their ions. A molecule and its ion are regarded as similar to each other if the corresponding atomic coordinates of the two entities differ less than the amplitude of vibration along this coordinate.

The final part of the paper gives an order-of-magnitude estimate of mobility for positive charge transfer. This treatment is a counterpart of a recent calculation which refers to electron transfer between hexafluorobenzene molecule and negative ion [3].

QUANTUM CHEMICAL CALCULATIONS

Wave functions and energies of the molecules and ions were calculated by making use of the semi-empirical CNDO/2 method in view of its moderate computer time requirement and the reliability of the geometrical information it renders.

The calculations were based on a developed version of the original CNDO/2 program [4]. Appropriate extensions were made for obtaining the self-consistent orbitals of open shell systems using the method of Pople and Nesbet [5]. The density and Fock matrices are divided into two parts according to the two possible spin states. Separate SCF iterations were performed for both parts in the form of two sets of Roothan equations, i.e.

$$\underline{F}^{\alpha} \underline{c}_i^{\alpha} = \epsilon_i^{\alpha} \underline{S} \, \underline{c}_i^{\alpha}$$

$$\underline{F}^{\beta} c_i^{\beta} = \epsilon_i^{\beta} \underline{S} \, c_i^{\beta}$$

(1)

where $\underline{c}_i^{\alpha}$ and $\underline{c}_i^{\beta}$ contain the coefficients of the φ_i^{α} and φ_i^{β} orbitals, ϵ_i^{α} and ϵ_i^{β} are the corresponding orbital energies, $\underline{F}^{\alpha}$ and $\underline{F}^{\beta}$ are the Fock matrices and $\underline{\underline{S}}$ contains the overlap integrals.

Having constructed the SCF wave functions and orbital energies we employed the geometry otpimization method of Nalewajski [6] to obtain a local optimal geometry. By this we mean a geometry which corresponds to a local minimum of the total energy without any change in the SCF Fock matrix. This optimal geometry is denoted by $r_{A-B}^{(1)}$ in the illustrative *Fig.1*.

The geometry obtained in this way was improved by calculating each force which acts on the j-th atom, P_j, and by making use of the force field method of Pulay and Török [7].

The expression

$$\underline{P}_j = -\text{grad}_j E$$

(2)

refers to each atom where E is the total energy of the molecule. If the forces are known it is possible to find a better geometry by displacing each nucleus in the direction of the force and with a distance which is proportional to the absolute value of the force. A new SCF iteration is then carried out with the new coordinates. After getting the new local optimal geometry the forces are determined again /cf. *Fig.1*/. This algorithm yields the energy-optimized geometry of the molecule together with the SCF wave function.

