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6. An Estimate of the Interatomic Distances in Monohaloacetylene Radical Cations from Photoelectron-spectroscopic Data1)

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(16. XI. 70)

Summary. A convenient method is given for the semiquantitative determination of those changes ΔS_i in internal coordinates, which describe the structure of the radical cation $M^+(\boldsymbol{\Psi})$ relative to the neutral molecule M in its electronic ground state. The changes ΔS_i correspond to those associated with the relaxation process which follows the ionisation $M + h\nu \rightarrow M^+(\boldsymbol{\Psi}) + e$, M^+ being in the electronic state $\boldsymbol{\Psi}$. The method, based on the procedure originally developped by *Smith & Warsop* [3], uses the spacing and relative intensity of the vibrational fine-structure components of the bands in the photoelectron spectrum of M. From these data are calculated the changes ΔQ_k in normal coordinates, which are then transformed into the ΔS_i by applying the $\mathbf{L}$-matrix.

The changes ΔR_{CX}, ΔR_{CC} and ΔR_{CH} which describe the structure of the radical cations of the four monohaloacetylenes I(X) (X = F, Cl, Br, I) in their $^2\Pi_\Omega(1)$ and $^2\Pi_\Omega(2)$ states have been determined. It is shown that the results are in agreement with theoretical expectation and that they confirm the band assignement proposed in a previous communication [2].

In many cases, the bands of high-resolution photoelectron spectra (PE. spectra) show a well resolved vibrational fine-structure. This fine-structure can be used for the determination of those changes in geometry which accompany the ionisation process

$$M \rightarrow M^+(\boldsymbol{\Psi}) + e, \qquad (1)$$

where M is the neutral molecule, M^+ the corresponding radical cation and $\boldsymbol{\Psi}$ the electronic state of the latter.

We wish to report the determination of the bondlength increments $\Delta R_{\mu\nu}(\boldsymbol{\Psi})$ which describe the structure of the monohaloacetylene radical cations $M^+(\boldsymbol{\Psi}) = I^+(\mathrm{X}, \boldsymbol{\Psi})$ relative to the structure of I(X), *i.e.* relative to the interatomic distances $R^0_{\mu\nu}$ of the neutral molecule in its electronic ground state $\mathbf{X} = {}^1\Sigma^+_g$.

$$\mathrm{H{-}C{\equiv}C{-}X} \qquad I(\mathrm{X}) \qquad \mathrm{X} = \mathrm{F, Cl, Br, I}.$$

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1) Part 18 of: 'Applications of Photoelectron-Spectroscopy'. Part 17 see ref. [1].

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The $\Delta R_{\mu\nu}(\Psi)$ are defined as follows:

$$R^{+}_{\mu\nu}(\Psi) = R^{0}_{\mu\nu} + \Delta R_{\mu\nu}(\Psi). \tag{2}$$

In the case of $I^{+}(X, \Psi)$ the symbol Ψ stands for the electronic ground state $\tilde{\mathbf{X}} \equiv {}^{2}\Pi_{\Omega}(1)$ or the first electronically excited state $\tilde{\mathbf{A}} \equiv {}^{2}\Pi_{\Omega}(2)$ [2] of the radical cation. The determination of $\Delta R_{\mu\nu}(\Psi)$ is based on a simple and convenient application of the *Franck-Condon* principle 3).

After describing the method we shall first apply it to some molecules for which the changes in interatomic distance on ionisation (or electronic excitation) are known from an analysis of their electronic spectra. We then proceed to determine the values $\Delta R_{\mu\nu}(\Psi)$ for the radical cations $I^{+}(X, \Psi)$. Finally these changes $\Delta R_{\mu\nu}(\Psi)$ and the frequencies $\nu = c\tilde{\nu}$ of those normal vibrations which are induced in the systems $I^{+}(X, \Psi)$ by the relaxation which follows process (1), will be correlated with changes in the corresponding characteristic quantities calculated according to the extended *Hückel* theory (EHT) of *Hoffmann* [4]. (Such a correlation has recently been applied in an investigation of the normal vibrations induced in the radical cation of 1,4-diazabicyclo[2.2.2]octane (DABCO) by the ionisation of the parent molecule [5].)

I. Description of the Method

a) General Theory

The method we shall use is a variation of the one described by *Smith & Warsop* [3].

The probability for photoionisation $P_{v'v''}$ is given in the *Born-Oppenheimer* approximation by the expression [6]

$$P_{v'v''} = \left|\overline{Re}\right|^{2} \langle \psi_{v'} | \psi_{v''} \rangle^{2} \tag{3}$$

In (3), $\overline{Re}$ stands for the mean value of the electronic transition moment, averaged over all vibrational distortions of the molecule M. The total vibrational eigenfunctions $\psi_{v'}$ and $\psi_{v''}$ are those of the radical cation $M^{+}(\Psi)$ (upper state with quantum number v') and of the neutral molecule M (lower state with quantum number v'') respectively. In the present context we are interested only in intensity variations among the vibrational components inside a single PE.-band, *i.e.* components which relate to the same state Ψ of M^{+}. In this case $|\overline{Re}|^{2}$ will be a constant and the (integrated) intensity $I_{v'v''}$ of a given component of the PE.-band will be directly proportional to the square of the *Franck-Condon* factor:

$$I_{v'v''} = A \langle \psi_{v'} | \psi_{v''} \rangle^{2} \tag{4}$$

The constant A includes, apart from $|\overline{Re}|^{2}$, all those contributions which are due to the design of the photoelectron spectrometer [7].

As usual, the vibrations of M and of $M^{+}(\Psi)$ are described in terms of normal coordinates Q_k under the assumption of a harmonic force field. The total vibrational functions ψ_v are therefore the product of $3N$-6 (for linear molecules $3N$-5) *Hermite* orthogonal functions Φ_k, N being the number of atoms in the system [8a]:

$$\psi_v = \Phi_{1,n_1}\Phi_{2,n_2}\Phi_{3,n_3}\ldots\Phi_{k,n_k}\ldots\Phi_{3N-6,n_{3N-6}}. \tag{5}$$

In (5), v stands for the set of quantum numbers $v = n_1, n_2, \ldots n_{3N-6}$.

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[3] For previous investigations of the geometry of excited molecules which are based on the *Franck-Condon* principle, see for example [3].

Each of the functions Φ_{k,n_k} is a solution of the *Schrödinger* equation of the one-dimensional harmonic oscillator,

$$\frac{d^2\,\Phi_{k,n_k}}{dQ_k^2} + 2\hbar^{-2}\left(E_{k,n_k} - \frac{\lambda_k}{2}\,Q_k^2\right)\Phi_{k,n_k} \equiv 0, \tag{6}$$

which corresponds to the normal mode **k**. In equation (6) λ_k is defined as

$$\lambda_k = 4\pi^2\nu_k^2, \tag{7}$$

where ν_k is the frequency of the classical oscillator associated with the normal coordinate Q_k. The eigenvalue

$$E_{k,n_k} = \mathrm{h}\nu_k\left(\mathrm{n}_k + \frac{1}{2}\right) \tag{8}$$

belongs to the eigenfunction

$$\Phi_{k,n_k}(\xi_k) = N_{k,n_k}\,H_{n_k}(\xi_k)\,\exp(-\xi_k^2/2), \tag{9}$$

for which the following abreviations have been used:

$$\xi_k = \alpha_k^{1/2}\,Q_k, \tag{10}$$

$$\alpha_k = (2\pi/\hbar)\,\nu_k = (2\pi c/\hbar)\,\tilde{\nu}_k, \tag{11}$$

$$N_{k,n_k} = \left\{\left(\frac{\alpha_k}{\pi}\right)^{1/2}\left(\frac{1}{2^{n_k}\,n_k!}\right)\right\}^{1/2}. \tag{12}$$

$H_{n_k}(\xi_k)$ is the n_kth *Hermite polynomial*.

In the following treatment we shall presume that both M and $M^+(\Psi)$ belong to the same symmetry group, *i.e.* that ionisation will affect all symmetry-equivalent internal coordinates S_i in the same way. In the particular case of $M = I(\mathrm{X})$ this implies that the ionisation process (1) is only accompanied by changes $\Delta R_{\mu\nu}(\Psi)$ in the equilibrium bond lengths (2) and by changes $\Delta k_{\mu\nu}(\Psi)$ in the corresponding stretching force constants

$$k_{\mu\nu}^{+}(\Psi) = k_{\mu\nu}^{0} + \Delta k_{\mu\nu}(\Psi), \tag{13}$$

but not by a departure of the equilibrium structure from linearity. Furthermore we shall make implicit use of the assumption that $\Delta R_{\mu\nu}(\Psi)$ and $\Delta k_{\mu\nu}(\Psi)$ are small compared to $R_{\mu\nu}^0$ and to $k_{\mu\nu}^0$.

