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Theoretical Calculation of the Time-Averaged Electron Density Distribution for Vibrating Ethyne Molecules in a Model Crystal Structure

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Calculations have been made on an ethyne model structure to investigate the influence of internal and external thermal motions of the molecules in a crystal on the time-averaged electron density distribution as obtained by X-ray diffraction. The density distributions in the chemical bonds have been studied from $D(\mathbf{r})=\varrho(\text{mol},\mathbf{r})-\varrho(\text{at},\mathbf{r})$ difference maps, where $\varrho(\text{at},\mathbf{r})$ is the density of the free-atom structure. Vibrations expected to occur at low temperatures reduce the difference densities at the centres of the C–C and C–H bonds by 12 and 23% respectively. Reliable time-averaged difference density distributions can be calculated from the static distributions obtained by theory by use of the root-mean-square deviations $\langle u^2\rangle^{1/2}$ of the atoms which can be determined by X-ray diffraction. Only negligibly small errors occur in the theoretical difference density maps if librations are accounted for by linear vibrations. In the experimental $[F_o-F_c]$ difference densities errors due to treating librations as linear vibrations are largely, but not completely, compensated by shifts of the atoms.

Introduction

Electron density distributions as obtained by X-ray diffraction have been used by several authors to study changes in the charge distribution due to chemical bonding. In our laboratory this method is being applied to investigate the density distributions in single, double and triple C–C bonds (Helmholdt, Ruysink, Reynaers and Kemper, 1972; Ruysink & Vos, 1974*a*). The observed densities are dynamic densities which means that they are time averages over the thermal motions of the atoms. On the other hand, densities calculated by quantum-theoretical methods are static densities as they are based on fixed configurations of the atomic nuclei. The observed densities can only be compared with theoretical results if in the latter the effect of thermal motion is taken into account.

Usually bonding effects are studied from difference maps which are directly related to the changes in charge distribution due to chemical bonding. The formula for the theoretical dynamic difference density map reads

$$D_d(\mathbf{r})=\varrho_d(\text{mol},\mathbf{r})-\varrho_d(\text{at},\mathbf{r})$$

where $\varrho_d(\text{mol},\mathbf{r})$ is the molecular dynamic density distribution and $\varrho_d(\text{at},\mathbf{r})$ the dynamic density distribution of the corresponding free-atom structure. The corresponding experimental quantity is the (F_o-F_c) X-ray diffraction difference map. In this map F_c is based on a model consisting of spherically symmetric atoms which should have the same parameters as the atoms in the molecule. Unfortunately this is not the case for the structure model obtained by normal X-ray diffraction refinement. In the atomic parameters systematic errors occur, as during the refinement a model consisting of spherically symmetric atoms is considered. Moreover librations are generally treated as linear vibrations.

The first aim of the present paper is a study of the effects of thermal vibrations on the density distribution. The study is done for a model structure consisting of ethyne, C_2H_2, molecules in which the intermolecular distances are so large that the molecules do not influence each other (for a description of the structure, see Ruysink & Vos, 1974*b*). Both internal and external vibrations of the molecules are considered in an investigation of how a reliable dynamic difference density distribution can be obtained from the static difference distribution calculated by quantum-mechanical methods. Secondly the errors caused by treating librations as linear vibrations will be discussed.

The consequences of the use of spherically symmetric atoms during the refinement are studied in the following paper (Ruysink & Vos, 1974*b*).

The static density

The wave function of the non-vibrating ethyne molecule with C–C = 2·2752 and C–H = 1·9956 a.u. (*Handbook of Chemistry and Physics*, 1960) has been obtained by the SCF–LCAO–MO method (Roothaan, 1951). The $2N$ electrons of the molecule form a closed shell: N molecular orbitals are each occupied by two electrons. Each molecular orbital χ_i is a linear combination of a number of basis functions φ_μ,

$$\chi_i=\sum_\mu \varphi_\mu c_{\mu i}\,. \tag{1}$$

$c_{\mu i}$ is the μth element of the ith SCF vector. As the molecular orbitals are orthonormal, the density distribution $\varrho(\mathbf{r})$ in the molecule is given by

$$\varrho(\mathbf{r})=2\sum_i \chi_i^*(\mathbf{r})\chi_i(\mathbf{r})=2\sum_i\sum_\mu\sum_\nu c_{\mu i}c_{\nu i}\varphi_\mu^*(\mathbf{r})\varphi_\nu(\mathbf{r})\,. \tag{2}$$

