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TRANSFERABILITY OF INTENSITY PARAMETERS

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ABSTRACT

The transferability of different kinds of intensity parameters is discussed. In order to transfer dipole moment derivatives with respect to internal or symmetry coordinates (dmd's) among similar modes in different molecules they must be split up into a mode-specific part (the dmd with respect to rotation-free reference coordinates) and a molecule-specific part (the rotational contribution). The calculation of reference coordinates and rotational contributions is discussed. The dmd's with respect to reference coordinates can be expressed in terms of first-order intensity parameters (bcp's or eop's). Expressions are given for CH_3's, propyne, butyne-2 and acetylene. The transferability of bcp's (or eop's) is tested by searching for a common set of bcp's for the following molecules: C_2H_2, C_2D_2, CH_3CCH, CD_3CCH, CH_3CCCH_3, CD_3CCCD_3. The final results are discussed in relation to the basic assumptions and the adopted constraints.

INTRODUCTION

Already during the first period of interest in infrared intensity studies the need of an intensity parameter theory was felt, leading to the development of zero-order bond moment theory. This theory is based upon a very simple model in which the molecular dipole moment is built up from effective bond moments formed by rigid point charges located at the atoms which form the bond. Dipole moment changes occur on stretching by displacement of the rigid charges and on bending by direction change of the bond moments. Unfortunately but not quite unexpectedly, this simple model was not very successful as clearly pointed out by several authors. In the well-known paper by Hornig and Mckean [1] it was concluded that intensity results reported in terms of zero-order parameters (viz. bond moments, μ_k, and bond moment derivatives with respect to bond length, $\partial\mu_k/\partial r_k$) may not only be in error but in some cases may be quite meaningless. One of the severe difficulties was that different values for the parameters were found from vibrations of different symmetry type within the same molecule. Dickson, Mills and Crawford [2] arrived at similar conclusions in their nice paper on the absolute intensities of CH_3-Cl, -Br and -I. Severe criticism on the results of zero-order theory was also given by Orville-Thomas and co-workers [3].

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The failure of zero-order bond moment theory made it inevitable to study the merits of first-order descriptions. The initial reluctance in applying first-order theory is very well understandable viewing the enormous increase in the number of parameters. In all but some small molecules this number is much larger than the number of independent experimental data from which the parameter values must be derived. Nevertheless, first-order theories were developed by several Russian scientists [4]. Their interesting results greatly stimulated new interest in intensity studies, especially facilitated by the English translation of Gribov's book [4a] in which the electro-optical theory is outlined in detail. Later, modifications of Gribov's theory were put forward by Decius (effective atomic charge model) [5], van Straten and Smit (bond charge model) [6] and Galabov and Orville-Thomas [7].

As mentioned before the number of first-order parameters in most cases substantially exceeds the number of experimental data. This arises the problem how to determine uniquely the parameter values. The two main approaches in solving this problem are i) the quantum-mechanical calculation of first-order intensity parameters and ii) the tranferability hypothesis of first-order intensity parameters. The latter approach will be discussed in this paper.

FIRST-ORDER INTENSITY THEORY

Confining us to electro-optical [4a] and bond charge [6] parameter theory the expressions for the dipole moment derivatives in terms of these parameters are

$$\partial\vec{\mu}_\xi/\partial R_j = \Sigma_k[(\partial\mu_k/\partial R_j)\vec{e}_{k\xi} + \mu_k(\partial\vec{e}_{k\xi}/\partial R_j)] \qquad (1)$$

$$\partial\vec{\mu}_\xi/\partial R_j = \Sigma_k[(\partial q_k/\partial R_j)\vec{r}_{k\xi} + q_k(\partial\vec{r}_{k\xi}/\partial R_j)] \qquad (2)$$

where $\vec{\mu}_\xi$ is the ξ-component of the molecular dipole moment (ξ = x,y or z), R_j is an internal coordinate, μ_k, $\vec{e}_k$ and q_k denote the bond moment, the unit vector and the bond charge of the k-th bond, respectively, while $\vec{r}_k = r_k\vec{e}_k$, r_k being the bond length.

The bond moment hypothesis formulated as

$$\vec{\mu} = \Sigma_k \mu_k \vec{e}_k \qquad (3)$$

is used for eqn.(1), whereas the formulation

$$\vec{\mu} = \Sigma_k q_k \vec{r}_k \qquad (4)$$

underlies eqn. (2).

Eqn. (1) is the basic equation of the electro-optical theory [4a] with the intensity parameters μ_k and $\partial\mu_k/\partial R_j$ (eop's), while eqn. (2) is the basic equation of the bond charge parameter theory [6] with the parameters q_k and $\partial q_k/\partial R_j$ (bcp's).

Obviously, the electro-optical and bond charge formulation are closely related as can be easily shown [6b]. The bond moment hypothesis can be written as

$$\vec{\mu} = \sum_k q_k r_k \vec{e}_k \quad , \tag{5}$$

revealing that

$$\mu_k = q_k r_k \quad , \tag{6}$$

while the derivatives are related by

$$\partial\vec{\mu}_k/\partial R_j = (\partial q_k/\partial R_j)\vec{r}_k + q_k \delta_{kj} \tag{7}$$

where the Kronecker δ represents the value of the derivative $\partial\vec{r}_k/\partial R_j$ which is identical to zero unless $R_j \equiv r_k$.

From the point of view of transferability studies the bcp's offer, in principle, an advantage over the eop's [6a] as is immediately clear from eqns. (6) and (7). First, the eop's depend on the bond length, r_k. Since the transferability of bond length and bcp's may differ, this may (slightly) obscure the transferability of eop's. Secondly, the transferability properties of q_k and $\partial q_k/\partial R_j$ may be different, hampering the interpretation of the transferability behaviour of $\partial\mu_k/\partial R_k$.

Before discussing the transferability of bcp's, however, it is worthwhile to realize that also the dipole moment derivatives with respect to internal or symmetry coordinates (dmd's) may be transferable to some extent. In spite of the fact that dmd's describe the change in the molecular dipole moment upon distortion along a symmetry coordinate (instead of changes in bond moments) the actual dipole change may be quite local for symmetry modes of functional groups like $-CH_3$, $-NH_2$, $-OH$, $-C\equiv CH$ etc. Therefore, in the next section some aspects of the transferability of dmd's will be discussed.

TRANSFERABILITY OF DMD'S

In the before mentioned paper of Dickson, Mills and Crawford [2] the explicit relations between the dmd's of a CH_3- molecule and the zero-order intensity parameters are given. These interesting expressions (collected in Table 1)

deserve further attention because of two reasons. First of all, the charm of the zero-order model is immediately clear from the nice simplicity of these expressions. The six experimental dmd's are expressed in terms of only three parameters, viz. μ_{CH}, $\partial\mu_{CH}/\partial r_{CH}$ and $\partial\mu_{CX}/\partial r_{CX}$. Table 2 shows how these expressions look like within the concepts of first-order bond charge parameter theory, the number of parameters now being 13. The second interesting feature is not immediately apparent from the expressions. Careful reading of the original paper [2] reveals that these expressions should be applied to dmd values corrected for the absolute rotational contributions. In other words, the dmd's in the expressions of Table 1 are derivatives with respect to a special set of rotation-free symmetry coordinates. Dickson, Mills and Crawford show in their paper that the symmetry coordinates of a CH_3X molecule in which the hydrogen atoms are replaced by hypothetical isotopes of zero-mass can be used for that purpose. Later, van Straten and Smit [8] proposed the use of hypothetical heavy isotopes instead of zero isotopes because of the more general applicability of such reference molecules.

Behind the use of reference molecules possessing the desired reference coordinates lies the fact that the actual atomic displacements along the same symmetry coordinate in different molecules are in many cases not identical. The reason for this results from the zero linear and angular momentum conditions imposed upon the vibrational motions of a molecule.