Under these conditions the ionisation process (1) can be visualised as follows. (To fix the ideas, we shall now refer to a linear triatomic model system $M = \mathrm{ABC}$. As both ABC and ABC$^+$ belong, by hypothesis, to the same symmetry group $C_{\infty v}$, the internal coordinate corresponding to the bending mode will be neglected.) If S_{AB}'' and S_{BC}'' are defined as the displacements from the equilibrium bond lengths R_{AB}^0 and R_{BC}^0 of ABC (see fig. 1), then a normal coordinate treatment will yield the normal coordinates Q_1'' and Q_2'' for the normal modes **1** and **2** of ABC. Upon ionisation (process (1)) the equilibrium bond lengths will change from R_{AB}^0 and R_{BC}^0 to R_{AB}^+ and R_{BC}^+, as indicated in (2). With respect to the coordinate systems S_{AB}'', S_{BC}'' or Q_1'', Q_2'' this corresponds to a shift of the origin by ΔS_{AB}, ΔS_{BC} or by ΔQ_1, ΔQ_2. If Δk_{AB} and Δk_{BC} (see (13)) are small, then the normal coordinates Q_1' and Q_2' of ABC$^+$ (*i.e.* of the ionised molecule ABC) are (practically) parallel to Q_1'' and Q_2''. This can be expressed in the following way: $Q_1'' = Q_1' + \Delta Q_1$, $Q_2'' = Q_2' + \Delta Q_2$. Numerical experiments have shown

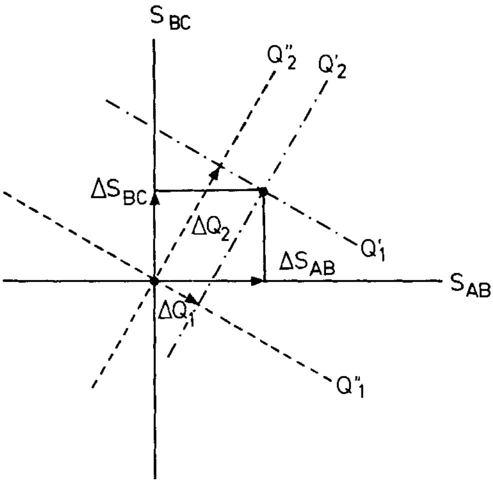


Fig. 1. *Relationship between internal coordinates* (S) *and normal coordinates* (Q) *for the neutral, linear molecule* ABC (Q'') *and the corresponding linear radical cation* ABC^+ (Q')

that even for changes $\Delta k_{\mu\nu}$ of the size encountered in the case of the monohaloacetylenes I(X), this is still a good approximation. In analogy one obtains in the general case of an arbitrary system M:

$$Q''_k = Q'_k + \Delta Q_k \tag{14}$$

An important simplification stems from the fact, that the increments ΔQ_k will be different from zero only if the normal coordinate Q_k belongs to a normal mode which is totally symmetric with respect to the symmetry group defined by M and $M^+(\boldsymbol{\Psi})$. These coordinates shall be designated by Q_l, where the lower index l spans the range $h \leqslant l \leqslant m$ corresponding to the set of normal modes $\boldsymbol{h} \cdots \boldsymbol{l} \cdots \boldsymbol{m}$ which belong to the totally symmetric irreducible representation of the group.

Each band in the PE. spectrum of M contains therefore vibrational progressions due to all or to some of the totally symmetric normal modes $\boldsymbol{h} \cdots \boldsymbol{l} \cdots \boldsymbol{m}$ of the ionised species $M^+(\boldsymbol{\Psi})$ (normal coordinates $Q_h' \ldots Q_l' \ldots Q_m'$). In the present approximation the transition probabilities $P_{v'v''}$ (formula (3)), associated with the components of a given progression due to the normal mode $\boldsymbol{l}$ (normal coordinate Q_l') are independent from those corresponding to the other normal modes $\boldsymbol{h} \cdots \boldsymbol{l} - 1$, $\boldsymbol{l} + 1 \cdots \boldsymbol{m}$ of the totally symmetric set. For this reason they can be measured individually, except in such cases where the components of two or more progressions overlap within their natural half-width or the resolution of the instruments used for the recording of the particular PE.-band. A final simplification is due to the fact that in the case of the molecules to be discussed in this contribution, only such fine-structure components will contribute to the progressions of a given PE.-band, for which the transition occurs from the vibrational ground state ψ_0 of M to a vibrationally singly excited state $\psi_{v'}$ of $M^+(\boldsymbol{\Psi})$:

$$\begin{array}{ll} M^+(\boldsymbol{\Psi}) & \psi_{v'} = \Phi'_{1,0}\,\Phi'_{2,0} \ldots \Phi'_{l,n_l} \ldots \Phi'_{3N-6,0} \\ \uparrow & \uparrow \\ M & \psi_0 = \Phi''_{1,0}\,\Phi''_{2,0} \ldots \Phi''_{l,0} \ldots \Phi''_{3N-6,0}. \end{array} \tag{15}$$

This means that each component can be described with reference to a single normal mode $\boldsymbol{l}$, as shown in fig. 2. The transition probability ratio P_{x0}/P_{y0} of two components with $n_l = x$ and $n_l = y$ in the progression associated with the excited normal mode $\boldsymbol{l}$ of $M^+(\Psi)$ (normal coordinates Q_l'' and Q_l') is according to (3), (4) and (5):

$$P_{x0}/P_{y0} = I_{x0}/I_{y0} = \langle \Phi'_{lx} | \Phi''_{l0} \rangle^2 / \langle \Phi'_{ly} | \Phi''_{l0} \rangle^2. \tag{16}$$

The *Franck-Condon* factors $\langle \Phi'_{lx} | \Phi''_{l0} \rangle$ and $\langle \Phi'_{ly} | \Phi''_{l0} \rangle$ are computed according to

$$\langle \Phi'_{ln} | \Phi''_{l0} \rangle = \frac{\varrho_l^{1/4} \sqrt{n\,!}}{\sqrt{2^{n-1}}\,(1+\varrho_l)} \exp\left[-2\,\delta_l^2 \left(\frac{\varrho_l}{\varrho_l+1}\right)\right] \times \sum_{p \geqslant 0}^{n} \left(\frac{-4\delta_l \sqrt{\varrho_l}}{1+\varrho_l}\right)^p \frac{1}{p!\,((n-p)/2)!} \left(\frac{\varrho_l - 1}{\varrho_l + 1}\right)^{(n-p)/2} \tag{17}$$

The summation extends only over even (odd) indices p in the interval $0 \leqslant p \leqslant n$ if n is even (odd).

In this formula, which is equivalent to the one given by *Ansbacher* [9], we have made use of the following definitions:

1. δ_l represents the change ΔQ_l relative to the generalised normal coordinate ξ_l (formulae (10) and (11)):

$$\delta_l = (\alpha^{1/2}/2)\Delta Q_l. \tag{18}$$

2. The parameter ϱ_l represents the ratio of the classical frequencies ν_l' and ν_l'' or of their corresponding wave-numbers $\tilde{\nu}_l'$ and $\tilde{\nu}_l''$ (see (7)) associated with Q_l' and Q_l'' respectively (cf. fig. 2):

$$\varrho_l = \nu_l'/\nu_l'' = \tilde{\nu}_l'/\tilde{\nu}_l'' \tag{19}$$

Formula (17) is computationally more convenient than the corresponding (more general) expression originally derived by *Hutchisson* [10], which yields of course the same numerical results for $\langle \Phi'_{ln} | \Phi''_{l0} \rangle$.

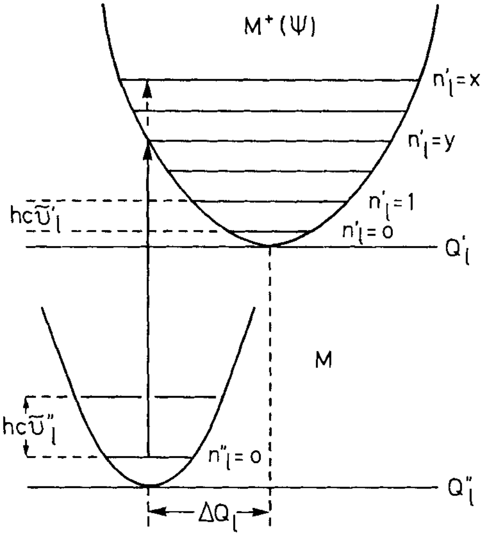


Fig. 2. *Harmonic potential for the normal mode Q_l'' of the molecule M and of the normal mode Q_l' of the corresponding radical cation $M^+(\Psi)$*

b) The Determination of Normal Coordinate Changes on Ionisation

Using equations (16) and (17), intensity ratios I_{x0}/I_{y0} (16) have been plotted for a wide range of frequency ratios $\nu'_l/\nu''_l = \varrho_l$ (see (19)) as a function of the displacement parameter δ_l defined in (18). For a given value of ϱ_l each plot consists of a family of curves:

$$F_{\varrho_l}(\delta_l) = 100\,(I_{x0}(\varrho_l, \delta_l)/I_{y0}(\varrho_l, \delta_l)), \tag{20}$$

where I_{y0} is defined as the intensity of the most intense component $n'_l = y$ of the progression in the particular range of δ_l (see fig. 2). Examples of such plots, which were used in the present investigation, are shown in fig. 3.