The calculations were done by Dr G. A. van der Velde with an extended basis set consisting of Hermite–Gaussian functions (Zivkovic & Maksic, 1968). A set (10, 6, 2/5, 2) consisting of ten s, six p and two d functions on carbon and of five s and two p functions on hydrogen was taken. For the calculation of the molecular orbitals the basis set (10, 6, 2/5, 2) was contracted to 6, 4, 2/4, 2) by replacing a number of individual basis functions of the same type and centred on the same atom by the linear combination found for the free atoms. The calculations were repeated with a small basis set (6, 3/3) during which no contraction was used. The coefficients $c_{\mu i}$ found for both cases are given by Ruysink (1973) and are available on request.

In Table 1 some results of our calculations are compared with accurate values given by McLean & Yoshimine (1967). For the extended basis set the agreement is good, for the small set somewhat less so. Comparison of the $\varrho(\text{mol},\mathbf{r})-\varrho(\text{at},\mathbf{r})$ maps calculated for the two sets shows that for the small basis set also a reasonable picture is obtained of the changes in the electron density distribution due to chemical bonding.

Table 1. C_2H_2 – *Theoretical data obtained for the different basis sets*

The values listed for r(C–C) and r(C–H) were adopted during the calculation, $D=\varrho(\text{mol})-\varrho(\text{at})$, $r_{\frac{1}{2}}(D)$ = half width of peak on the centre of C–C, perpendicular to C–C.

	McLean	Present work	
	(1967)	Extended set	Small set
Orbital type	S.T.F.	G.T.F.	G.T.F.
Basis set used	5,4,1,1/2,1,1	10,6,2/5,2	6, 3/3
r(C–C) in a.u.	2·281	2·2752	2·2752
r(C–H) in a.u.	2·002	1·9956	1·9956
E(a.u.)	−76·8540	−76·8476	−76·6737
ϱ(mol) at C in e a.u.$^{-3}$	126·2	121·7	106·9
D(C nucleus)	−1·413	−1·440	−1·214
D(H nucleus)	0·109	0·099	0·078
D(centre C–C)	0·124	0·125	0·110
D(max on C–H)*	0·121	0·110	0·096
$r_{\frac{1}{2}}(D)$	0·83	0·80	0·75

* Lies close to H (see Fig. 1.)

The dynamic density

Introduction

The geometry of the molecule changes with time owing to the internal vibrational modes, whereas its position and orientation in the crystal change as a result of external translations and librations. The dynamic density is the time-averaged density for all molecular geometries, positions and orientations. In this section we shall consider the changes in the density distribution due to external and internal vibrations.

Method of calculation

To obtain a feasible calculation of the dynamic density distributions the following assumptions have been made.

(*a*) The SCF vectors found for the static molecule are used for all molecular geometries (apart from the normalization factors C_i discussed below). This is an extension of the convolution approximation introduced by Coulson & Thomas (1971) and Thomas (1972) for diatomic molecules. The figures in their papers show that at short distances from the nuclei, where the density changes due to internal vibrations are appreciable, the convolution approximation gives reliable dynamic difference density distributions. No figures are given for the centres of the bonds. On the basis of recent accurate calculations on H_2^+ by Thomas (1973) it is expected that in the case of internal vibrations the static and dynamic densities in the centres of the bonds will be hardly different.