Consider the complete set of coordinates of motion (S_i, ρ_j), the subset S_i representing the 3N-6 vibrational coordinates whereas the subset ρ_j contains the six translations and rotations. Another complete set is formed by the 3N Cartesian displacement coordinates x_i. In matrix form the transformation from x_i to (S_i, ρ_i) is given by

$$\left|\frac{S}{\rho}\right| = \left|\frac{B}{\tilde{B}}\right| x \tag{8}$$

and the inverse transformation by

$$x = |A:a| \left|\frac{S}{\rho}\right| \tag{9}$$

From the orthogonality conditions

$$\left|\frac{B}{\tilde{B}}\right| |A:a| = |A:a| \left|\frac{B}{\tilde{B}}\right| = E_{3N} \tag{10}$$

we obtain the following conditions in terms of the submatrices:

Table 1. Dipole moment derivatives[a] of CH_3X expressed in zero-order bond moment parameters[b]

$$\partial\vec{\mu}/\partial S_1{}^{c} = 3^{\frac{1}{2}} \cos\beta\ (\partial\mu_{CH}/\partial r_{CH})\vec{e}_z$$
$$\partial\vec{\mu}/\partial S_2 = 3[3(1+\kappa^2)]^{-\frac{1}{2}} \sin\beta\ \mu_{CH}\ \vec{e}_z$$
$$\partial\vec{\mu}/\partial S_3 = -(\partial\mu_{CX}/\partial r_{CX})\ \vec{e}_z$$
$$\partial\vec{\mu}/\partial S_{4x} = -2^{-\frac{1}{2}} \cdot 3^{\frac{1}{2}} \sin\beta\ (\partial\mu_{CH}/\partial r_{CH})\vec{e}_x$$
$$\partial\vec{\mu}/\partial S_{5x} = -2^{\frac{1}{2}} \cos\tfrac{1}{2}\alpha\mu_{CH}\ \vec{e}_x$$
$$\partial\vec{\mu}/\partial S_{6x} = -6^{\frac{1}{2}} \cos\beta\ \mu_{CH}\ \vec{e}_x$$
$$\kappa = -3 \sin\beta \cos\beta / \sin\alpha$$

[a] With respect to rotation-free symmetry coordinates

[b] The expressions given here are completely identical to those given by Dickson, Mills and Crawford [2].

[c] For a definition of the symmetry coordinates in terms of internal coordinates see e.g. Ref. 10.

Table 2 Dipole moment derivatives[a,b] of CH_3X expressed in bond charge parameters

$$\partial\vec{\mu}/\partial S_1 = 3^{\frac{1}{2}}\{r_{11}\cos\beta[(\partial q_{11}/\partial r_{11}) + 2(\partial q_{11}/\partial r_{21})] - r_{41}(\partial q_{41}/\partial r_{11}) + \cos\beta q_{11}\}\vec{e}_z$$
$$\partial\vec{\mu}/\partial S_2 = 3[3(1+\kappa^2)]^{-\frac{1}{2}}\{r_{11}\cos\beta\kappa[(\partial q_{11}/\partial\alpha_1)+2(\partial q_{11}/\partial\alpha_2)] - r_{11}\cos\beta[(\partial q_{11}/\partial\beta_1) + 2(\partial q_{11}/\partial\beta_2)] - \kappa r_{41}(\partial q_{41}/\partial\alpha_1) + r_{41}(\partial q_{41}/\partial\beta_1) + r_{11}\sin\beta q_{11}\}\vec{e}_z$$
$$\partial\vec{\mu}/\partial S_3 = \{3r_{11}\cos\beta(\partial q_{11}/\partial r_{41}) - r_{41}(\partial q_{41}/\partial r_{41}) - q_{41}\}\vec{e}_z$$
$$\partial\vec{\mu}/\partial S_{Red} = 3[3(1+\kappa^2)]^{-\frac{1}{2}}\{r_{11}\cos\beta[(\partial q_{11}/\partial\alpha_1)+2(\partial q_{11}/\partial\alpha_2)] + r_{11}\cos\beta\kappa[(\partial q_{11}/\partial\beta_1) + 2(\partial q_{11}/\partial\beta_2)] - r_{41}(\partial q_{41}/\partial\alpha_1) - \kappa r_{41}(\partial q_{41}/\partial\beta_1)\}\vec{e}_z$$
$$\partial\vec{\mu}/\partial S_{4x} = -2^{-\frac{1}{2}} \cdot 3^{\frac{1}{2}}\{r_{11}\sin\beta[(\partial q_{11}/\partial r_{11}) - (\partial q_{11}/\partial r_{21})] + \sin\beta q_{11}\}\vec{e}_x$$
$$\partial\mu/\partial S_{5x} = -2^{-\frac{1}{2}} \cdot 3^{\frac{1}{2}}\{r_{11}\sin\beta[(\partial q_{11}/\partial\alpha_1) - (\partial q_{11}/\partial\alpha_2) + 2 \cdot 3^{-\frac{1}{2}} r_{11}\cos\tfrac{1}{2}\alpha q_{11}\}\vec{e}_x$$
$$\partial\mu/\partial S_{6x} = -2^{-\frac{1}{2}} \cdot 3^{\frac{1}{2}}\{r_{11}\sin\beta[(\partial q_{11}/\partial\beta_1) - (\partial q_{11}/\partial\beta_2)] + 2r_{11}\cos\beta q_{11}\}\vec{e}_x$$

[a] With respect to (4,5) heavy isotope reference coordinates

[b] See Ref. 10 for definition of the symmetry coordinates

$$BA = E_{3N-6} \qquad \beta\alpha = E_6 \qquad AB + \alpha\tilde{A} = E_{3N}$$
$$B\alpha = O_{3N-6,6} \qquad \beta A = O_{6,3N-6} \tag{11}$$

The last relation of eqn. (11) directly shows that the form of the symmetry coordinate displacements (as given by the columns of the A matrix) depends on the β matrix. The β matrix represents the six approximate "linear and angular momentum" coordinates or Eckart coordinates which have the following form:

$$\rho_1(T_x) = M^{-1}\sum_i m_i x_i$$
$$\rho_2(T_y) = M^{-1}\sum_i m_i y_i$$
$$\rho_3(T_z) = M^{-1}\sum_i m_i z_i$$
$$\rho_4(R_x) = I_{xe}^{-1}\sum_i m_i(-z_{ie}y_i + y_{ie}z_i) \tag{12}$$
$$\rho_5(R_y) = I_{ye}^{-1}\sum_i m_i(z_{ie}x_i - x_{ie}z_i)$$
$$\rho_6(R_z) = I_{ze}^{-1}\sum_i m_i(-y_{ie}x_i + x_{ie}y_i)$$

where M denotes the molecular mass, m_i the mass of atom i, I_{xe}, I_{ye} and I_{ze} the principal moments of inertia belonging to the equilibrium configuration, x_{ie}, y_{ie} and z_{ie} the components of the equilibrium position vector of atom i with respect to the center of gravity, and x_i, y_i and z_i are the Cartesian displacement coordinates of atom i.

In matrix form eqn. (12) becomes

$$\rho = \beta x \tag{13}$$

which is already included in eqn. (8).

The effect of the last condition of eqn. (11) is that small amounts of translation and/or rotation are mixed into the vibrational displacements as given by the columns of the A matrix. Inspection of eqn. (12) reveals that the translation and rotation coordinates strongly depend on the masses and equilibrium geometry of the molecule under consideration. From the point of view of intensity studies the interesting point is the possibility that small amounts of rotation may be built into a given vibrational mode since in case of molecules with a non-zero permanent moment the mixed-in rotational motion may contribute to the dipole moment change. Such contributions only occur for modes which transform according to the same symmetry type as one of the

rotations. Clearly, the rotational contribution to a certain dmd is molecule dependent and differs even among isotopically related molecules. Therefore, in order to study the transferability properties of dmd's the experimental dmd values have to be split into two parts, a molecule-specific part and a mode-specific part. This can be achieved by the use of rotation-free reference coordinates which bring about the necessary changes in bond lengths and interbond angles without inclusion of rotational motion. Such pure geometrical distortions, denoted by S_g, are found in heavy isotope reference molecules in which properly placed heavy isotopes prevent rotational motion to be mixed-in. The A matrix of such a molecule, denoted as A_g, contains the form of the reference coordinates. Several methods to obtain reference coordinate displacements, including the heavy isotope method were outlined and discussed by Bode, van Straten and Smit [9], each method having its own merits [9c]. However, among them, the heavy (or zero) isotope method forms an easy and elegant way to calculate these quantities.

In order to split the dmd's of actual molecules in their mode-specific and molecule-specific parts one proceeds as follows After the proper Ag matrix has been obtained the absolute rotational contributions are straight forwardly calculated from the matrix equation [9a]

$$V = -P_\rho \mathcal{E} A_g \tag{14}$$

where the elements of the matrix V are the rotational contributions and the matrix P_ρ contains the components of the molecular dipole moment [9a]. The last step is to subtract the rotational contributions from the observed dmd's yielding the desired mode-specific derivatives. In matrix formalism

$$P_{Sg} = P_S - V \tag{15}$$

where the polar tensor P_S contains the observed dmd's. The mode-specific derivatives contained in P_{Sg} are the appropriate quantities for the comparison of similar dmd's in different molecules. Moreover, these quantities can be easily expressed in terms of first-order intensity parameters (see Tables 1-5). These expressions are extremely useful in deciding which first-order parameters have to be taken into account in the refinement procedure as will be discussed in the next section.