It can be shown that $F_{\varrho_l}(\delta_l)$ is a slowly varying function of ϱ_l. For our purposes it proved sufficient to compute plots of $F_{\varrho_l}(\delta_l)$ for ϱ_l-values spaced by 0.05 units and to use the one with the parameter ϱ_l nearest to the ϱ-value obtained experimentally from the spectroscopic data (ν'_l and ν''_l).

The determination of δ_l is carried out as follows: The vibrational fine-structure of the band in the PE. spectrum of M, which corresponds to $M^+(\boldsymbol{\Psi})$, is analysed in terms of progressions which are associated with the totally symmetrical modes $\boldsymbol{h} \cdots \boldsymbol{l} \cdots \boldsymbol{m}$ of $M^+(\boldsymbol{\Psi})$. It is self-evident that even for small polyatomic molecules, only a few normal modes out of the totally symmetric set $\boldsymbol{h} \cdots \boldsymbol{m}$ will yield progressions which can be detected with some confidence in a given PE.-band. Some of the reasons which prevent a more complete analysis are the lack of intensity in the higher components with $n'_l > 0$, accidental degeneracy with the components of a more intense mode ($\nu'_l = r\nu'_j$, $r =$ whole number) or simply lack of resolution. For those modes which dominate in the PE.-band, the analysis yields two quantities:

1. The vibrational frequency $\nu'_l = c\tilde{\nu}'_l$ of the normal mode $\boldsymbol{l}$ of $M^+(\boldsymbol{\Psi})$.
2. The intensity I_{n_l0} of the fine-structure components of the particular progression.

(In this work we have taken the intensities I_{n_l0} to be proportional to the heights of the fine-structure maxima, *i.e.* under the implicit assumption of a constant half-width of the components.)

The infrared- and/or *Raman*-spectra of M yield the frequency $\nu''_l = c\tilde{\nu}''_l$ of the normal mode $\boldsymbol{l}$ of the neutral molecule M, that is the normal mode which according to (14) (see fig. 1) has its normal coordinate Q''_l parallel to Q'_l. From $\tilde{\nu}'_l$ and $\tilde{\nu}''_l$ one calculates the ratio ϱ_l, as defined in (19). Finally the normalised intensity ratios $100\,(I_{x0}/I_{y0})$, see (16) and (20), are determined, y referring to the most intense component of the progression.

One now choses the theoretically derived plot $F_{\varrho_l}(\delta_l)$ (formula (20), fig. 3) whose ϱ_l-value is nearest to the one obtained from the experimentally determined frequencies (or wave-numbers) ν'_l and ν''_l of the normal mode $\boldsymbol{l}$. From this plot one reads the δ_l-value for which optimal agreement between the computed and the experimentally observed intensity ratios I_{x0}/I_{y0} is obtained. The displacement parameter δ_l so obtained yields, according to (18), the shift ΔQ_l of the origin of the normal coordinate Q''_l relative to $Q'_l = 0$ (see fig. 1).

The above procedure is carried through for all those normal modes $\boldsymbol{l}$ of the set $\boldsymbol{h} \cdots \boldsymbol{m}$ which can be picked up in a particular band of the PE. spectrum of M.

It is obvious that under the implicit assumption of a harmonic force field, both for M and $M^+(\boldsymbol{\Psi})$, the changes δ_l and thus the shifts ΔQ_l are only determined up to

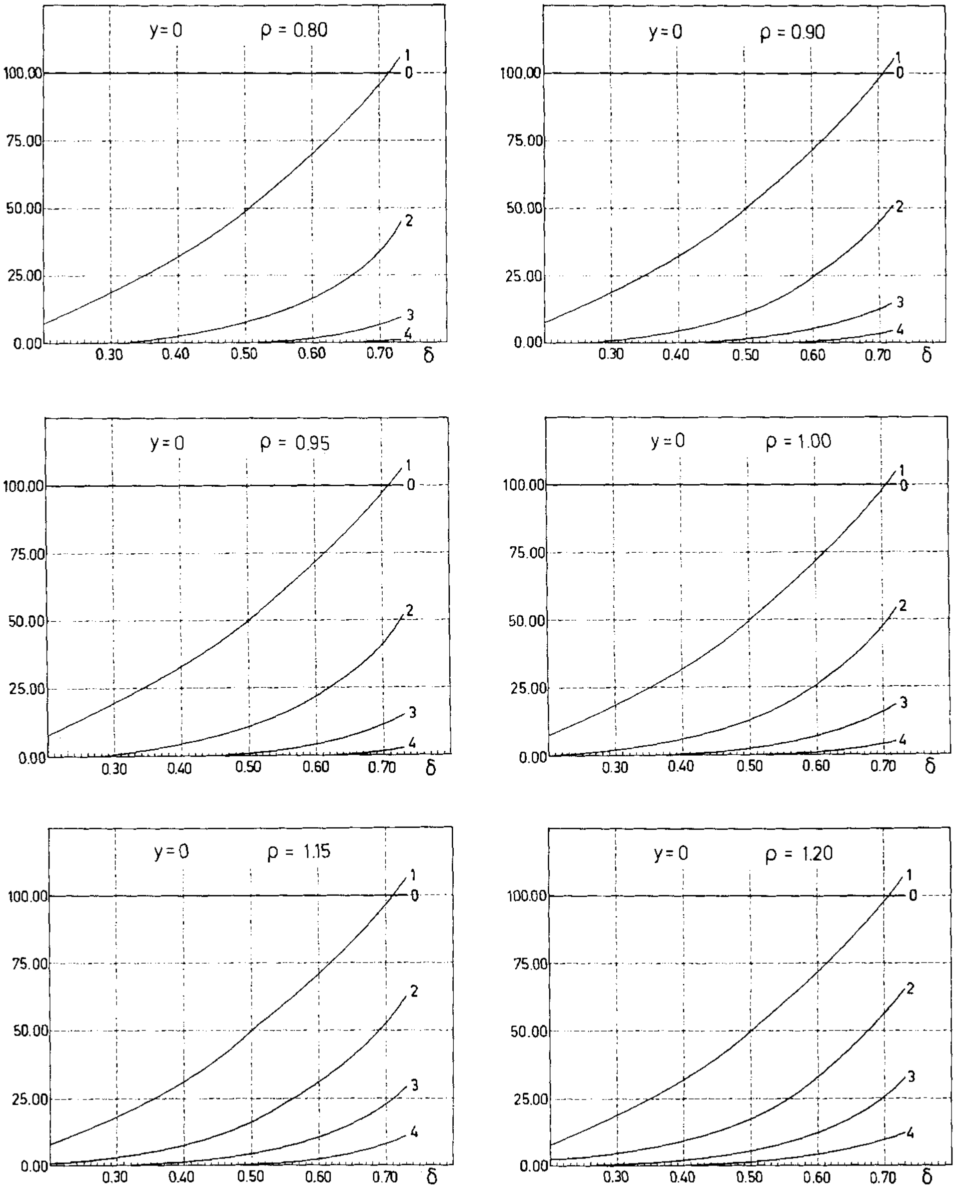
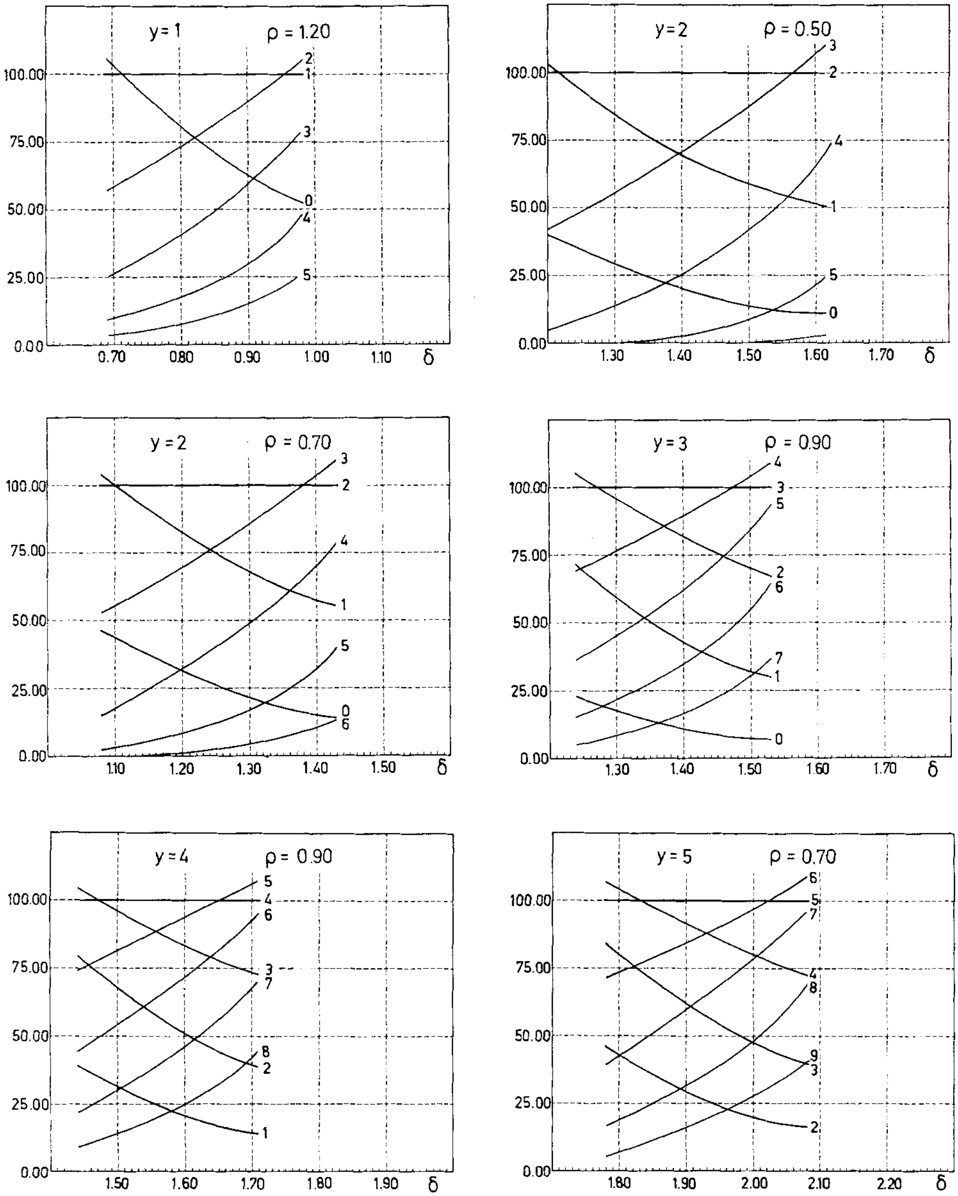