Since the overlap of basis functions depends on the molecular geometry, the normalization factors of the molecular orbitals χ_i are functions of the molecular geometry. We have approximated these normalization factors, which should be calculated for each geometry G, by averaged normalization factors C_i defined by

$$C_i^2\int\langle\chi_i^*(\mathbf{r},G)\chi_i(\mathbf{r},G)\rangle_G\mathrm{d}\mathbf{r}=1\ . \tag{3}$$

(*b*) The vibrations are harmonic and independent of each other. For the ith linear vibration the distribution function $P(\mathbf{u}_i)$ for an atom, taken as a standard atom, is given by

$$P(\mathbf{u}_i)\mathrm{d}\mathbf{u}_i=(g_{xi}g_{yi}g_{zi})^{1/2}\pi^{-3/2}\exp\left[-g_{xi}u_{xi}^2-g_{yi}u_{yi}^2-g_{zi}u_{zi}^2\right]\mathrm{d}\mathbf{u}_i\ . \tag{4}$$

$g_{xi}=\langle 2u_{xi}^2\rangle^{-1}$, $\mathbf{u}_i$ is the deviation from the equilibrium position, $\mathrm{d}\mathbf{u}_i=\mathrm{d}u_{xi}\mathrm{d}u_{yi}\mathrm{d}u_{zi}$. In case the deviation of an atom κ is coupled with that of the standard atom with a coupling constant $k_{\kappa i}$, its deviation is given by

$$\mathbf{u}_{\kappa i}=k_{\kappa i}u_i \tag{5}$$

and the distribution function obeys the relation

$$P(k_{\kappa i}\mathbf{u}_i)\mathrm{d}(k_{\kappa i}\mathbf{u}_i)\mathrm{d}\mathbf{u}_i=P(\mathbf{u}_i)\mathrm{d}\mathbf{u}_i\ . \tag{6}$$

The total displacement of an atom κ undergoing m independent vibrations is given by

$$\mathbf{u}_\kappa=\sum_{i=1}^{m}\mathbf{u}_{\kappa i}=\sum_{i=1}^{m}k_{\kappa i}\mathbf{u}_i\ . \tag{7}$$

From (6) and the fact that the vibrations are independent, it follows that the distribution function of atom κ obeys the formula

$$P(\mathbf{u}_{\kappa 1}\ \ldots\ \mathbf{u}_{\kappa m})\ \mathrm{d}\mathbf{u}_{\kappa 1}\ \ldots\ \mathrm{d}\mathbf{u}_{\kappa m}=\prod_{i=1}^{m}P(\mathbf{u}_i)\mathrm{d}\mathbf{u}_i\ . \tag{8}$$

With the assumptions discussed above the dynamic density $\varrho_d(\mathbf{r})$, found by averaging over all molecular geometries and positions G, is given by

$$\varrho_d(\mathbf{r})=2\sum_i\sum_\mu\sum_\nu C_i^2c_{\mu i}c_{\nu i}\varrho_{d,\,\mu\nu}(\mathbf{r}) \tag{9}$$

with

$$\varrho_{d,\mu\nu}(\mathbf{r}) \equiv \langle \varphi_\mu(\mathbf{r},G)\varphi_\nu(\mathbf{r},G)\rangle_G$$
$$= \int_{u_i} \ldots \int_{u_m} \prod_i P(\mathbf{u}_i)\varphi_\mu(\mathbf{r}-\mathbf{u}_\kappa)\varphi_\nu(\mathbf{r}-\mathbf{u}_\lambda)\mathrm{d}\mathbf{u}_1 \ldots \mathrm{d}\mathbf{u}_m\,, \qquad (10)$$

where κ or λ indicates the atomic nucleus on which the basis function φ_μ or φ_ν is centred.

Owing to the favourable properties of the Hermite–Gaussian (HG) functions used for the basis functions φ_μ and φ_ν, (10) can be worked out in analytical form. A HG function of s type is defined by

$$f(s \text{ type}) = \exp\, -\alpha((\mathbf{r}-\mathbf{A})^2 \qquad (11)$$

where α is the orbital exponent, $\mathbf{r}$ = position vector in space and $\mathbf{A}$ = position vector of nucleus on which the basis function is centred. Functions of p type are obtained from (11) by differentiation with respect to the relevant component of $\mathbf{A}$, for instance

$$f(p_x \text{ type}) = \frac{\partial}{\partial A_x}[\exp\, -\alpha(\mathbf{r}-\mathbf{A})^2]$$
$$= 2\alpha(r_x - A_x)\exp\, -\alpha(\mathbf{r}-\mathbf{A})^2. \qquad (12)$$

Functions of d type are derived in an analogous way by taking second derivatives.