The calculated equilibrium bond lengths of the molecules, given in Table I, are in fair agreement with the experimental data. The same result would have been obtained without using Nalewajski's method as was demonstrated by earlier trial calculations on a few smaller molecules. With larger
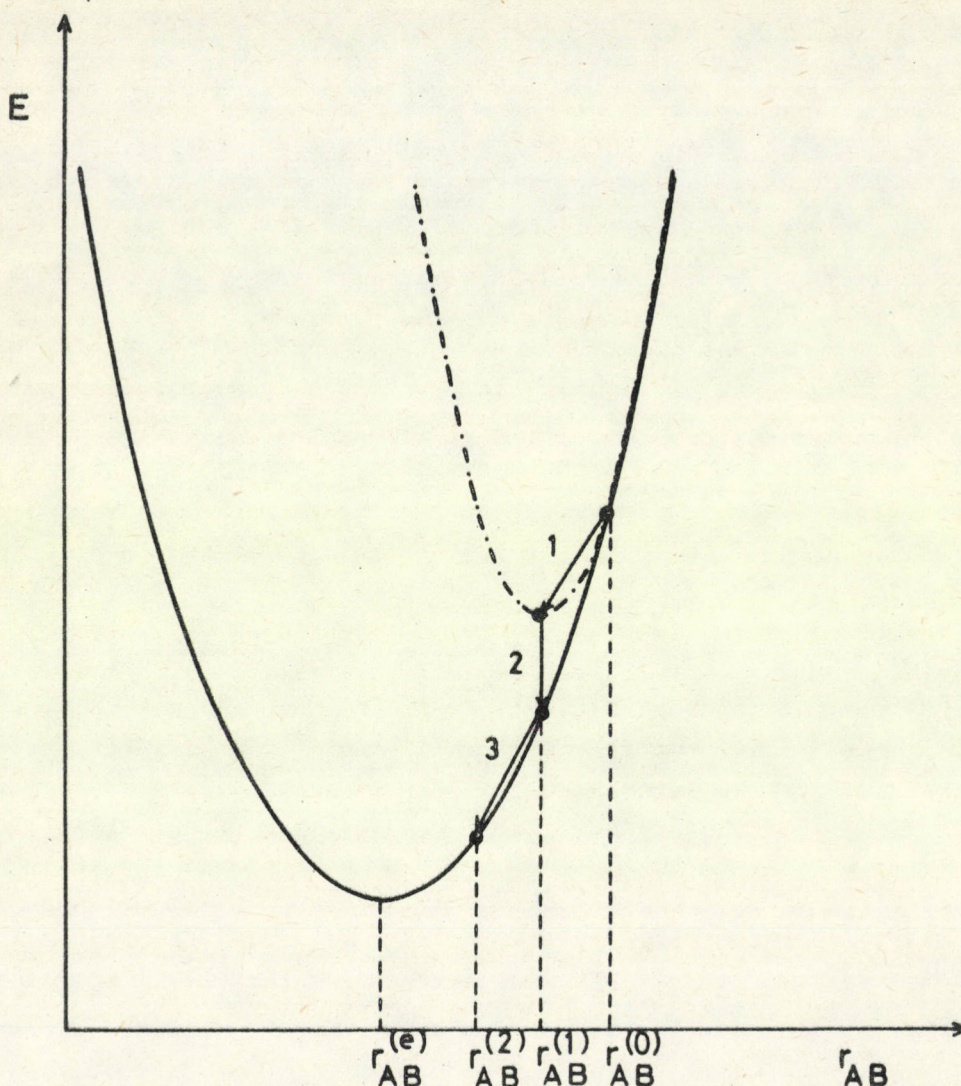
Fig. 1. *Illustration of nesting of Nalevajski's method [6] into the force field method.*
Energy versus bond length diagram of a hypothetical diatomic molecule. Continuous line: CNDO/2 total energy as a function of bond length, minimum energy at $r^{(e)}_{AB}$.
Dotted line: minimum at $r^{(1)}_{AB}$ obtained by the Fock matrix which corresponds to the initial distance $r^{(o)}_{AB}$.

Step 1 improves this geometry by Nalewajski's method; step 2 represents an SCF iteration which yields the new Fock matrix; step 3 is the computation of forces acting upon the atoms by making use of the force field method by Pulay and Török [7] obtaining the next distance $r^{(2)}_{AB}$.

systems, however, the method makes the algorithm more effective by reducing the number of time-consuming SCF iterations.

RESULTS AND DISCUSSION

Using the method briefly outlined in the previous section four molecules were studied: these being hexafluorobenzene methane, *cyclo*-hexene and *cyclo*-pentane. The results obtained for equilibrium geometries of the neutral molecules and the corresponding ions are listed in Tables II-V. (Only those internuclear distances are given where the mean vibrational amplitudes are known from experiment).

A common feature observed in all four cases is that the symmetry of the neutral molecule decreses upon ion formation in accordance with the Jahn-Teller theorem [8]. The sic C-C bonds, for example, of C_6F_6 and C_6F_{12}, cease to be equivalent in the respective negative or positive ions: a threefold splitting occurs.

The equilibrium geometry of the $C_6F_6^-$ ion was found to be slightly non-planar by us with out-of-plane angles as small as a few tenths of a degree. The chair-like structure proposed by Symons et al. [9] was found to be unstable, successive geometrical optimization steps having brought the ion close to the planar form.