Fig. 3. *Plots of the intensity ratios* $F_\varrho(\delta) = 100\,(I_{x0}(\varrho, \delta)/I_{y0}(\varrho, \delta))$, *see formula (20)*

Each curve is labelled by the number x of the fine-structure component, $x = y$ corresponding to the most intense component in the range of δ investigated. For definition of δ and ϱ see formulae (18) and (19)

the sign. In other words, displacements of $+|\delta_l|$ and of $-|\delta_l|$ will result in identical *Franck-Condon* factors. In the present investigation the sign of δ_l was determined according to the following two methods:



1. In the case of diatomic molecules, or of molecules in which a given normal mode $\boldsymbol{l}$ can be described in a first approximation in terms of two essentially rigid parts of the molecule moving against each other, the positive sign $(+|\delta_l|)$ is chosen if $\nu_l' < \nu_l''$, and the negative $(-|\delta_l|)$ if $\nu_l' > \nu_l''$.

2. In the more general case the sign of δ_l can be derived with some confidence from the computed changes $\Delta OP_{\mu\nu}$ of the overlap populations (OP) of the bonds involved in the normal mode $\boldsymbol{l}$, under the well established assumption that $\Delta R_{\mu\nu} \propto -\Delta OP_{\mu\nu}$.

(In the present investigation such differences $\Delta OP_{\mu\nu}$ have been calculated by the EHT procedure [4].)

c) *The Transformation to Internal Coordinate Changes*

The transformation from normal coordinates Q_k to internal coordinates S_i is given by the matrix equation [8b]

$$\mathbf{S} = \mathbf{LQ}. \tag{21}$$

$\mathbf{S}$ is a column vector whose elements S_i are the internal coordinates. The elements of the column vector $\mathbf{Q}$ are the $3N$-6 normal coordinates Q_k ($3N$-5 in the case of linear molecules). Column k of the matrix $\mathbf{L}$ is the amplitudes vector $\mathbf{L}_k$ of the internal coordinates contributing to the normal mode $\boldsymbol{k}$. The matrix $\mathbf{L}$ is normalised in the sense that

$$\mathbf{L}_k^{\dagger}\,\mathbf{FL}_k = \lambda_k, \tag{22}$$

$\mathbf{F}$ being the matrix of the force constants [8].

The transformation (21) reads $\mathbf{S}'' = \mathbf{L}''\mathbf{Q}''$ and $\mathbf{S}' = \mathbf{L}'\mathbf{Q}'$ for M and $\mathrm{M}^+(\Psi)$ respectively. In the present treatment we make the assumption that

$$\mathbf{L}'' = \mathbf{L}' = \mathbf{L}. \tag{23}$$

It has been shown by numerical experiments that the approximation (23) does not affect significantly the semiquantitative results of the investigation reported in this paper. Therefore we write for M and $M^+(\Psi)$:

$$\mathbf{S}'' = \mathbf{LQ}''; \; \mathbf{S}' = \mathbf{LQ}'. \tag{24}$$

Using the relation (14) in the form $\mathbf{Q}'' = \mathbf{Q}' + \Delta\mathbf{Q}$, and in analogy

$$\mathbf{S}'' = \mathbf{S}' + \Delta\mathbf{S}, \tag{25}$$

we obtain from (24) the expression

$$\Delta\mathbf{S} = \mathbf{L}\Delta\mathbf{Q}. \tag{26}$$

In formula (26) $\Delta\mathbf{Q}$ is a column vector in which only the elements ΔQ_l ($h \leqslant l \leqslant m$) corresponding to the totally symmetric modes $\boldsymbol{h} \cdots \boldsymbol{l} \cdots \boldsymbol{m}$ can assume values different from zero [11]. These elements ΔQ_l are obtained as described in section I, b, through the use of formula (18).

d) *Determination of the Matrix* $\mathbf{L}$

In view of the assumption (23) it is sufficient to compute $\mathbf{L}$ only for the neutral molecule M. The numerical solution of this vibrational problem was obtained using a modified version of the program of *Slezak & Wait* [12]. The eigenvalues λ_k and the properly normalised eigenvectors $\mathbf{L}_k$ (see (21)) of the $\mathbf{GF}$-matrix are calculated by a matrix iteration/matrix deflation method [8c], [13]. The refinement of the force constants k_i corresponding to the internal coordinates S_i, and of the $\mathbf{L}$-matrix, is carried out iteratively in an automatic process, until the desired agreement between the computed and the experimentally determined frequencies ν_k is obtained. The whole procedure is based on a perturbation treatment [8d].

For all cases reported in this paper we have used a diagonal valence force field. In view of the fact that the totally symmetric modes of acetylene and of the monohaloacetylenes have well separated frequencies, the neglect of interaction terms seems to be a rather well justified approximation. Indeed, in all instances the calculated frequencies obtained after the last iteration were identical within 1 cm^{-1} with the experimental values. In a few instances the same treatment has been applied to $M^{+}(\Psi)$ to test the validity of the simplifying assumption (23).

II. Results for some Test Cases

a) Diatomic Radical Cations

The method has first been tested by calculating the changes $\Delta R_{AB}(\Psi)$ which occur in the bond length R^{0}_{AB} of a diatomic molecule AB after ionisation (see (1)). In these cases the values derived from the PE. spectra can be compared to the known interatomic distances $R^{+}_{AB}(\Psi)$, which have been obtained from an analysis of the rotational fine-structure of the electronic spectra of the radical cations AB^{+} [14]. The results are summarised in tab. 1. As can be seen from this table, the present method yields reasonably accurate estimates of $\Delta R_{AB}(\Psi)$. The largest error, in the case on the $^{4}\Pi_{u}$-state of O_2^{+}, amounts to 0.03 Å.