If both φ_μ and φ_ν in (10) are s-type functions, it can be seen from (11), (4) and (8) that $\varrho_{d,\mu\nu}(\mathbf{r})$ can be factorized according to

$$\varrho_{d,\mu\nu}(\mathbf{r}) = \varrho_d(x)\varrho_d(y)\varrho_d(z) \qquad (13)$$

with

$$\varrho_d(x) = \prod_i \left[\frac{g_i}{\pi}\right]^{1/2} \int_{u_1} \ldots \int_{u_m} \exp\,[-a(x-A-\sum_i k_i u_i)^2$$
$$-b(x-B-\sum_i l_i u_i)^2 - \sum_i g_i u_i^2]\mathrm{d}u_1 \ldots \mathrm{d}u_m\,. \qquad (14)$$

In the latter relation the indices μ, ν and x have been omitted for clarity, $a(b)$ stands for the orbital exponent of atom $\kappa(\lambda)$, $A(B)$ for its nuclear equilibrium position and $k(l)$ for the coupling constant of (5). From the definition of the HG functions and the fact that A and B are constants for the integration of (10), it follows that $\varrho_d(x)$ values for p or d-type functions can easily be obtained from (14) by differentiating the integrated expression with respect to the relevant components of A or B.

Results

With the formulae listed above dynamic difference density maps

$$D_d(\mathbf{r}) = \varrho_d(\text{mol},\mathbf{r}) - \varrho_d(\text{at},\mathbf{r})$$

have been calculated for ethyne. These maps have cylindrical symmetry around $\mathbf{z}$ (lying along C–C). In Fig. 1 the following $D(\mathbf{r})$ values along $\mathbf{z}$ are shown.

(*a*) The static density (for comparison purposes).

(*b*) The dynamic density based on the internal vibrations found by spectroscopic work (Meisingseth & Cyvin, 1961; Cyvin & Meisingseth, 1961) plus rigid-body translations along $\mathbf{x}$, $\mathbf{y}$ and $\mathbf{z}$. These translations are taken such that the total thermal motion of the carbon atoms corresponds to an isotropic temperature factor $B = 8\pi^2\langle u^2\rangle = 1{\cdot}07$ Å^2. A thermal motion of approximately this magnitude is expected for organic compounds at low temperatures (Cruickshank, 1956*c*). $\langle u^2\rangle$ values and coupling constants k of the vibrations used in the calculation of $\varrho_d(\text{mol},\mathbf{r})$ are given in Table 2. It should be noted that $\varrho_d(\text{at},\mathbf{r})$, which is composed of free atoms, is not influenced by the coupling assumed for the vibration, as the density distributions of the free atoms are independent of each other.

(*c*) The dynamic density corresponding to the $\langle u^2(\text{total})\rangle$ values of (*b*) for each of the atoms and each direction, but interpreted as rigid-body translations

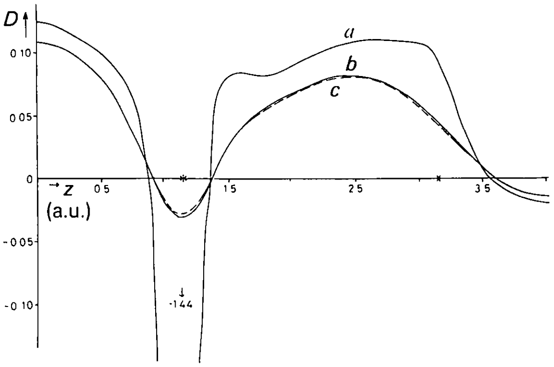

Fig. 1. C_2H_2. Difference densities $D(\mathbf{r}) = \varrho(\text{mol}) - \varrho(\text{at})$ along $\mathbf{z}$ in e a.u.$^{-3}$. The inversion centre of the molecule is taken as origin, $*$ = C and × = H. a = static difference density; b and c are dynamic difference densities; details are given in the text.