Three short examples may further clarify the use of reference coordinates. First, consider the methylgroups in methylbromide and propyne. In order to study the transferability of the dmd's describing the methylmodes in both molecules (see Tables 2 and 3) [10,11] we must use reference coordinates for the E-type

modes. These are easily provided by properly chosen heavy isotope molecules viz. heavy C and Br atoms in CH_3Br and heavy C_4 and C_5 atoms in propyne (see Fig. 1). Obviously, however, every choice of two heavy isotopes along the threefold axis in propyne is formally correct Secondly, consider the two expressions given for $\partial\vec{\mu}/\partial S_{9x}$ in Table 3. As indicated in the Table $\partial\vec{\mu}/\partial S_{9x}(4,5)$ means that the S_{9x} reference coordinate is taken from the propyne molecule with heavy atoms on the C_4 and C_5 positions, whereas $\partial\vec{\mu}/\partial S_{9x}$ (5,6) belongs to the reference molecule with heavy C_5 and C_6 atoms. As can be easily verified from the Table

$$\partial\vec{\mu}/\partial S_{9x}(4,5) - \partial\vec{\mu}/\partial S_{9x}(5,6) = (3\cos\beta r_{11}q_{11} - r_{42}q_{42} - r_{51}q_{51} + r_{61}q_{61})\vec{e}_x \qquad (16)$$

The expression for the dipole moment of propyne in terms of bond charges reads

$$\vec{\mu}_{pro} = (3\cos\beta r_{11}q_{11} - r_{42}q_{42} - r_{51}q_{51} + r_{61}q_{61})\vec{e}_z \qquad (17)$$

showing that the magnitude of the R.H.S. of eqn. (16) equals the magnitude of the permanent moment of propyne. From eqns. (15), (16) and (17) we obtain

$$|V_{9x}(5,6) - V_{9x}(4,5)| = |\mu_{pro}| \qquad (18)$$

Eqn. (18) is exactly confirmed by the calculated values for the rotational contributions based on the indicated reference molecules:

$$V_{9x}(5,6) = -0.42883\ D\text{Å}^{-1} \quad , \quad V_{9x}(4,5) = 0.32117\ D\text{Å}^{-1}$$

This result is easily understandable if one realizes that combining these two forms of S_{9x}, viz. $S_{9x}(4,5)$ and $S_{9x}(5,6)$, in the sense of eqn. (16) just results in a rotation of the whole molecule leading to a dipole moment change with the magnitude of μ_{pro}.

As a third example consider $\partial\vec{\mu}/\partial\theta_{1x}$ of acetylene (see Table 4) and $\partial\vec{\mu}/\partial S_{9x}$ of propyne. Proper comparison of these derivatives requires the use of a (4,5) reference molecule for propyne, while in comparing $\partial\vec{\mu}/\partial S_{12x}$ of butyne-2 (see Table 5) and $\partial\vec{\mu}/\partial S_{9x}$ of propyne a (5,6) reference coordinate should be used. In order to avoid confusion it should be remarked that comparison of $\partial\vec{\mu}/\partial\theta_{1x}$ and $\partial\vec{\mu}/\partial S_{9x}$ is mentioned here just for the sake of illustrating the use of reference molecules; in practice, comparison of $\partial\vec{\mu}/\partial\theta_{2x}$ (or $\partial\vec{\mu}/\partial\theta_{1x}$) of acetylene and $\partial\vec{\mu}/\partial S_{10x}$ of propyne is more useful, in which case either the (4,5) or the (5,6) reference coordinates may be used.

Table 3. Symmetry coordinates[a] and dipole moment derivatives[b] of propyne expressed in bond charge parameters.

A_1 $S_1 = 3^{-\frac{1}{2}}(\Delta r_{11} + \Delta r_{21} + \Delta r_{31})$

$S_2 = [3(1+\kappa^2)]^{-\frac{1}{2}} R\{\kappa(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) - (\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)\}$

$S_3 = \Delta r_{42}$

$S_4 = \Delta r_{51}$

$S_5 = \Delta r_{61}$

$S_{Red} = [3(1+\kappa^2)]^{-\frac{1}{2}} R\{(\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3) + \kappa(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)\}$

E $S_{6x} = 6^{-\frac{1}{2}}(2\Delta r_{11} - \Delta r_{21} - \Delta r_{31})$

$S_{7x} = 6^{-\frac{1}{2}} R(2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)$

$S_{8x} = 6^{-\frac{1}{2}} R(2\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3)$

$S_{9x} = R\Delta\omega_{1x}$

$S_{10x} = R\Delta\theta_{2x}$

$\partial\vec{\mu}/\partial S_1 = 3^{\frac{1}{2}}\{r_{11}\cos\beta[(\partial q_{11}/\partial r_{11}) + 2(\partial q_{11}/\partial r_{21})] - r_{42}(\partial q_{42}/\partial r_{11}) - r_{51}(\partial q_{51}/\partial r_{11}) + r_{61}(\partial q_{61}/\partial r_{11}) + \cos\beta q_{11}\}\vec{e}_z$

$\partial\vec{\mu}/\partial S_2 = 3[3(1+\kappa^2)]^{-\frac{1}{2}}\{r_{11}\cos\beta\kappa[(\partial q_{11}/\partial\alpha_1) + 2(\partial q_{11}/\partial\alpha_2)] - r_{11}\cos\beta[(\partial q_{11}/\partial\beta_1) + 2(\partial q_{11}/\partial\beta_2)] - \kappa r_{42}(\partial q_{42}/\partial\alpha_1) + r_{42}(\partial q_{42}/\partial\beta_1) - \kappa r_{51}(\partial q_{51}/\partial\alpha_1) + r_{51}(\partial q_{51}/\partial\beta_1) + \kappa r_{61}(\partial q_{61}/\partial\alpha_1) - r_{61}(\partial q_{61}/\partial\beta_1) + r_{11}\sin\beta q_{11}\}\vec{e}_z$

$\partial\vec{\mu}/\partial S_3 = \{3r_{11}\cos\beta(\partial q_{11}/\partial r_{42}) - r_{42}(\partial q_{42}/\partial r_{42}) - q_{42} - r_{51}(\partial q_{51}/\partial r_{42}) + r_{61}(\partial q_{61}/\partial r_{42})\}\vec{e}_z$

$\partial\vec{\mu}/\partial S_4 = \{3r_{11}\cos\beta(\partial q_{11}/\partial r_{51}) - r_{42}(\partial q_{42}/\partial r_{51}) - r_{51}(\partial q_{51}/\partial r_{51}) - q_{51} + r_{61}(\partial q_{61}/\partial r_{51})\}\vec{e}_z$

$\partial\vec{\mu}/\partial S_5 = \{3r_{11}\cos\beta(\partial q_{11}/\partial r_{61}) - r_{42}(\partial q_{42}/\partial r_{61}) - r_{51}(\partial q_{51}/\partial r_{61}) + r_{61}(\partial q_{61}/\partial r_{61}) + q_{61}\}\vec{e}_z$

$\partial\vec{\mu}/\partial S_{Red} = 3[3(1+\kappa^2)]^{-\frac{1}{2}}\{r_{11}\cos\beta[(\partial q_{11}/\partial\alpha_1) + 2(\partial q_{11}/\partial\alpha_2)] + r_{11}\cos\beta\kappa[(\partial q_{11}/\partial\beta_1) + 2(\partial q_{11}/\partial\beta_2) - r_{42}(\partial q_{42}/\partial\alpha_1) - \kappa r_{42}(\partial q_{42}/\partial\beta_1) - r_{51}(\partial q_{51}/\partial\alpha_1) - \kappa r_{51}(\partial q_{51}/\partial\beta_1) + r_{61}(\partial q_{61}/\partial\alpha_1) + \kappa r_{61}(\partial q_{61}/\partial\beta_1)\}\vec{e}_z$

$\partial\vec{\mu}/\partial S_{6x} = -2^{-\frac{1}{2}} \cdot 3^{\frac{1}{2}}\{r_{11}\sin\beta[(\partial q_{11}/\partial r_{11}) - (\partial q_{11}/\partial r_{21})] + \sin\beta q_{11}\}\vec{e}_x$