Table 1. *Bond length changes $\Delta R_{AB}(\Psi)$ for several diatomic molecules AB.* (See formulae (1) and (2))

					$\Delta R_{AB}(\Psi)$ in Å		
AB^{+}		ϱ a)	ϱ^{*} b)	δ c)	PES d)	El. Sp. e)	Ref. PES f)
H_2^{+}	$^{2}\Sigma_{g}^{+}$	0.52	0.50	1.40	0.35	0.33	[15]
O_2^{+}	$^{2}\Pi_{g}$	1.19	1.20	0.88	–0.09	–0.08	[15]
O_2^{+}	$^{4}\Pi_{u}$	0.66	0.70	1.93	0.20	0.17	[15]
O_2^{+}	$^{4}\Sigma_{g}^{-}$	0.76	0.80	0.70	0.07	0.07	[15]
CO^{+}	$^{2}\Sigma^{+}$	0.80	0.80	0.51	0.05	0.04	[7]
CO^{+}	$^{2}\Pi_{i}$	0.72	0.70	1.28	0.12	0.12	[7]

a) See definition (19). Values for ν' and ν'' from ref. [14].

b) Rounded value of ϱ which characterises the plot of fig. 2 used in the determination of δ.

c) See definition (18). The value of δ was determined as described in section I, b. The separation between the minima of the upper and lower quadratic potential curves amounts to 2δ when expressed in units of ξ (formula (10)) of the lower curve.

d) Calculated from the PE spectra by the method described in section I.

e) From an analysis of the rotational fine-structure of the electronic spectra.

f) References for the primary PE. data.

b) Interatomic Distances of Acetylene in its $^{1}\Pi_{u}$-State (3R)

As a second test we have computed the changes ΔR_{CH} and ΔR_{CC} of acetylene, on excitation from the electronic ground state $^{1}\Sigma_{g}^{+}$ to the electronically excited state $^{1}\Pi_{u}$. Note that in both these states the molecule has $D_{\infty h}$ symmetry [16]. In this case the

Table 2. *Bond length changes for the transition $^{1}\Pi_{u} \leftarrow {}^{1}\Sigma_{g}^{+}$ of acetylene*

For the meaning of the symbols see footnotes of tab. 1. The normal modes are defined in ref. [16]. ΔR-values in Å.

	Wave-numbers in cm^{-1}						
State	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$	ϱ_2	δ_2	ΔR_{CC}	ΔR_{CH}
$^{1}\Sigma_{g}^{+}$ a)	3372	1973	3294				
$^{1}\Pi_{u}$ (3R)		1849		0.937	0.285	0.027	0.009

a) The values for the ground state vibrational frequencies are those given in ref. [16].

intensity ratios I_{x0}/I_{y0} (formula (16)) have been taken from the photoelectric recording of the absorption spectrum of acetylene reported by *Nakayama* & *Watanabe* [17]. The value $\Delta R_{CC} = +\ 0.027$ Å obtained from the calculations summarised in tab. 2 is in perfect agreement with $\Delta R_{CC} = +\ 0.03$ Å deduced by *Price* [18] from the electron-spectroscopic data.

c) Interatomic Distances of the Acetylene Radical Cation in its $^2\Pi_\Omega(1)$ Ground State

A further test is provided by the calculation of the changes ΔR_{CH} and ΔR_{CC} which occur after an electron has been ejected from the top occupied orbital π_u of acetylene (formula (1) with $M = C_2H_2$ and $\Psi = {}^2\Pi_\Omega(1)$). This problem has been dealt with some time ago by *Sharp* & *Rosenstock* [3], who have made use of the photoionisation curve of acetylene recorded by *Dibeler* & *Reese* [19]. They have obtained an optimal simulation of this curve under the assumption that $\Delta R_{CC}\,({}^2\Pi_\Omega(1)) = 0.05 \pm 0.005$ Å. The agreement between the observed and the calculated band envelope was insensitive to changes $\Delta R_{CH}({}^2\Pi_\Omega(1))$, which lead to a bond length $R^+_{CH}\,({}^2\Pi_\Omega(1))$ in the range of 1.06 to 1.08 Å.

The method used by *Sharp* & *Rosenstock* involves the calculation of the *Franck-Condon* factors for a given set of changes in internal coordinates ΔS_i. The resultant band shape is compared to the experimental one and the ΔS_i are varied until optimal agreement is observed. In a sense this is the reverse approach to the one described in section I.

The PE. spectrum of acetylene has been reported by *Baker* & *Turner* [15], [20]. It indicates that only the ν_2-mode is excited when an electron is removed from the orbital π_u, due to the weakening of the CC-π-bond. The relevant data are collected in tab. 3, which also summarises the results of our treatment. The value $\Delta R_{CC}({}^2\Pi_\Omega(1)) = +\ 0.04$ Å so obtained corresponds nicely to the one found by *Sharp* & *Rosenstock* (0.05 Å). In addition we find a small lengthening $\Delta R_{CH}({}^2\Pi_\Omega(1))$ of 0.01 Å for the CH-bonds in $C_2H_2^+$ (${}^2\Pi_\Omega(1)$) relative to C_2H_2 in its ${}^1\Sigma_g^+$ ground state, as predicted by theoretical calculations (see discussion of section III).

Table 3. *Bond length changes* $\Delta R_{CC}({}^2\Pi_\Omega(1))$ *and* $\Delta R_{CH}({}^2\Pi_\Omega(1))$ *of* $C_2H_2^+$

For the meaning of the symbols see foortnotes of tab. 1. The normal modes are defined in ref. [16]. ΔR-values in Å.

State	Wave-numbers in cm^{-1}						
	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$	ϱ_2	δ_2	ΔR_{CC}	ΔR_{CH}
C_2H_2; ${}^1\Sigma_g{}^{+\,a)}$	3372	1973	3294				
$C_2H_2{}^+$; ${}^2\Pi_\Omega(1)$		1830		0.927	0.425	0.041	0.013

a) The values for the ground state vibrational frequencies are those given in ref. [16].

III. Interatomic Distances in the Monohaloacetylene Radical Cations

a) General Remarks

Before describing the results obtained for the monohaloacetylene radical cations $I^+(X, \Psi)$, it seems worthwhile to summarise briefly the simplifications that have been introduced into the derivation developped in section I. This will prevent us from overestimating the numerical precision that can be attained under the experimental conditions prevailing in the present investigation.

1. The factor A in formula (4) has been assumed to be a constant, at least inside a given PE.-band. However, this is not the case for our instrument, which shows a marked fall-off in count rate with increasing ionisation potential. As a consequence, the intensity ratios (16) derived from the experimental curves will overestimate the intensity of the components with lower quantum numbers n'_l relative to those with higher quantum numbers.

2. It should be emphasised again that formula (14) and its counterpart $\mathbf{Q}'' = \mathbf{Q}' + \Delta\mathbf{Q}$ used in the derivation of (26) are only approximately true. In general, the postulated parallelism between the normal coordinates Q'_k and Q''_k (see fig. 1) will be no longer valid if large changes in internal coordinates S_i and/or force constants k_i occur on ionisation.

3. The same applies to the postulate (23). The latter clearly presupposes that the eigenvectors of $\mathbf{F}$ (formula (22)) which one would obtain for M and for $M^+(\Psi)$ do not differ significantly. In particular the signs of the matrix elements L_{ik} should be the same.

4. Finally, for purely technical reasons, we have assumed that the heights of the individual components in a given progression are reliable measures of the integrated intensities I_{x0} and I_{y0} (see (16)).

In addition there are two further simplifications that have to be introduced if the method is applied in practice. These are due to restrictions which can not be eliminated by a more precise reformulation of the theory:

5. In many cases we are in the presence of overlapping progressions which cannot be resolved within the resolution obtainable on the particular photoelectron spectrometer. As a consequence, the intensities of such overlapping components cannot be measured independently and, furthermore, assumption 4) is necessarily wrong. This is especially true if the vibrational spacing ν'_l of the progression due to a given mode $\boldsymbol{l}$ is a multiple of ν'_m, the spacing of the progression due to another mode $\boldsymbol{m}$ in the same PE.-band.

A rather special case of this type of difficulty occurs if a particular PE.-band is split into two bands as a consequence of spin-orbit coupling and if the magnitude of this split is accidentally the same as the spacing between the components of the dominant progression (or a multiple thereof). An example for this kind of degeneracy is provided by the first PE.-band of bromoacetylene I(Br).

6. As mentioned in section I, not all normal modes $\boldsymbol{l}$ will give rise to a progression that can be recognised in a given PE.-band. This will be the case if δ_l and thus ΔQ_l are too small to yield components (other than the $0 \leftarrow 0$ one) of sufficient intensity. In these cases we have assumed $\Delta Q_l = 0$ to be a valid approximation. However, it should be noted that this simplification can introduce serious errors into the change ΔS_i of an internal coordinate S_i if the matrix element L_{il} of $\mathbf{L}$ is large (see formula (26)).