Computing the differences, Δd, between the bond lengths in the cyclic molecules and those in the corresponding ions one finds all of them to be smaller than the mean-squere amplitudes along the bond /cf. Tables II-V/. Thus as far as bond lengths are concerned the Franck-Condon factor of electron transfer between cyclic molecules and their ions is about 1. The non-bonded distances also comply with the requirement of similarity in the case of hexafluorobenzene and *cyclo*-pentane, i.e. the differences between the non-bonded distances are smaller than the corresponding vibrational amplitudes of the molecules. With *cyclo*-hexane, however, the situation is somewhat different. Here the Δd values for the second and third neighbour C atoms are somewhat larger than the molecular amplitudes.

Methane shows strikingly different features. The tetrahedral symmetry of the neutral molecule is completely lost in the positive ion and the differences both in the C-H bond lengths and in the H...H distances are three to four times larger than the amplitudes of molecular vibrations. One may safely conclude to a very low Franck-Condon factor of electron transfer between CH_4 and CH_4^+.

The fulfiment of the admittedly too strict requirement of similarity between C_6F_6 and $C_6F_6^-$ is in good agreement with the observed electron transport in hexafluorobenzene. The same finding regarding C_5H_{10} and $C_5H_{10}^+$ leaves some room to speculation.

The fact that electron transfer between positive ion and molecule has not been observed in *cyclo*-pentane [1/a] indicates that a./ our condition if met, renders not the necessity only but the possibility that charge transfer or b./ some experimental difficulty has prevented one observing this process. As to the latter, impurity effects or an electron transfer

which happens to be not much faster than the motion of a molecular ion might serve as an explanation. The *cyclo*-hexane data strongly suggest that the similarity of bond lengths is sufficient for a fast charge transfer to take place. Distances between non-bonded atoms do not seem to influence decisively the Franck-Condon factor of this process.

Admittedly the weakest point of the present method lies in its numerical nature, i.e. no general predictions can be made and the molecules in question have to be examined individually. Technically speaking, the method is suitable only for relatively small molecules because of computer time limitations. Furthermore, the condition of geometrical similarity refers only to the entropy factor of the rate of charge transfer. The energy factor may play an equally important role.

In spite of these shortcomings we believe that the method used here casts some light on the problem why intermolecular charge transfer between corresponding ions and molecules is that sensitive to the properties of the molecules. The present results support the suggestion made by the Delft group [1], nevertheless much work is needed to investigate the role of other factors and to calculate vibrational overlap integrals.

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APPENDIX. ESTIMATION OF HOLE MOBILITY

The geometrical similarity between ion and molecule, as defined and computed above, implies that charge transfer between adjacent ion and molecule does not require any intramolecular rearrangement. Nothing has been said, however, about the intermolecular orientation of the two entities. We try now to estimate charge mobility due to resonance transfer in terms of the relative position of ion and molecule. Using the more familiar language of activated complex theory one may regard charge transfer as a chemical reaction the activated complex of which gets formed through appropriate orientation of a certain bond of the molecule with respect to a bond of the ion. No internal rearrangement of either of the reactants is involved in complex formation.

As an important difference from activated complex theory it is complex formation and not complex decomposition that we regard as the rate determining step. We do this because complex formation means motion of entities of molecular size whereas complex decomposition, i.e. charge transfer proper, is an electron transfer process many times faster than any sort of diffusive displacement of molecules.

Let the probability of an activated ion-molecule complex formation, W, be defined as the probability of finding a C-C bond of the ion relative to that of molecule within the solid angle element $\sin \vartheta \delta \vartheta \delta \varphi$. The angle of

orientation is the only important parameter of the complex since intermol-
ecular distances in a liquid are practically constant. The probability W
can be written as $W = (n/2\pi)\sin \vartheta\delta\vartheta\delta\varphi$, where n is the number of equivalent
pairs of bonds.

Since the overlap of the electron wave functions of ion and molecule
is the greatest if the bonds are nearly parallel, $\vartheta\approx\delta\vartheta$ holds. The spread
$\delta\vartheta\approx\delta\varphi$ cannot be smaller than that defined by the uncertainty relation, i.e
$\delta\vartheta>\hbar/M$, where M is the angular momentum with reference to the bond in ques-
tion. With this one finds

$$W > \frac{n}{2\pi} \left(\frac{\hbar}{M}\right)^3 \tag{3}$$

The frequency of a valence electron, ν_o, is about E_i/h with E_i being
the ionization potential of the molecule. The frequency of electron transfer
ν, is equal to the probability of complex formation multiplied by electron
frequency, $\nu = W\nu_o$. If we insert ν into the Einstein relation the lower
bound of charge mobility is

$$\mu = \frac{e\nu\ell^2}{6kT} > \frac{e\hbar^2}{24\pi^2 kT} \frac{nE_i\ell^2}{M^3} \tag{4}$$

where ℓ is the average jump distance.