$\partial\vec{\mu}/\partial S_{7x} = -2^{-\frac{1}{2}} \cdot 3^{\frac{1}{2}}\{r_{11}\sin\beta[(\partial q_{11}/\partial\alpha_1) - (\partial q_{11}/\partial\alpha_2)] + 2.3^{-\frac{1}{2}} r_{11}\cos\frac{1}{2}\beta q_{11}\}\vec{e}_x$

$\partial\vec{\mu}/\partial S_{8x} = -2^{-\frac{1}{2}} \cdot 3^{\frac{1}{2}}\{r_{11}\sin\beta[(\partial q_{11}/\partial\beta_1) - (\partial q_{11}/\partial\beta_2)] + 2r_{11}\cos\beta q_{11}\}\vec{e}_x$

$\partial\vec{\mu}/\partial S_{9x}(4,5) = \{-r_{11}\sin\beta[(\partial q_{11}/\partial\omega_{1x}) - (\partial q_{21}/\partial\omega_{1x})] - r_{51}q_{51} + r_{61}q_{61}\}\vec{e}_x$

$\partial\vec{\mu}/\partial S_{9x}(5,6) = \{-r_{11}\sin\beta[(\partial q_{11}/\partial\omega_{1x}) - (\partial q_{21}/\partial\omega_{1x})] - 3\cos\beta r_{11}q_{11} + r_{42}q_{42}\}\vec{e}_x$

$\partial\vec{\mu}/\partial S_{10x} = \{-r_{11}\sin\beta[(\partial q_{11}/\partial\theta_{2x}) - (\partial q_{21}/\partial\theta_{2x})] + r_{61}q_{61}\}\vec{e}_x$

[a] See Figure 1 for definition of the internal coordinates.

[b] With respect to (4,5) and / or (5,6) reference coordinates.

Table 4. Dipole moment derivatives[a] of acetylene expressed in bond charge parameters.

$$\partial\vec{\mu}/\partial S_3 = 2^{\frac{1}{2}}(-r_{43}(\partial q_{43}/\partial r_{61}) - r_{52}(\partial q_{52}/\partial r_{61}) + r_{61}(\partial q_{61}/\partial r_{61}) + q_{61})\vec{e}_z$$
$$\partial\vec{\mu}/\partial S_{5x} = 2^{\frac{1}{2}} r_{61} q_{61}\vec{e}_x$$
$$\partial\vec{\mu}/\partial r_{61} = 2^{-\frac{1}{2}}\partial\vec{\mu}/\partial S_3$$
$$\partial\vec{\mu}/\partial\theta_{1x} = 2^{-\frac{1}{2}}\partial\vec{\mu}/\partial S_{5x}$$

[a] With respect to symmetry and internal coordinates

Table 5. Dipole moment derivatives[a] of butyne-2 expressed in bond charge parameters

$$\begin{aligned}\partial\vec{\mu}/\partial S_6 = {} & 6^{\frac{1}{2}}(r_{11}\cos\beta[(\partial q_{11}/\partial r_{11}) + 2(\partial q_{11}/\partial r_{21})] - r_{42}(\partial q_{42}/\partial r_{11}) \\ & - r_{52}(\partial q_{52}/\partial r_{11}) + r_{62}(\partial q_{62}/\partial r_{11}) \\ & - r_{71}\cos\beta[(\partial q_{71}/\partial r_{11}) + 2(\partial q_{71}/\partial r_{21})] + \cos\beta q_{11})\vec{e}_z\end{aligned}$$

$$\begin{aligned}\partial\vec{\mu}/\partial S_7 = {} & 2^{\frac{1}{2}} \cdot 3[3(1+\kappa^2)]^{-\frac{1}{2}}(r_{11}\cos\beta\kappa[(\partial q_{11}/\partial\alpha_1) + 2(\partial q_{11}/\partial\alpha_2)] \\ & - r_{11}\cos\beta[(\partial q_{11}/\partial\beta_1) + 2(\partial q_{11}/\partial\beta_2)] - \kappa r_{42}(\partial q_{42}/\partial\alpha_1) \\ & + r_{42}(\partial q_{42}/\partial\beta_1) - \kappa r_{52}(\partial q_{52}/\partial\alpha_1) + r_{52}(\partial q_{52}/\partial\beta_1) \\ & + \kappa r_{62}(\partial q_{62}/\partial\alpha_1) - r_{62}(\partial q_{62}/\partial\beta_1) - r_{71}\cos\beta\kappa[(\partial q_{71}/\partial\alpha_1) \\ & + 2(\partial q_{71}/\partial\alpha_2)] + r_{72}\cos\beta[(\partial q_{71}/\partial\beta_1) + 2(\partial q_{71}/\partial\beta_2)] + r_{11}\sin\beta q_{11})\vec{e}_z\end{aligned}$$

$$\begin{aligned}\partial\vec{\mu}/\partial S_8 = {} & 2^{\frac{1}{2}}(3r_{11}\cos\beta(\partial q_{11}/\partial r_{42}) - r_{42}(\partial q_{42}/\partial r_{42}) - q_{42} - r_{52}(\partial q_{52}/\partial r_{42}) \\ & + r_{62}(\partial q_{62}/\partial r_{42}) - 3r_{71}\cos\beta(\partial q_{71}/\partial r_{42}))\vec{e}_z\end{aligned}$$

$$\begin{aligned}\partial\vec{\mu}/\partial S_{Red2} = {} & 2^{\frac{1}{2}} \cdot 3[3(1+\kappa^2)]^{-\frac{1}{2}}(r_{11}\cos\beta[(\partial q_{11}/\partial\alpha_1) + 2(\partial q_{11}/\partial\alpha_2)] \\ & + \kappa r_{11}\cos\beta[(\partial q_{11}/\partial\beta_1) + 2(\partial q_{11}/\partial\beta_2)] - r_{42}(\partial q_{42}/\partial\alpha_1) \\ & - \kappa r_{42}(\partial q_{42}/\partial\beta_1) - r_{52}(\partial q_{52}/\partial\alpha_1) - \kappa r_{52}(\partial q_{52}/\partial\beta_1) \\ & + r_{62}(\partial q_{62}/\partial\alpha_1) + \kappa r_{62}(\partial q_{62}/\partial\beta_1) - r_{71}\cos\beta[(\partial q_{71}/\partial\alpha_1) \\ & + 2(\partial q_{71}/\partial\alpha_2)] - \kappa r_{71}\cos\beta[(\partial q_{71}/\partial\beta_1) + 2(\partial q_{71}/\partial\beta_2)])\vec{e}_z\end{aligned}$$

$$\begin{aligned}\partial\vec{\mu}/\partial S_{9x} = {} & -3^{\frac{1}{2}}(r_{11}\sin\beta[(\partial q_{11}/\partial r_{11}) - (\partial q_{11}/\partial r_{21})] \\ & + r_{71}\sin\beta[(\partial q_{71}/\partial r_{11}) - (\partial q_{71}/\partial r_{21})] + \sin\beta q_{11})\vec{e}_x\end{aligned}$$

$$\begin{aligned}\partial\vec{\mu}/\partial S_{10x} = {} & -3^{\frac{1}{2}}(r_{11}\sin\beta[(\partial q_{11}/\partial\alpha_1) - (\partial q_{11}/\partial\alpha_2)] \\ & + r_{71}\sin\beta[(\partial q_{71}/\partial\alpha_1) - (\partial q_{71}/\partial\alpha_2)] + 2 \cdot 3^{-\frac{1}{2}} r_{11}\cos\frac{1}{2}\alpha q_{11})\vec{e}_x\end{aligned}$$

$$\begin{aligned}\partial\vec{\mu}/\partial S_{11x} = {} & -3^{\frac{1}{2}}(r_{11}\sin\beta[(\partial q_{11}/\partial\beta_1) - (\partial q_{11}/\partial\beta_2)] \\ & + r_{71}\sin\beta[(\partial q_{71}/\partial\beta_1) - (\partial q_{71}/\partial\beta_2)] + 2r_{11}\cos\beta q_{11})\vec{e}_x\end{aligned}$$

$$\begin{aligned}\partial\vec{\mu}/\partial S_{12x} = {} & 2^{\frac{1}{2}}(-r_{11}\sin\beta[(\partial q_{11}/\partial\omega_{1x}) - (\partial q_{21}/\partial\omega_{1x})] - 3r_{11}\cos\beta q_{11} + r_{42}q_{42} \\ & - r_{71}\sin\beta[(\partial q_{71}/\partial\omega_{1x}) - (\partial q_{81}/\partial\omega_{1x})])\vec{e}_x\end{aligned}$$

[a] See Ref. 15 for definition of the symmetry coordinates.