To summarise, it is obvious that the method, as applied in this work, is semiquantitative at best. Nevertheless it is quite useful for the assessment of the magnitude and of the relative sign of those changes in structure (*i.e.* changes in internal coordinates S_i) which accompany process (1). This in turn allows for a more significant correlation with theoretical data, such as changes in overlap populations or computed changes in topography, and provides therefore a sounder basis for band assignments and band correlations than the simple matching of ionisation potentials with calculated orbital energies.

b) Interatomic Distances of the Monohaloacetylene Radical Cations $I^+(\mathrm{X}, \tilde{\Psi})$

Tab. 4 contains the wave-numbers $\tilde{\nu}_l$ of the three totally symmetrical stretching modes $l = \mathbf{1, 2, 3}$ of the monohaloacetylenes $I(\mathrm{X})$ in their electronic ground state $\mathbf{X} \equiv {}^1\Sigma^+$ [21]. The optimised force constants $f_{\mathrm{CH}}, f_{\mathrm{CC}}$ and f_{CX} are those obtained from the normal coordinate treatment (see section I, d). They reproduce the $\tilde{\nu}_l$-values to better than 1 cm^{-1}. The **L**-matrices are given in tab. 8 of the appendix. For comparison the results for acetylene itself ($I(\mathrm{X})$ with X = H) are also included. (It should be noted that in this case the normal mode **3** ($\tilde{\nu}_3 = 3294$ cm^{-1}) is the antisymmetric stretch vibration belonging to the irreducible representation A_u of $D_{\infty h}$.) The interatomic distances R^0_{CH}, R^0_{CC} and R^0_{CX} are those given by *Hunt* & *Wilson* [21].

Table 4. *Force constants, interatomic distances and wave-numbers for the totally symmetric stretching modes of the monohaloacetylenes* $I(\mathrm{X})$ *in their electronic ground state*

Force constants $f_{\mu\nu}$ in 10^5 dyne cm^{-1}. Interatomic distances $R^0_{\mu\nu}$ in Å. Wave-numbers $\tilde{\nu}_l$ in cm^{-1}.

X	f_{CH}	f_{CC}	f_{CX}	R^0_{CH}	R^0_{CC}	R^0_{CX}	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$
F	6.002	16.080	8.468	1.058	1.200	1.275	3355	2255	1055[a])
Cl	5.966	15.015	5.522	1.058	1.211	1.632	3340	2110	756[a])
Br	5.912	14.965	4.697	1.058	1.200	1.800	3325	2085	618[a])
I	5.899	15.335	3.134	1.058	1.200	2.000	3320	2075	490[b])[c])
H	5.937	15.661		1.06	1.20		3372	1973	(3294)[d])

[a]) See ref. [21]. [b]) See ref. [22]. [c]) For $\tilde{\nu}_3$ of $I(\mathrm{I})$ see ref. [2]. [d]) Antisymmetric vibration.

As shown in a previous communication [2], the PE. spectra of $I(\mathrm{X})$ contain two PE.-bands which correspond to an ionisation process (1) in which an electron has been ejected from one or the other of the pairs of top-occupied π-orbitals $\pi_\lambda(1)$ or $\pi_\lambda(2)$. The index λ, which can take the values +1 or −1, refers to the associated angular momentum. The resultant states $\tilde{\Psi}$ of the radical cations $I^+(\mathrm{X}, \tilde{\Psi})$ are ${}^2\Pi_\Omega(1)$ and ${}^2\Pi_\Omega(2)$ respectively, with total angular monumentum quantum numbers $\Omega = 3/2$ or $1/2$. As a consequence the two PE.-bands are split into two sub-bands due to spin-orbit coupling. In the following we shall make use of the abbreviations $\tilde{\mathbf{X}} = {}^2\Pi_\Omega(1)$ and $\tilde{\mathbf{A}} = {}^2\Pi_\Omega(2)$ for the electronic states, without referring explicitely to the quantum number Ω. (The tilde (~) refers henceforth to a state of the ion).

The result of the analysis of the fine-structure of these PE.-bands (as described in section I) is summarised in tab. 5. They are derived from PE. spectra recorded on a scale of 0.5 eV/inch (see fig. 4). In the case of large splits due to spin-orbit coupling, the intensities were taken from the first sub-band ($\Omega = 3/2$).

In the case of $I(\mathrm{F})$ only the PE.-band at 11 eV, corresponding to the transition $\tilde{\mathbf{X}} \leftarrow \mathbf{X}$, can be analysed. The second PE.-band (transition $\tilde{\mathbf{A}} \leftarrow \mathbf{X}$) is found in the vicinity of 18 eV and overlaps the band due to the transition $\tilde{\mathbf{B}} \leftarrow \mathbf{X}$ ($\tilde{\mathbf{B}} = {}^2\Sigma(\,?)$) in which the photoelectron has vacated a σ-orbital. The latter orbital can be thought of as a linear combination of the semilocalised CH and CC σ-orbitals. As mentioned above, the first PE.-band of I(Br) can not be analysed, as the split of this band due to spin-orbit coupling (0.14 eV) coincides with twice the spacing of the progression due to the normal mode **3** ($\tilde{\nu}_3 = 620$ cm$^{-1} \approx 0.07_5$ eV). As a consequence, the fine-structure components of the two sub-bands overlap extensively and it becomes impossible to measure the individual intensities with any accuracy. On the other hand the observed spacings $\tilde{\nu}_2$ and $\tilde{\nu}_3$ correspond nicely to those expected on theoretical grounds (see [2]).

Table 5. *Analysis of the fine-structure of the π-bands in the PE. spectra of the monohaloacetylenes* I(X)
$\tilde{\mathbf{X}}$ = ground state $^2\boldsymbol{\Pi}_\Omega(1)$ and $\tilde{\mathbf{A}}$ = first excited state $^2\boldsymbol{\Pi}_\Omega(2)$ of the radical cation of I(X); $(\tilde{\nu}_l\boldsymbol{\Psi})$ = wave-number of mode $\boldsymbol{l}$ of $I^+(\mathrm{X}, \boldsymbol{\Psi})$ in cm^{-1}; ϱ_l = frequency ratio (19); $100(I_{x0}/I_{y0})$ = intensity ratios (16) as a function of x.

	process			100(I_{x0}/I_{y0})								
X	(1)			0	1	2	3	4	5	6	7	8
F	$(\tilde{\mathbf{X}}) \leftarrow (\mathbf{X})$	$\tilde{\nu}_2(\tilde{\mathbf{X}}) = 2180$	$\varrho_2 = 0.97$	100	84	35	10					
		$\tilde{\nu}_3(\tilde{\mathbf{X}}) = 1210$	$\varrho_3 = 1.15$	100	9							
Cl	$(\tilde{\mathbf{X}}) \leftarrow (\mathbf{X})$	$\tilde{\nu}_2(\tilde{\mathbf{X}}) = 2040$	$\varrho_2 = 0.97$	100	28							
		$\tilde{\nu}_3(\tilde{\mathbf{X}}) = 900$	$\varrho_3 = 1.19$	100	42							
	$(\tilde{\mathbf{A}}) \leftarrow (\mathbf{X})$	$\tilde{\nu}_3(\tilde{\mathbf{A}}) = 560$	$\varrho_3 = 0.74$		71	100	95					
Br	$(\tilde{\mathbf{A}}) \leftarrow (\mathbf{X})$	$\tilde{\nu}_3(\tilde{\mathbf{A}}) = 560$	$\varrho_3 = 0.91$			74	90	100	98	72	55	32[a]
I	$(\tilde{\mathbf{X}}) \leftarrow (\mathbf{X})$	$\tilde{\nu}_2(\tilde{\mathbf{X}}) = 1850$	$\varrho_2 = 0.89$	100	20							
		$\tilde{\nu}_3(\tilde{\mathbf{X}}) = 560$	$\varrho_3 = 1.14$	100	65	22						
	$(\tilde{\mathbf{A}}) \leftarrow (\mathbf{X})$	$\tilde{\nu}_3(\tilde{\mathbf{A}}) = 420$	$\varrho_3 = 0.86$	13	42	84	100	95				
H[b]	$(\tilde{\mathbf{X}}) \leftarrow (\mathbf{X})$	$\tilde{\nu}_2(\tilde{\mathbf{X}}) = 1830$	$\varrho_2 = 0.93$	100	36							

[a] The onset of the $^2\boldsymbol{\Pi}_{1/2}(2)$ progression coincides probably with the fifth vibrational component of $^2\boldsymbol{\Pi}_{3/2}(2)$; see [2].

[b] Acetylene; $\mathbf{X} \equiv {}^1\Sigma_g^+$; $\tilde{\mathbf{X}} \equiv {}^2\boldsymbol{\Pi}_u$.