Table 2. *Vibrational amplitudes* (a.u.) *and coupling constants k for the ethyne molecule* H(1)–C(1)–C(2)–H(2)

Rigid-body translations are given by T_{ii}.

Vibration	Direction	$\langle u^2(C)\rangle^{1/2}$	k(C1)	k(C2)	k(H1)	k(H2)
Σ_g	$\mathbf{z}$	0·034	1	−1	−2·904	2·904
Σ_u	$\mathbf{z}$	0·014	1	1	−6	−6
π_g	$\mathbf{x}(\mathbf{y})$	0·057	1	−1	−2·179	2·179
π_u	$\mathbf{x}(\mathbf{y})$	0·030	1	1	−6	−6
T_{33}	$\mathbf{z}$	0·217	1	1	1	1
$T_{11} = T_{22}$	$\mathbf{x}(\mathbf{y})$	0·210	1	1	1	1

as far as possible. Residual $\langle u^2 \rangle$ values for the hydrogen atoms are assumed to be due to vibrations which are independent of each other and of the rigid-body translations.

In calculation (*c*) the in-phase coupling of the atoms for the external vibrations is taken into account. For the internal vibrations the coupling of the atoms is neglected. The resulting errors in the dynamic density are expected to be small, as, owing to the small internal vibrational amplitudes of the carbon atoms, the lengths assumed by C–C and C–H during the vibrations are only slightly affected by the coupling constants of the internal motions. We see that the curve (*c*) obtained shows good agreement with curve (*b*). This result is encouraging as it shows that for the present example theoretical dynamic difference densities can be calculated reliably from static densities by making use of the $\langle u^2(\text{total})\rangle$ values, which can be obtained from X-ray diffraction. It therefore seems probable that spectroscopic data are not required for this type of work.

To check whether it is possible to neglect the coupling between the atoms for the external vibrations as well as for the internal vibrations, a calculation has been carried out with the assumption that the $\langle u^2(\text{total}\rangle$ values of the atoms can be ascribed to independent vibrations. At some places the deviations from curve (*b*) are of the order of 0·01 e a.u.$^{-3}$= 0·07 e Å^{-3} and thus considerably larger than observed for curve (*c*). These deviations are approximately equal to the standard deviations of present accurate low-temperature X-ray diffraction studies (cyanuric acid, σ=0·06 e Å^{-3}; Verschoor & Keulen, 1971) and larger than the standard deviations expected for future very accurate work. To obtain theoretical dynamic density distributions for which the errors are small in comparison with the experimental errors, it is thus necessary to account for the coupling between the atoms for the external vibrations.

Fig. 1 shows that detailed features present in the static density disappear owing to the thermal vibrations. Especially in the region around the carbon nucleus the change is large, the cusp of −1·44 e a.u.$^{-3}$ disappearing to a large extent. For both cases (*b*) and (*c*) the difference density on the centre of the C–C bond is reduced by 12% and that on the centre of the C–H bond by 23%. The remaining density is 0·108 e a.u.$^{-3}$ and 0·083 e a.u.$^{-3}$ respectively.

Errors caused by treating librations as linear vibrations

Introduction

In X-ray diffraction studies thermal librations are usually treated as linear vibrations. It may be questioned, however, whether $(F_o - F_c)$ maps obtained in this way show reliable values for the bonding maxima in the centres of the bonds. For a diatomic molecule, for instance, we expect the maxima to be too high as the F_c values are deduced from a model in which the electrons follow the thermal motion of the nuclei, whereas actually the electrons in the centre of the bond do not move if only librational motions are considered. To study the errors due to treating librations as vibrations we have calculated the difference map

$$D_d(\text{at}) = \varrho_d(\text{at, libration}) - \varrho_d(\text{at, vibration})$$

for the free-atom structure corresponding to the ethyne molecule.

Finally we have investigated the effect of describing librations by linear vibrations on theoretical dynamic difference density maps.

Method of calculation

We assume that the molecule librates around its inertial axes (for ethyne around **x** and **y** perpendicular to the C–C bond of the molecule). Fig. 2 shows the situation for libration around **x**. The dynamic density in a point *P* is calculated as the time average of the densities of the static molecule seen by *P* when librating around *O*. The librations are assumed to be harmonic

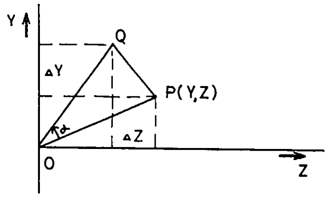

Fig. 2. Libration around **x**.