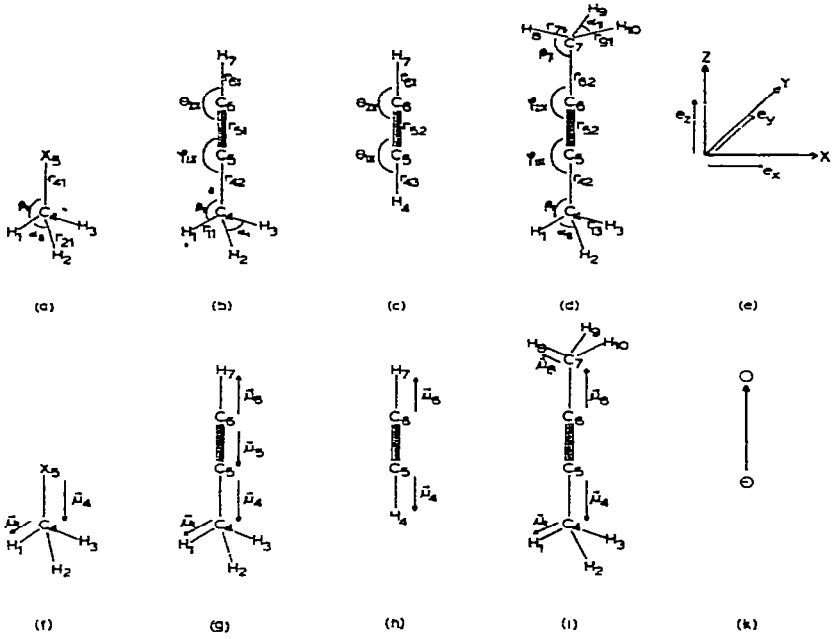

Figure 1. Definition of internal coordinates (a-d), Cartesian axis system and unit vectors (e), bond moment directions (f-i) and dipole moment direction (k).

DETERMINATION OF A COMMON SET BCP'S FOR ACETYLENE, PROPYNE AND BUTYNE-1

Eqns. (1) and (2) show that, in principle, each $\partial\mu/\partial R_j$ is expressed in all q_k (or μ_k) and all $\partial q_k/\partial R_j$ (or $\partial\mu_k/\partial R_j$) For a non-cyclic, N atomic molecule k runs from 1 to N-1, so the number of bcp's for one dmd is 2N-2. Further, it is important to note that the q_k occur in each dmd, whereas the $\partial q_k/\partial R_j$ only occur in $\partial\mu/\partial R_j$. Therefore, the total number of bcp's in the dmd expressions of a molecule amounts to

$$(3N-6)(N-1) + N-1 = (3N-5)(N-1) \qquad (19)$$

In general, this number is considerably larger than the number of dmd values from which the parameters must be determined. Consider, for instance, a moderate

size molecule like propyne (N=7). The number of bcp's, according to eqn. (19), amounts up to 96 However, taking full advantage of the C_{3v} symmetry of this molecule, this number reduces to 35. The number of data from which these parameters must be determined amounts to 12, namely 10 intensity data (5 non-degenerate A_1-type modes and 5 doubly-degenerate E-type modes), $\partial\mu/\partial S_{Red}$ (only if S_{Red} has the same symmetry as one of the infrared active modes) and μ_{pro}. Solving for all 35 parameters would only be possible by quantum-mechanical calculations. The feasibility of such calculations is beyond the scope of this paper and will not be discussed here. As mentioned before, a second approach, on which we focuss in this paper, is based upon the transferability hypothesis of first-order intensity parameters. In this approach we assume that the q_k's are transferable to similar bonds (here similarity includes to some extent the nature of the adjacent bonds). The same holds for the charge-flux parameters, $\partial q_k/\partial R_j$. The assumption of transferability of the charge-flux bcp's necessarily means that they are assumed to have a local character, implying that zero values are assigned to bond charge derivatives with respect to remote coordinates. If only the bond charge derivatives with respect to their own bond length and with respect to adjacent bond lengths and interbond angles are taken into account, the number of bcp's for propyne reduces to 21. Even this reduced parameter number largely exceeds the number of available data for propyne. Therefore successful determination of the parameter values requires the simultaneous use of intensity data for a number of closely related molecules. In this paper we consider the following molecules: $CH_3C{\equiv}CH$, $CD_3C{\equiv}CH$, $HC{\equiv}CH$, $DC{\equiv}CD$, $CH_3C{\equiv}CCH_3$ and $CD_3C{\equiv}CCD_3$. By use of a non-linear least-squares fitting procedure we will try to find a common set bcp's for these molecules. The procedure starts from the well-known relation between the absolute intensities A_i and the dipole moment derivatives with respect to normal coordinates, $\partial\vec{\mu}/\partial Q_i$, which reads

$$A_i = \frac{N_o \pi g_i}{3c^2} \frac{\nu_i}{\omega_i} (\partial\vec{\mu}/\partial Q_i)^2 \qquad (20)$$

where N_o is Avogadro's number, g_i is the degree of degeneracy, c is the velocity of light, ν_i and ω_i are the observed and harmonic frequencies. The $\partial\vec{\mu}/\partial Q_i$'s can be written in terms of internal coordinates and subsequently expressed in terms of bcp's according to eqn. (2) The general form of the expressions can be given in matrix notation by

$$\partial\vec{\mu}/\partial Q_i = \tilde{c}_i P_q \qquad (21)$$

where the entries of the column matrix P_q are the bcp's taken into account in

the refinement procedure and $\tilde{c}_l$ is a row matrix containing the coefficients of the bcp's. In determining the common bcp values we not only use the absolute intensities of the molecules considered, but also the non-zero equilibrium dipole moments and the $\partial\vec{\mu}/\partial S_{Red}$ quantities (derivatives with respect to redundant symmetry coordinates, see Tables 3-5) which belong to the same symmetry species as the infrared active modes. Both dipole moments and $\partial\vec{\mu}/\partial S_{Red}$ quantities can be expressed in terms of bcp's according to eqn. (21) and thus can be treated as pseudo $\partial\vec{\mu}/\partial Q$ quantities. It should be noted that propyne-d_o and propyne-d_3 each provide 10 intensity values giving 20 $\partial\vec{\mu}/\partial Q_l$ expressions but provide together only 2 pseudo $\partial\vec{\mu}/\partial Q_l$ expressions, viz. one for $\vec{\mu}_{pro}$ and one for $\partial\vec{\mu}/\partial S_{Red}$. The series of molecules considered in this work provides 41 experimental data (C_2H_2 and C_2D_2 [12,13]. $4A_1$, $CH_3C{\equiv}CH$ and $CD_3C{\equiv}CH$ [11,14] $20A_1$, $\vec{\mu}_{pro}$ and $\partial\vec{\mu}/\partial S_{Red}$, $CH_3C{\equiv}CCH_3$ and $CD_3C{\equiv}CCD_3$ [15] $14A_1$ and $\partial\vec{\mu}/\partial S_{Red2}$).