Let us evaluate the mobility for *cyclo*-hexane. Taking n=6, E_i=9.9 eV,
ℓ=7 Å which is the Wigner-Seitz radius of the liquid, and M = $(kTI)^{1/2}$,
where I=3.38x10^{-45}kg/m^2 is the moment of inertia with reference to a C-C
bond we find μ=1.33x10^{-7}m^{2}V^{-1}sec^{-1}. This is indeed a lower bound to the
experimentally observed mobility, 1x10^{-6} [1/b] differing significantly from
the mobility of positive molecular ions in *cyclo*-hexane which is as low as
3x10^{-8} [11]. Thus, although eq.(4) gives a lower estimate, the expression
seems to have some predictive power.

ACKNOWLEDGEMENTS

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Calculated and measured bond lengths

Table I

Substance	Bond	$d_{calc.}$ /Å/	$d_{exp.}$ /Å/
CH_4	C-H	1.114	1.107±0.001[a]
C_5H_{10}	C-C	1.482	1.546±0.001[b]
	C-H	1.125	1.113±0.001[b]
C_6H_{12}	C-C	1.477	1.536±0.002[c]
	C-H	1.126	1.121±0.004[c]
C_6F_6	C-C	1.392	1.394±0.007[d]
	C-H	1.345	1.327±0.007[d]

a./ Ref. /14/
b./ Ref. /13/
c./ Ref. /12/
d./ Ref. /10/

All experimental bond lengths are measured by electron diffraction.

Internuclear distances and root mean square amplitudes
for C_6F_6 and $C_6F_6^-$

Table II

	d_n	d_i	Δd	A_n
C-C	1.392	1.420 1.388 1.392	0.028	0.030
C-F	1.345	1.352 1.353 1.347	0.007 0.008 0.002	0.031
C···C second neighbours	2.411	2.431 2.416 2.429	0.020 0.005 0.018	0.046
C...C third neighbours	2.784	2.802 2.803 2.797	0.018 0.019 0.013	0.057
F···F first neighbours	2.737	2.763 2.746 2.744	0.026 0.009 0.007	0.085
F···F second neighbours	4.740	4.766 4.764 4.765	0.026 0.024 0.025	0.067
F···F third neighbours	5.473	5.506 5.508 5.492	0.033 0.035 0.019	0.063

d_n = distance in the molecule, d_i = distance in the ion,
$\Delta d = |d_n - d_i|$, A_n = mean vibrational amplitude of the atoms
indicated in the molecule. A_n values are taken from Ref. 10.
All values are in A°

Internuclear distances and root mean square
amplitudes for C_6H_{12} and $C_6H_{12}^+$. /For notation
see Table II/.

Table III

	d_n	d_i	Δd	A_n
C-C	1.477	1.452 1.480 1.479	0.025 0.003 0.002	0.07
C-H	1.126	1.121 1.123 1.137	0.005 0.003 0.011	0.08
C...C second neighbours	2.450	2.286 .. 2.436	0.014 .. 0.164	0.11
C...C third neighbours	2.863	2.693 .. 3.023	0.15 .. 0.17	0.08
C...H second neighbours	2.145	2.124 .. 2.192	0.021 .. 0.047	0.11