Table 6. *Summary of the computation of changes $\Delta R_{\mu\nu}(\boldsymbol{\Psi})$ in interatomic distances for the monohaloacetylenes* I(X)

Symbols for the electronic states, see tab. 5. ΔQ_l in units of $10^{-20}\mathrm{g}^{1/2}$ cm; $\Delta R_{\mu\nu}$ ($\boldsymbol{\Psi}$) in Å.

X	process (1)			ΔR_{CH}	ΔR_{CC}	ΔR_{CX}
F	$(\tilde{\mathbf{X}}) \leftarrow (\mathbf{X})$	$\delta_2 = 0.65$	$\Delta Q_2 = 0.205$	0.021	0.053	−0.062
		$\delta_3 = -0.22$	$\Delta Q_3 = -0.096$			
Cl	$(\tilde{\mathbf{X}}) \leftarrow (\mathbf{X})$	$\delta_2 = 0.37$	$\Delta Q_2 = 0.120$	0.010	0.026	−0.067
		$\delta_3 = -0.46$	$\Delta Q_3 = -0.250$			
	$(\tilde{\mathbf{A}}) \leftarrow (\mathbf{X})$	$\delta_3 = 1.32$	$\Delta Q_3 = 0.715$	0.006	0.029	0.129
Br	$(\tilde{\mathbf{A}}) \leftarrow (\mathbf{X})$	$\delta_3 = 1.59$	$\Delta Q_3 = 0.956$	0.006	0.028	0.154
I	$(\tilde{\mathbf{X}}) \leftarrow (\mathbf{X})$	$\delta_2 = 0.32$	$\Delta Q_2 = 0.105$	0.009	0.025	−0.078
		$\delta_3 = -0.56$	$\Delta Q_3 = -0.378$			
	$(\tilde{\mathbf{A}}) \leftarrow (\mathbf{X})$	$\delta_3 = 1.39$	$\Delta Q_3 = 0.940$	0.004	0.017	0.150
H	$(\tilde{\mathbf{X}}) \leftarrow (\mathbf{X})$	$\delta_2 = 0.43$	$\Delta Q_2 = 0.143$	0.013	0.041	0.013

From the plots of fig. 3, with ϱ-values nearest to those given in tab. 5, and from the intensity ratios $100(I_{x0}/I_{y0})$ one obtains the shifts δ_l and ΔQ_l shown in tab. 6. The latter yield according to (26) the increments $\Delta R_{\mu\nu}(\Psi)$ listed in the same table. (The matrices **L** are given in tab. 8.) The data for acetylene I(H) from tab. 3 have been included for the sake of completeness.

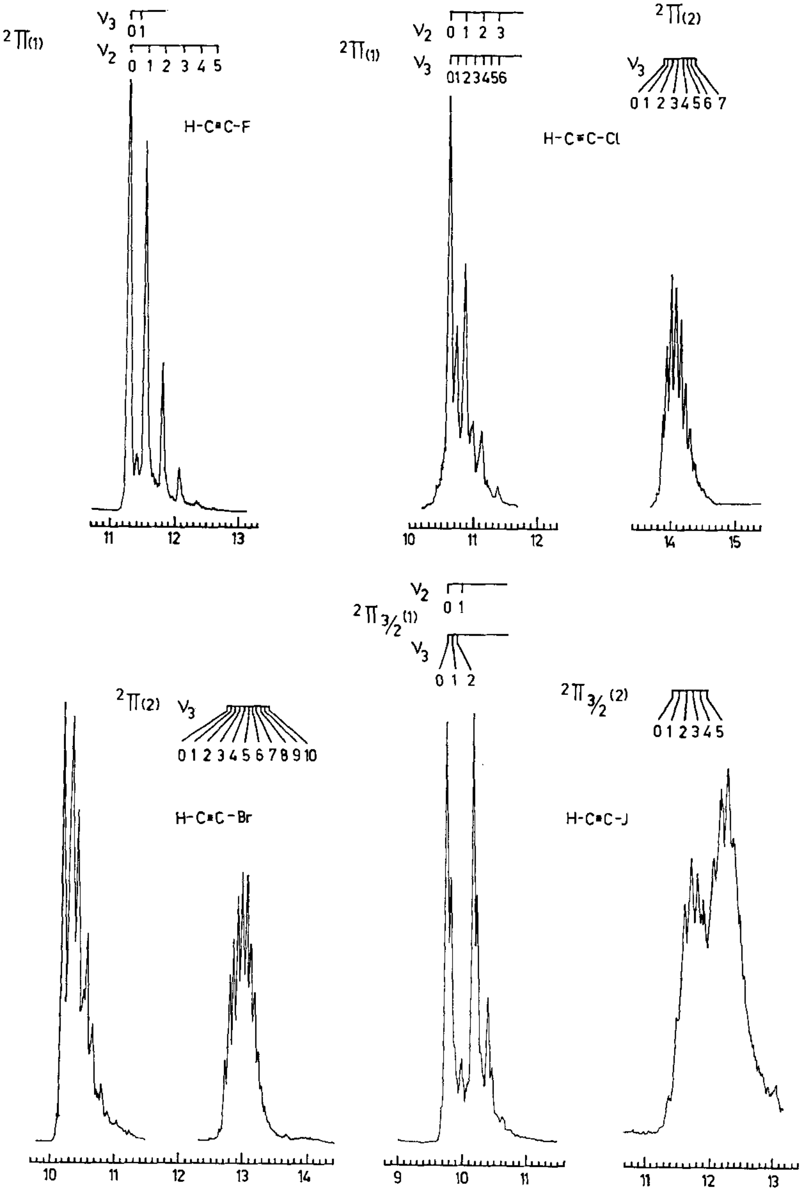


Fig. 4. *PE.-bands of the monohaloacetylenes* $I(X)$
Abscissa: ionisation potentials in eV. Ordinate: count rates

c) *Discussion of the Results*

Ab initio calculations for acetylene I(H) have been performed by *McLean & Yoshimine* [23] (see also [24]) by *Palke & Lipscomb* [25], by *Buenker, Peyerimhoff & Whitten* [26] and by *Griffith & Goodman* [27]. The latter authors have also included the acetylene radical cation $I^+(\mathrm{H}, \tilde{\mathrm{X}})$ in its electronic ground state in their investigation, under the assumption that the interatomic distances are the same as in the neutral, closed shell parent compound. The reason for this assumption was, that *Griffith & Goodman* were only interested in the purely electronic reorganisation which follows the vertical ionisation process.

The vertical ionisation potentials for the ejection of a π-electron can be derived from the π-orbital energies of I(H) obtained by the four groups of authors under the assumption of the validity of *Koopmans'* theorem. The values agree fairly well with the observed ionisation potential $I_v(\pi) = 11.4$ eV [15] (11.2 eV [23], [24], [26], 11.0 eV [25], 10.7 eV [27]). On the other hand the difference in total energies compiled by *Griffith & Goodman* [27] for $I^+(\mathrm{H}, \tilde{\mathrm{X}})$ and I(H) (both of same topography) yields only 9.8 eV. Obviously this value would be changed if both $I^+(\mathrm{H}, \tilde{\mathrm{X}})$ and I(H) were allowed to relax to their mutual geometry of minimum energy.

From the point of view of the present investigation the most important result obtained by *Griffith & Goodman* is, that ejection of an electron from the π-orbital induces a σ-density shift from the C-H region towards the C-C region. In this way the loss in π-density is partially compensated at the expense of the electron density near and at the hydrogen atoms. From this drift of σ-electrons, calculated for fixed interatomic distances, one can conclude that the relaxation of the radical cation $I^+(\mathrm{H}, \tilde{\mathrm{X}})$ will involve a lengthening of both the CC and the CH distances. Such a conclusion is strongly supported by calculations due to *Haselbach* [28], using the MINDO/2 procedure [29]. He predicts $\Delta R_{\mathrm{CC}} = 0.04$ Å and $\Delta R_{\mathrm{CH}} = 0.03$ Å, in good semiquantitative agreement with the results summarised in tab. 3 and 6.

As far as the monohaloacetylenes I(X) are concerned, only the orbitals of I(F) and of I(Cl) have been calculated by an *ab initio* method. *McLean & Yoshimine* [23] obtained the following orbital energies for the three top-occupied orbitals, which agree reasonably well with our experimental ionisation potentials [2]:

I(F)			I(Cl)		
Orbital	Predicted [23]	Observed [2]	Orbital	Predicted [23]	Observed [2]
$\pi(1)$	−11.4	−11.3	$\pi(1)$	−10.7	−10.6
$\sigma(1)$	−19.8	−18	$\pi(2)$	−15.0	−14.1
$\pi(2)$	−20.7		$\sigma(1)$	−18.3	−16.8

(All values in eV).