In order to obtain the relations between the absolute intensities (including pseudo-intensities) and the bcp's we proceed as follows

$$(\partial\vec{\mu}/\partial Q_l)^2 = \tilde{c}_l P_q \tilde{P}_q c_l \qquad (22)$$

Let us define the column matrix

$$A = DP \qquad (23)$$

where the entries of A are the experimental data A_l (intensities and pseudo-intensities) and D is a diagonal matrix containing the coefficients

$$D_l = \frac{N_o \pi g_l}{3c^2} \frac{\nu_l}{\omega_l}$$

In the case of pseudo-intensities $g_l \nu_l/\omega_l = 1$. P is a column matrix containing the quantities

$$P_l = \tilde{c}_l P_q \tilde{P}_q c_l$$

A somewhat different formulation of these relations is given in Ref. 16

The refinement procedure starts with an initial set bcp values chosen within the range of physically acceptable values. Arbitrary chosen values lead very often to unacceptable results as reported already by Saeki and Tanabe [17,18]. As will be discussed later, however, even acceptable sets may result in unacceptable solutions. From the initial set a first set of intensities is calculated, A(calc 1), giving the first difference matrix

$$\Delta A(1) = A(exp) - A(calc\ 1) \qquad (24)$$

On differentiating the relations contained in eqn (23) one obtains a first-order expression for ΔA_i in terms of ΔP_q.

$$\Delta A_i = 2D_i\tilde{c}_i P_q \tilde{c}_i \Delta P_q = K_i \Delta P_q \tag{25}$$

where

$$\Delta A_i = \Sigma_j \partial A_{ij} \tag{26}$$

The quantities ∂A_{ij} of eqn. (26) denote the change in A_i upon a unit change in bond charge parameter P_{qj}. The index i runs from 1 to m, m being the total number of experimental data. The index j runs from 1 to n, n being the total number of bcp's that have to be refined. The elements of the column matrix ΔP_q are the changes in the bcp's, viz. ∂P_{qj} (j = 1,n).
The row matrix

$$K_i = 2D_i\tilde{c}_i P_q \tilde{c}_i \tag{27}$$

contains n elements K_{ij} (j = 1,n). Collecting the ΔA_i in the column matrix ΔA gives

$$\Delta A = K\Delta P_q \tag{28}$$

leading to the least-squares equation

$$\Delta P_q = (\tilde{K}WK)^{-1}\tilde{K}W\Delta A \tag{29}$$

where W is a square diagonal matrix containing the statistical weights assigned to the experimental data. Inserting $\Delta A(1)$ of eqn. (24) into eqn. (29) gives a first set of corrections to the bcp's, viz. $\Delta P_q(1)$. These corrections are added to P_q, leading to $\Delta A(2)$ and $\Delta P_q(2)$. The procedure stops when $[S(k+1) - S(k)]/S(k)$ becomes smaller than a preset value. S(k) denotes the least-squares sum of the k-th iteration step, the sum being defined by

$$S = \sum_{i=1}^{m} (\Delta A_i)^2 W_{ii} \tag{30}$$

Due to dependencies among the relations of eqn. (23) the matrix $\tilde{K}K$ (or $\tilde{K}WK$) may be singular or near-singular, a well known problem in refinement procedures. Such singularities must be properly removed. For that purpose we have adopted the procedure described in Ref. 19. Other procedures are possible and have been used [20]. The chance that singularities occur strongly depends on the number

of parameters that have to be refined in relation to the number of experimental data. Generally spoken, the number of parameters must be considerably smaller than the number of experimental data. However, in judging that situation, one should keep in mind that a) the experimental data very often are only a function of a limited number of parameters (see Tables 1-5) and b) some parameters always occur in fixed combinations with other parameters; in such cases the combinations must sometimes be treated as a single parameter.

In the case of acetylene, propyne and butyne-2 the situation is as follows The number of local bcp's in propyne is 21, in acetylene 3, while the infrared active dmd's of butyne-2 contain 14 parameters. All butyne-2 and acetylene bcp's occur in propyne so that the total number of parameters equals 21. In order to start the refinement procedure we need an initial set parameter values. However, before discussing the evaluation of a starting set, a very important observation has to be made.

In principle, the relations of Tables 3, 4 and 5 allow the determination of almost all local bcp's. From $\partial\vec{\mu}/\partial S_1$, $\partial\vec{\mu}/\partial S_{6x}$(pro) and $\partial\vec{\mu}/\partial S_6$, $\partial\vec{\mu}/\partial S_{9x}$(bu) values can be obtained for q_{11}, $\partial q_{11}/\partial r_{11}$, $\partial q_{11}/\partial r_{21}$ and $\partial q_{42}/\partial r_{11}$ Similarly, values for q_{11}, $\partial q_{11}/\partial\alpha_1$, $\partial q_{11}/\partial\alpha_2$, $\partial q_{42}/\partial\alpha_1$, $\partial q_{11}/\partial\beta_1$, $\partial q_{11}/\partial\beta_2$ and $\partial q_{42}/\partial\beta_1$ can be derived from $\partial\vec{\mu}/\partial S_2$, $\partial\vec{\mu}/\partial S_{Red}$, $\partial\vec{\mu}/\partial S_{7x}$, $\partial\vec{\mu}/\partial S_{8x}$(pro) and $\partial\vec{\mu}/\partial S_7$, $\partial\vec{\mu}/\partial S_{Red2}$, $\partial\vec{\mu}/\partial S_{10x}$, $\partial\vec{\mu}/\partial S_{11x}$(bu). The bond charges q_{61} and q_{51} follow from $\partial\vec{\mu}/\partial S_{9x}(4,5)$, $\partial\vec{\mu}/\partial S_{10x}$(pro) and $\partial\vec{\mu}/\partial S_{5x}$(ace) In principle, q_{11}, q_{51} and q_{61} being determined, a value for q_{42} follows from the expression for $\vec{\mu}_{prc}$, whereas $\partial\vec{\mu}/\partial S_{9x}(5,6)$(pro) and $\partial\vec{\mu}/\partial S_{12x}$(bu) serve as a check. Further, from $\partial\vec{\mu}/\partial S_5$(pro) and $\partial\vec{\mu}/\partial S_3$(ace) we obtain values for $\partial q_{61}/\partial r_{61}$ and $\partial q_{51}/\partial r_{61}$. The remaining dmd's are $\partial\vec{\mu}/\partial S_3$(pro) and $\partial\vec{\mu}/\partial S_8$(bu), containing $\partial q_{42}/\partial r_{42}$, $\partial q_{11}/\partial r_{42}$, $\partial q_{51}/\partial r_{42}$ and $\partial q_{52}/\partial r_{42}$. Additional relations are necessary to solve for all these parameters. Finally we have $\partial\vec{\mu}/\partial S_4$(pro) with $\partial q_{51}/\partial r_{51}$, $\partial q_{42}/\partial r_{51}$ and $\partial q_{61}/\partial r_{51}$ Here we need two constraints to solve for the parameters.

In practice, the solving procedure described above fails completely. The values obtained are physically unacceptable in most cases and the results for the same parameter obtained from different sets of equations are inconsistent. For instance, the q_{11} values independently obtained from the methyl stretching dmd's, the α bending dmd's and the β bending dmd's are very different, namely 2.8, -35.8 and -22.4 $D\text{Å}^{-1}$ respectively. The spread in these values indicates that the systematic and/or random errors in the dmd values are too large to find acceptable and consistent solutions. Close inspection of the $\partial\vec{\mu}/\partial S$ expressions reveals that the differences in the relations containing the same non-zero bcp's (e.g. $\partial\vec{\mu}/\partial S_1$(pro) and $\partial\vec{\mu}/\partial S_6$(bu)) result from the small differences in the values of the geometrical parameters. Therefore these relations can only be successfully applied to solve for the bcp's if the errors in the dmd's are of the same order as the uncertainties in the geometry data of the molecules. In

practice, we are far from that accuracy and it is highly unlikely that as far as random errors are considered the situation will improve to that level within the next twenty years. Moreover, systematic errors may play an important role. First, in several cases Fermi resonance corrections have to be applied to the measured intensities. Some of these corrections may be in error since the intrinsic anharmonic intensity of the overtones or combination bands involved is not always taken into account. Secondly, the tranferability hypothesis (zero values for the bond charge derivatives with respect to remote coordinates) might not be valid for some molecules. Especially in the case of symmetric molecules like acetylene and butyne-2, the in-phase stretching and bending modes of the terminal groups (≡C-H, ≡C-CH_3) may lead to non-zero values for non-local bcp's ("long-range" bcp's). The large differences in the values for $\partial\vec{\mu}/\partial S_1$(pro) and $\partial\vec{\mu}/\partial S_6$(bu) and also $\partial\vec{\mu}/\partial S_{9x}$(5,6)(pro) and $\partial\vec{\mu}/\partial S_{12x}$(bu) point to that direction (see Table 6). The situation is not clear-cut, however, viewing the good correspondence between $\partial\vec{\mu}/\partial S_{10x}$(pro) and $\partial\vec{\mu}/\partial S_{5x}$(ace). Thirdly, errors in the L matrix elements may influence the obtained results.

TABLE 6

Dmd values for propyne, butyne-2 and acetylene. Units $D\text{Å}^{-1}$.

Propyne[a,b]		Butyne-2[c]		Acetylene[d]	
A_1	0.618	A_2''	0.83	Σ_u	
	0.089		0.09		
	-0.052		-0.11		
	-1.228				
	0.871				0.894
E	0.381	E'	0.44	π_u	
	-0.424		-0.39		
	0.249		0.17		
	1.557		1.37		
	1.074				1.052

[a] E-type dmd's with respect to a (5,6) reference coordinate.
[b] Ref. 11.
[c] Ref. 15; dmd values divided by √2 to allow direct comparison with propyne.
[d] Average values taken from Refs. 12 and 13; average dmd values divided by √2.