Internuqlear distances and root mean square amplitudes
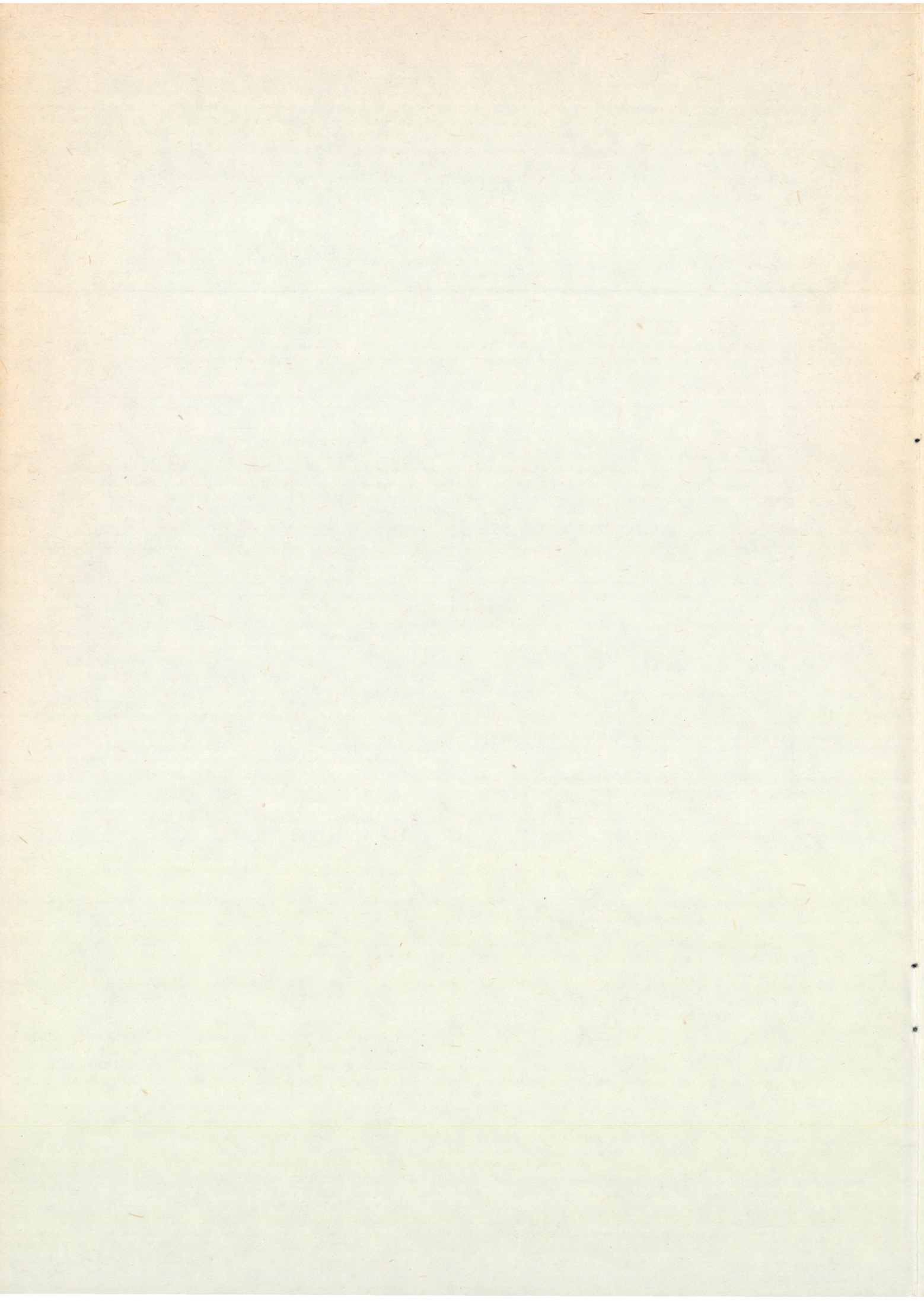for C_5H_{10} and $C_5H_{10}^+$. /For notation see Table II/.
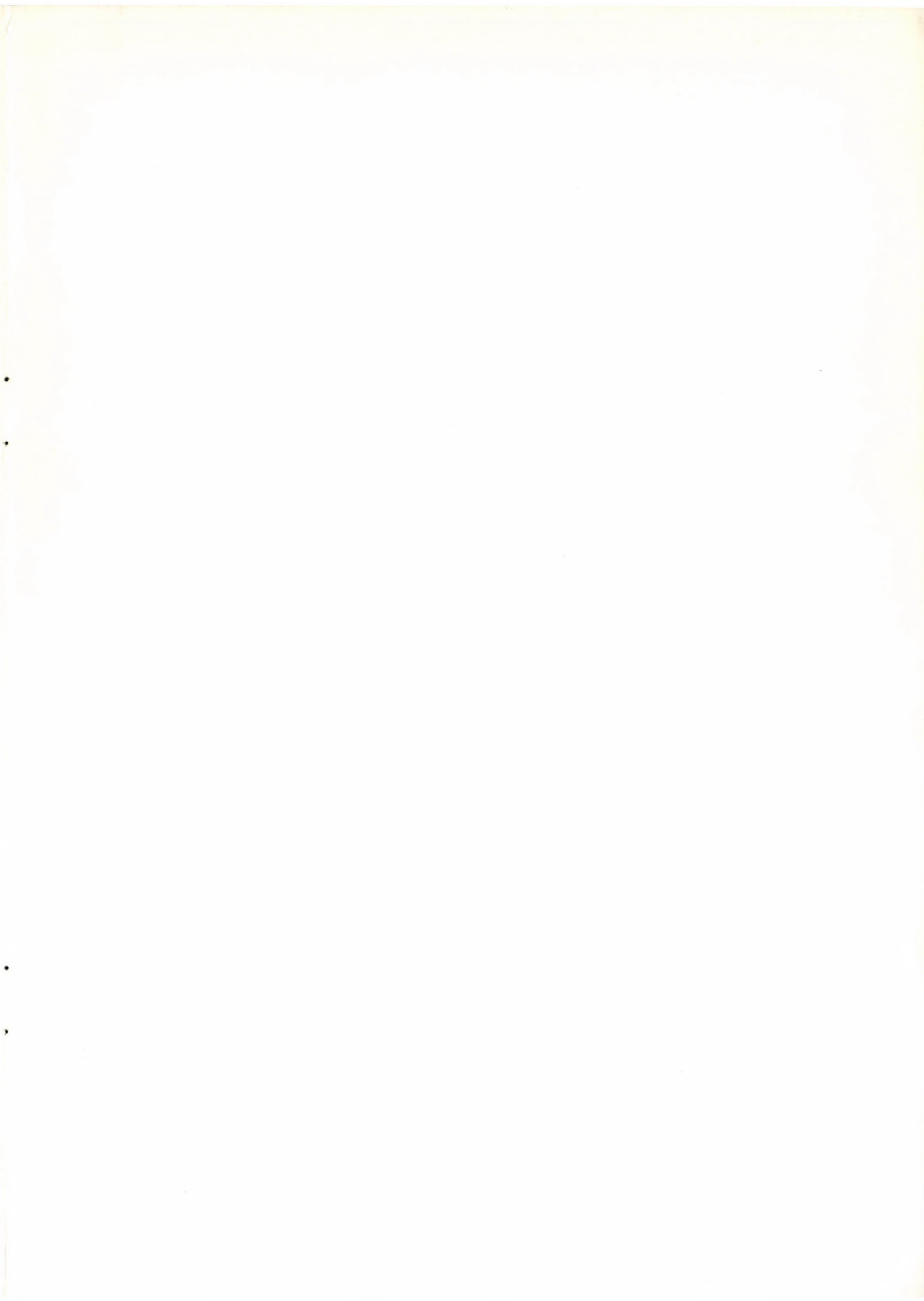
Table IV

	d_n	d_i	Δd	A_n
C-C	1.482	1.436 1.465 1.484	0.046 0.017 0.002	0.053
C-H	1.125	1.145 1.125 1.123	0.020 0.000 0.002	0.081
C···C second neighbours	2.400 2.390 2.408	2.364 2.368 2.399	0.036 0.022 0.009	0.071
C...H second neighbours	2.159 2.168	2.153 2.223	0.006 0.055	0.110
C...H third neighbours	3.204	3.288	0.084	0.113

Internuclear distances and root mean square amplitudes
for CH_4 and CH_4^+. /For notation see Table II/.

Table V

	d_n	d_i	Δd	A_n
C-H	1.114	1.327 1.278	0.213 0.164	0.078
H...H	1.819	1.38 ... 2.08	0.13 ... 0.44	0.125