Note that for I(F) the sequence of the orbitals from the top is π, σ, π and for I(Cl) π, π, σ. Furthermore the first σ-orbital energy and the second π-orbital energy of I(F) are very close to each other. As can be seen from the correlation diagram shown in fig. 3 of our previous communication [2], the essential correctness of these predictions is confirmed by the PE.-spectroscopic investigation.

It seemed of interest to correlate the $\Delta R_{CC}(\Psi)$ and $\Delta R_{CX}(\Psi)$ values of tab. 6 with data derived from a theoretical model. To this end extended *Hückel* calculations (EHT) [4] have been carried out for acetylene I(H) and the four monohaloacetylenes I(X). The parameters used are listed in tab. 9 of the appendix II. The EHT model of $I^+(\mathrm{X}, \tilde{\mathbf{X}})$ is obtained by removing an electron from the top-occupied π-orbital $\pi(1)$ and that of $I^+(\mathrm{X}, \tilde{\mathbf{A}})$ by ejecting an electron from the π-orbital $\pi(2)$ of I(X) (see fig. 2 of ref. [2]). Tab. 7 contains the differences ΔOP_{CC} and ΔOP_{CX} between the overlap populations OP_{CC} and OP_{CX} for the radical cation $I^+(\mathrm{X}, \Psi)$ in the states $\tilde{\mathbf{X}}$ and $\tilde{\mathbf{A}}$, and for the neutral molecule I(X). It is to be expected that the differences

$$\Delta OP_{\mu\nu} = OP_{\mu\nu}(\Psi) - OP_{\mu\nu}(\mathbf{X}) \tag{27}$$

correlate qualitatively with $\Delta R_{\mu\nu}$, positive changes in overlap population corresponding to bond shortening and negative changes to bond lengthening. As seen from tab. 7, this is indeed the case as far as the bonds with π-character are concerned.

Table 7. *Changes in bond lengths* $\Delta R_{\mu\nu}(\Psi)$ (in Å) *and changes in overlap population* $\Delta OP_{\mu\nu}$ (according to EHT)

		$(\tilde{\mathbf{X}}) \leftarrow (\mathbf{X})$			$(\tilde{\mathbf{A}}) \leftarrow (\mathbf{X})$		
I(H)	$\Delta OP_{\mu\nu}$		-0.25				
		H —— C	C ≡ C	C —— H			
	$\Delta R_{\mu\nu}$	0.01	0.04				
I(F)	$\Delta OP_{\mu\nu}$		-0.25	0.04		-0.002	-0.05
		H —— C	C ≡ C	C —— F	H —— C	C ≡ C	C —— F
	$\Delta R_{\mu\nu}$	0.02	0.05	-0.06			
I(Cl)	$\Delta OP_{\mu\nu}$		-0.21	0.08		-0.03	-0.10
		H —— C	C ≡ C	C —— Cl	H —— C	C ≡ C	C —— Cl
	$\Delta R_{\mu\nu}$	0.01	0.03	-0.07	0.01	0.03	0.13
I(Br)	$\Delta OP_{\mu\nu}$		-0.07	0.05		-0.16	-0.10
		H —— C	C ≡ C	C —— Br	H —— C	C ≡ C	C —— Br
	$\Delta R_{\mu\nu}$				0.01	0.03	0.15
I(I)	$\Delta OP_{\mu\nu}$		-0.01	0.01		-0.21	-0.07
		H —— C	C ≡ C	C —— I	H —— C	C ≡ C	C —— I
	$\Delta R_{\mu\nu}$	0.01	0.02	-0.08	0.00	0.02	0.15

It is obvious that the EHT model will yield $\Delta OP_{\mathrm{CH}} = 0$ for all π-ionisation processes. However, in analogy to the results quoted above for acetylene [27], one expects that the decrease in π-population on the carbon atom carrying the hydrogen will again induce a drift in the σ-frame which results in a lengthening of the CH bond.

If the photoelectron vacates the orbital $\pi(1)$, *i.e.* if the radical cation $I^+(\mathrm{X}, \tilde{\mathbf{X}})$ is formed in its electronic ground state, then ΔOP_{CC} increases from -0.25 to -0.01 along the series I(F) to I(I). This is in qualitative agreement with the observed trend in the lengthening of the CC bond: $\Delta R_{\mathrm{CC}} = 0.05$ Å in I(F) to $\Delta R_{\mathrm{CC}} = 0.02$ Å in I(I). On the other hand ΔOP_{CX} increases in all cases, and again this prediction is borne out by the observed bond shortening $\Delta R_{\mathrm{CX}} = -0.06$ to -0.08 Å. That the magnitude of ΔOP_{CX} does not correlate well with that of the increments ΔR_{CX} is probably due to the fact that the CX bond shortening is also affected by the change in σ-population, as discussed above in the case of the CH bond.

Ejection of an electron from the orbital $\pi(2)$ results in the radical cation $I(\mathrm{X}, \tilde{\mathrm{A}})$. This ionisation process is accompanied by a decrease of both overlap populations OP_{CC} and OP_{CX}. Again this prediction is borne out by the observed bond lengthenings ΔR_{CC} and ΔR_{CX}.

To conclude, the observed changes in bond lengths on ionisation for the four monohaloacetylenes $I(\mathrm{X})$ support the assignement of the π-bands in the PE. spectra proposed in a previous communication [2].

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Appendix I. – In tab. 8 are listed the **L**-matrices for acetylene $I(\mathrm{H})$ and for the four mono haloacetylenes $I(\mathrm{X})$. The dimensions of the matrix elements L_{ik} have been chosen in such a way, that the elements ΔR_i of the column vector $\boldsymbol{\Delta S}$ of (26) are obtained in Å-units if the elements ΔQ_k of $\boldsymbol{\Delta Q}$ are in units of cm $g^{1/2}$.

Table 8. **L**-*matrices for acetylene and the four monohaloacetylenes*

Dimension of the matrix elements $[L_{ik}]$ = Å $g^{-1/2}cm^{-1}$. Order of columns: ΔQ_1, ΔQ_2, ΔQ_3; Order of rows: ΔR_{CH}, ΔR_{CC}, ΔR_{CX}.

$$10^{20}\begin{pmatrix} .5617 & .0912 & .5690 \\ -.1357 & .2861 & .0000 \\ .5617 & .0912 & -.5690 \end{pmatrix} = \mathbf{L}(\mathrm{H{-}C{\equiv}C{-}H}) \qquad I(\mathrm{H})$$

$$10^{20}\begin{pmatrix} .7967 & .1123 & .0164 \\ -.1052 & .2901 & .0710 \\ .0257 & -.2105 & .1920 \end{pmatrix} = \mathbf{L}(\mathrm{H{-}C{\equiv}C{-}F}) \qquad I(\mathrm{F})$$

$$10^{20}\begin{pmatrix} .7987 & .0982 & .0082 \\ -.0998 & .2978 & .0400 \\ .0210 & -.1855 & .1797 \end{pmatrix} = \mathbf{L}(\mathrm{H{-}C{\equiv}C{-}Cl}) \qquad I(\mathrm{Cl})$$

$$10^{20}\begin{pmatrix} .7987 & .0982 & .0059 \\ -.0997 & .2991 & .0292 \\ .0205 & -.1765 & .1615 \end{pmatrix} = \mathbf{L}(\mathrm{H{-}C{\equiv}C{-}Br}) \qquad I(\mathrm{Br})$$

$$10^{20}\begin{pmatrix} .7984 & .1008 & .0037 \\ -.1007 & .2997 & .0181 \\ .0207 & -.1700 & .1599 \end{pmatrix} = \mathbf{L}(\mathrm{H{-}C{\equiv}C{-}I}) \qquad I(\mathrm{I})$$

Appendix II. – The parameters used in the EHT calculations for the atomic orbitals of hydrogen and carbon atoms were those recommended in the original paper by *Hoffmann* [4], with the exception of the STO exponent ζ of the hydrogen 1s-orbital, for which $\zeta = 1.3$ was used. For

Table 9. *STO exponents* (ζ) *and valence state ionisation potentials* ($H_{\mu\mu}$) *of halogen atomic orbitals*

Atom	Orbital	ζ	$H_{\mu\mu}$ (eV)
F	2*s*	2.6	–40.0
F	2*p*	2.6	–18.1
Cl	2*s*	2.033	–30.0
Cl	2*p*	2.033	–15.0
Br	2*s*	2.054	–24.05
Br	2*p*	2.054	–12.52
I	2*s*	1.9	–18.0
I	2*p*	1.9	–11.4

the halogen atomic orbitals, the STO exponents ζ and the valence state ionisation potentials $H_{\mu\mu}$ are listed in tab. 9. This set of parameters has been suggested by *Gleiter* [30] on the basis of previous values given by other authors [31].

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