Therefore, physically meaningful solutions may not be expected from a least-squares refinement procedure based on experimental intensity data regardless the physical quality of the initial set. This is clearly shown by the results given in Table 7. The independent bcp's for the molecules considered in this work are shown in the first column. The last three bcp's are combinations as indicated in the footnote to Table 7. The initial set I was obtained from propyne, butyne and acetylene, using the following constraints:

$$\begin{aligned} \partial q_{11}/\partial r_{21} &= 0.2\ \partial q_{11}/\partial r_{11} \\ \partial q_{11}/\partial \alpha_2 &= -2.5\ \partial q_{11}/\partial \alpha_1 \\ \partial q_{11}/\partial \beta_2 &= -0.6\ \partial q_{11}/\partial \beta_1 \\ q_{42} &= 0.5\ q_{11} \end{aligned} \qquad (31)$$

The first constraint is taken from the paper of Jona, Gussoni and Zerbi [21] in which a quite similar calculation is reported. The second and third one are taken from our work on CH_3Br [10] and the last one from ab initio results on propyne reported by Newton and Lipscomb [22] and used already in our earlier work on propyne [11,23]. Initial set II is obtained by using the same constraints on $\partial q_{11}/\partial r_{21}$, $\partial q_{11}/\partial \alpha_2$ and $\partial q_{11}/\partial \beta_2$ and adopting the values for the bond charges as reported by Jona et al. [21]. The final sets obtained from the initial sets are almost identical as can be seen from the Table.

TABLE 7

Two almost identical final sets of common bcp's for acetylene, propyne and butyne-2 obtained from two different initial sets[a]

bcp	initial set		final set	
	I	II	I	II
q_{11}	0.797	0.474	-0.654	-0.648
q_{42}	0.401	0.694	1.518	1.513
q_{51}	0.224	0.206	0.275	0.275
q_{61}	0.987	1.002	0.991	0.991
$\partial q_{11}/\partial r_{11}$	-1.308	-0.943	-6.235	-6.234
$\partial q_{11}/\partial r_{12}$	-0.262	-0.189	-6.505	-6.500
$\partial q_{42}/\partial r_{11}$	0.010	-0.049	5.003	4.997
$\partial q_{11}/\partial \alpha_1$	-0.073	-0.006	0.982	0.970
$\partial q_{11}/\partial \alpha_2$	0.183	0.016	0.194	0.186
$\partial q_{42}/\partial \alpha_1$	0.180	0.135	-0.621	-0.612
$\partial q_{11}/\partial \beta_1$	0.271	0.119	-0.281	-0.256
$\partial q_{11}/\partial \beta_2$	-0.163	-0.071	0.366	0.387
$\partial q_{42}/\partial \beta_1$	-0.228	-0.130	0.124	0.105
$\partial q_{42}/\partial r_{42}$[b]	-0.218	-0.418	-0.991	-0.989
$\partial q_{51}/\partial r_{51}$[b]	0.832	0.847	0.799	0.800
$\partial q_{61}/\partial r_{61}$[b]	-0.109	-0.124	-0.098	-0.098

[a] See text for choice of initial sets; the calculation of the final sets was based on the experimental data of Refs. 11, 12, 13 and 15.

[b] The last three bcp's denote the following combinations:

$\partial q_{42}/\partial r_{42} \equiv (\partial q_{42}/\partial r_{42}) - 3(r_{11}/r_{42})\cos\beta(\partial q_{11}/\partial r_{42}) + (r_{51}/r_{42})(\partial q_{51}/\partial r_{42})$

$\partial q_{51}/\partial r_{51} \equiv (\partial q_{51}/\partial r_{51}) + (r_{42}/r_{51})(\partial q_{42}/\partial r_{51}) - (r_{61}/r_{51})(\partial q_{61}/\partial r_{51})$

$\partial q_{61}/\partial r_{61} \equiv (\partial q_{61}/\partial r_{61}) - (r_{51}/r_{61})(\partial q_{51}/\partial r_{61})$.

Quite similar final sets were obtained by varying q_{11} and q_{42} over a number of intermediate values indicating that all these initial sets are refined to the same unique solution pertaining to the experimental data used. Both the

intensity data and the dmd values are rather well predicted by this common parameter set (see Table 9). Obviously, however, the final parameter values are unacceptable (with a few exceptions) from a physical point of view. As expected, the final values are in line with the results obtained by solving directly the dmd expressions. An interesting feature of the solution obtained is that both the intensities and dmd's are satisfactorily predicted. This confirms that indeed the correct dmd sets have been selected for propyne [11,14] and butyne-2 [15] and indicates that use of the transferability properties of dmd's may be very helpful in the determination of sign and magnitude of dmd quantities.

It is clear, however, that the simultaneous refinement of all independent bcp's will not lead to physically acceptable solutions. The question arises how such a solution can be obtained. In fact, the initial sets of Table 7 are examples of acceptable solutions. The quality of these sets depends on the quality of the intensity data used in this work and on the physical reality of the constraints used. The adopted constraint on q_{11} and q_{42} is of major importance since the q_k terms represent the larger part of most intensities. It is therefore of the utmost importance to find physical arguments to select values for q_{11} and q_{42}. The experimental intensity data for acetylene ($\partial\vec{\mu}/\partial S_{5x}$) and propyne ($\partial\vec{\mu}/\partial S_{9x}(4,5)$ and $\partial\vec{\mu}/\partial S_{10x}$) satisfactorily fix the values for q_{51} and q_{61}, but, as shown before, reliable values for q_{11} and q_{42} can not be obtained from the available intensity data. Although the ab initio results of Newton and Lipscomb [22] very well predict $\vec{\mu}_{pro}$, q_{61} and q_{51} [11,23] this does not guarantee that also the predictions for q_{11} and q_{42} are of the same quality. The other constraint on q_{11} and q_{42}, taken from Jona et al. [21], was not provided with physical arguments in that paper. However, recently Gussoni, Jona and Zerbi [24] presented some correlations between the C-H bond charge and other physical parameters, like bond length [24b] and force constants. These correlations are in favour of the q_{11} value as given by Jona et al. [21]. Such correlations provide at least some of a physical basis for the q_k values of initial set II. Since other evidence for the selection of q_k values is not available, we have performed some additional calculations with the initial sets I and II of Table 7. In these calculations the q_k values were fixed on their initial values. Also $\partial q_{42}/\partial r_{11}$ was kept on its initial value to prevent the first three charge flux parameters from taking unlikely large values (see Table 7). The remaining charge flux parameters were fitted to two sets of experimental data as indicated in Table 8. So by using the two different starting sets we end up with the four final sets shown in Table 8. Inspection of that Table leads to the following conclusions: (1) changing the propyne intensities of Bode et al. [11] by those of Kondo and Koga [14] has a considerable influence on a number of charge flux parameters.

TABLE 8

Four different sets[a] of common bcp's for acetylene, propyne and butyne-2.

bcp	Ia	Ib	IIa	IIb
q_{11}(n.r.)[b]	0 797	0.797	0.474	0.474
q_{42}(n.r.)	0.401	0.401	0.694	0.694
q_{51}(n.r.)	0.224	0.224	0.206	0.206
q_{61}(n.r.)	0.987	0.987	1.002	1.002
$\partial q_{11}/\partial r_{11}$	-1.294	-1.301	-0.932	-0 936
$\partial q_{11}/\partial r_{21}$	-0.244	-0.248	-0.174	-0.175
$\partial q_{42}/\partial r_{11}$(n.r)	0.010	0.010	-0.049	-0.049
$\partial q_{11}/\partial \alpha_1$	-0.089	-0.142	0.258	0.379
$\partial q_{11}/\partial \alpha_2$	0.148	0.069	0.207	0 315
$\partial q_{42}/\partial \alpha_1$	0.201	0.256	-0.038	-0.128
$\partial q_{11}/\partial \beta_1$	-0 014	-0.049	0 124	0.250
$\partial q_{11}/\partial \beta_2$	-0.413	-0.44o	-0.047	0.082
$\partial q_{42}/\partial \beta_1$	-0.020	0.006	-0 143	-0.246
$\partial q_{42}/\partial r_{42}$[c]	-0.221	-0.220	-0.428	-0.428
$\partial q_{51}/\partial r_{51}$[c]	0 871	0.854	0.858	0.851
$\partial q_{61}/\partial r_{61}$[c]	-0 103	-0 099	-0 109	-0.108

[a] Final sets Ia and IIa based upon the experimental data of Refs 11, 12, 13 and 15, sets Ib and IIb based on data of Refs. 12, 13, 14 and 15. Start set I of Table 7 was used for the calculation of Ia and Ib, start set II of Table 7 was used for IIa and IIb

[b] n.r. = not refined.

[c] The last three bcp's are the combination parameters given in Table 7.

Since the intensities of Refs. 11 and 14 are in good mutual correspondence with the exception of υ_2 it must be concluded that the charge flux bcp's are very sensitive to small changes in intensity data. Moreover, magnitude and direction of this sensitivity depends on the choice of q_k values. (11) As expected, the choice of q_k values strongly influences the values of the charge flux parameters The only parameters which are determined quite well from the experimental data are q_{51}, q_{61}, $\partial q_{51}/\partial r_{51}$ and $\partial q_{61}/\partial r_{61}$. The other charge flux parameters strongly depend on the chosen values for q_{11} and q_{42}.

In Table 9 the predicted intensities with the common parameter sets of Tables 7 and 8 are shown. It is clear that by far the best prediction results from the (almost identical) common sets of Table 7. The other sets are not very different although sets Ia and Ib are slightly better than the other two.

In general it can be concluded that a good fit of the observed intensities can be obtained by a simultaneous refinement of all independent bcp's (sets I and II of Table 7) The physical meaning of such a set will, in general, be very limited. However, such sets may be useful in predicting the correct sign combinations of the dmd's of related molecules. It is very difficult to find common sets with improved physical meaning, at one hand because of the lack of arguments to select physically acceptable regions for the parameter values, at

TABLE 9

Experimental and predicted intensities (km mole^{-1}) for propyne, butyne-2 and acetylene.

	A_i(obs)[a]	A_i(calc) - A_i(obs)				
		I,II[b]	Ia[c]	Ib[c,d]	IIa[c]	IIb[c,d]
pro-d_o	19.5	-3.8	-0.9	4.3	-0.2	4.6
	1.42	-0.7	-0.7	-0.8	-0.7	-0.8
	0.65	-0.02	-0.06	-0.54	-0.01	-0.17
	5.2	-0.1	0.3	-0.1	-0.05	-0.3
	43.2	3.1	2.5	0.8	3.0	1.1
	0.00[e]	0.00	0.00	0.00	0.00	0.00
	15.4	1.7	0.8	-1.4	0.9	-1.2
	17.8	-0.7	0.7	4.5	10 1	12.0
	0.25	-0.12	0.40	0.48	0 35	0.32
	15.6	-3.5	-1.5	-2.5	-0.1	-1.2
	88.5	-1.8	-3.5	-2.3	-1.8	-0.6
μ_{pro}	-0.75[f]	0.01	0.02	0.02	0.00	0.00
pro-d_3	0.69	0.08	0.40	0.70	0.55	0.75
	0.19	-0.01	0.00	-0.01	0.00	-0.01
	0.44	-0.01	0.01	0.04	-0.03	0.01
	12.4	0.00	1.7	1.7	1.5	1.0
	48.4	-2.1	-2.6	1.2	-2.1	1.5
	8.2	1.8	1.0	1.1	0.8	1.1
	9.6	-1.0	0 01	1.1	4.7	4.8
	0.87	0.5	-0.08	-0.13	0 19	0.16
	12.3	-2.5	-0.7	-1.9	0.5	-0.8
	92.3	-7.2	-8.9	-6.1	-7.3	-4.5
bu-d_o	62.2	-6.9	-22.2	-21.0	-21.6	-21.2
	2.2	-0.9	-0.5	-0.6	-0 6	-0.6
	0.25	-0.19	-0.10	-0.09	-0.14	-0.14
	0.00[e]	0.00	0.00	0.00	0.00	0.00
	39.6	-7.3	-4.5	-4.2	-5.2	-4.9
	33.6	-0.1	2.5	10.1	20.9	24.9
	1.41	-0.1	2.0	2.7	1.9	2.4
	18.5	2.4	5.1	5.2	6.5	6.5
bu-d_6	27.7	0.4	-7.6	-6.9	-7.3	-7.1
	0.84	-0.30	-0.06	-0.06	0.32	0.32
	0.40	0.18	0.10	0.10	0.16	0.16
	21.6	-3.3	-2.2	-2.5	-3.0	-3.0
	16.6	0.5	2.3	6.4	11.8	13.9
	0.52	-0.25	-0.52	-0.51	-0.49	-0.51
	14.3	2.0	4.1	4.2	5.3	5.3
ace-d_o	70.8	-1.8	-3.4	-2.7	-2.0	-1.8
	176.0	-1.6	-3.0	-3.0	2.3	2.3
ace-d_2	37.6	-0.05	-0.9	-0.5	-0.2	-0.05
	93.7	0.5	-0.3	-0.3	2.7	2.7

[a] Experimental intensities taken from Ref. 11(pro), Ref. 15(bu), Ref. 12 and 13 (ace, average values).
[b] Predicted with final sets of Table 7.
[c] Predicted with final sets of Table 8.
[d] The ΔA_1 values refer to the propyne intensity values of Ref. 14.
[e] Redundant intensity.
[f] Unit: D.

the other hand because of the fact that the uncertainties in the intensity data may cause large deviations from the starting sets, regardless their physical quality.

In our opinion it is impossible, therefore, to present a definite common set of bcp values for the molecules considered in this work. Unfortunately, this statement seems to have a quite general validity. The nature of the relationships as given in Tables 3-5 does not allow a satisfactorily accurate determination of first order intensity parameters (bcp's or eop's) as discussed before. Nevertheless, such sets have been presented, recently also for the molecules considered here [21,25].

For comparison the common parameter values given by Jona et al. [21] and Gribov and Novoselova [25] are collected in Table 10 together with two final sets taken from the present work, namely set I, being the average of sets Ia and Ib of Table 8, and set II, being the average of sets IIa and IIb of Table 8.

TABLE 10

Comparison of four sets common bcp's for acetylene, propyne and butyne-2

bcp	This work		Jona et al.[c]	Gribov et al.[d]
	I[a]	II[b]		
q_{11}	0.797	0.474	0.474	0.25
q_{42}	0.401	0.694	0.694	0.30
q_{51}	0.224	0.206	0.206	-0.74
q_{61}	0.987	1.002	1.002	0.94
$\partial q_{11}/\partial r_{11}$	-1.297	-0.934	-1.027	0.42
$\partial q_{11}/\partial r_{21}$	-0.246	-0.174	-0.245	0.26
$\partial q_{42}/\partial r_{11}$	0.010	-0.049	-0.010	-
$\partial q_{11}/\partial \alpha_1$	-0.115	0.268	-0.008	-0.22
$\partial q_{11}/\partial \alpha_2$	0.108	0.261	0.015	-0.51
$\partial q_{42}/\partial \alpha_1$	0.229	-0.083	0.114	-
$\partial q_{11}/\partial \beta_1$	-0.031	0.187	0.076	-0.26
$\partial q_{11}/\partial \beta_2$	-0.430	0.017	-0.048	-0.25
$\partial q_{42}/\partial \beta_1$	-0.007	-0.195	-0.114[e]	-
$\partial q_{42}/\partial r_{42}$	-0.220	-0.428	-0.361	0.14 (-0.14)[f]
$\partial q_{51}/\partial r_{51}$	0.862	0.855	0.745	0.45
$\partial q_{61}/\partial r_{61}$	-0.101	-0.109	-0.104	-0.05

[a] Average of sets Ia and Ib of Table 8

[b] Average of sets IIa and IIb of Table 8.

[c] Ref. 21.

[d] Ref. 25

[e] Jona et al. have used the constraint $\partial q_{42}/\partial \alpha_1 = -\partial q_{42}/\partial \beta_1$ (private communication).

[f] For this parameter two values are given in Ref. 25, viz. 0.14(pro) and -0.14(bu).

It is almost of no use to comment in any detail on the differences in parameter values, at one hand because of the fact that the necessary details of the calculation procedures and adopted constraints are missing in Refs. 21 and 25, at the other hand because of the fact that the parameter values are based on different experimental data and force field. Anyhow, the large differences confirm the conclusion of this paper that definite sets with a clear physical significance can not be obtained from experimental intensity data. It is therefore of the utmost importance to state clearly which additional arguments have been used to determine the final values of a common parameter set.

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