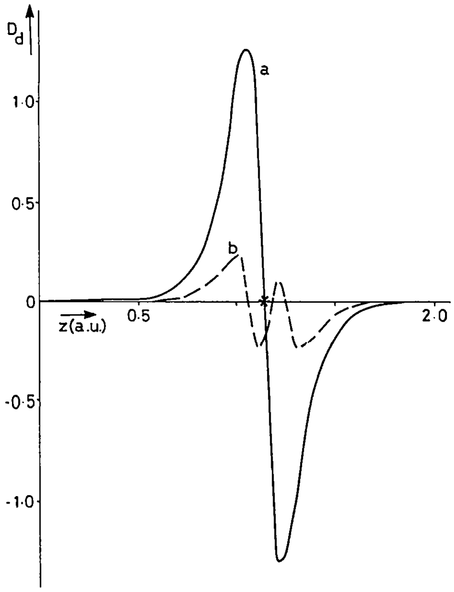

Fig. 3. Difference density $D_d(\text{at}) = \varrho_d(\text{at, libration}) - \varrho_d(\text{at, vibration})$ along **z**, in e a.u.$^{-3}$; $*$=C(libration), $\langle\alpha^2\rangle^{1/2} = \langle\beta^2\rangle^{1/2} = 4°$. (*a*) $z(\text{C, vibration}) = z(\text{C, libration})$. (*b*) $z(\text{C, vibration}) = z(\text{C, libration}) - 0{\cdot}0055$ a.u. (=0·0029 Å). For $z > 2$ a.u. the differences are small and are not shown in the Figure,

and independent of the linear vibrations. The probability $P(\alpha)\mathrm{d}\alpha$ for a deviation between α and $\alpha+\mathrm{d}\alpha$ from the equilibrium position is given by

$$P(\alpha)\mathrm{d}\alpha=g_\alpha^{1/2}\pi^{-1/2}\exp\left(-g_\alpha\alpha^2\right) \tag{15}$$

with $g_\alpha=\langle 2\alpha^2\rangle^{-1}$. Analogous functions can be derived for libration around **y** and **z**.

From Fig. 2 it can be deduced that for rotations of α, β and γ around **x**, **y** and **z** respectively, the displacement vector **v** for P is given by

$$\mathbf{v}=\mathbf{L}\,.\,\mathbf{r}\,, \tag{16}$$

where **r** gives the position of P, and **L** obeys the relation

$$\mathbf{L}=\begin{pmatrix} \cos\beta+\cos\gamma-2 & \sin\gamma & -\sin\beta \\ -\sin\gamma & \cos\alpha+\cos\gamma-2 & \sin\alpha \\ \sin\beta & -\sin\alpha & \cos\alpha+\cos\beta-2 \end{pmatrix}. \tag{17}$$

Comparison of (16) with (7) and consideration of (14) shows that the formula for the dynamic density $\varrho_d(\mathbf{r})$ reads

$$\varrho_d(\mathbf{r})=\iiint P(\alpha)P(\beta)P(\gamma)\exp\left[-a(\mathbf{r}-\mathbf{A}-\mathbf{L}\,.\,\mathbf{r})^2 - b(\mathbf{r}-\mathbf{B}-\mathbf{L}\,.\,\mathbf{r})^2\right]\mathrm{d}\alpha\mathrm{d}\beta\mathrm{d}\gamma\,. \tag{18}$$

In this case the integral cannot be factorized to a product of one-dimensional terms. The formula can be worked out, however, by assuming that $\langle\alpha^2\rangle^{1/2}$, $\langle\beta^2\rangle^{1/2}$ and $\langle\gamma^2\rangle^{1/2}$ are small. This assumption is valid for structures determined at low temperatures, where root-mean-square values of approximately 4° have been observed (Keulen, 1969, p. 66).

Results

To study $D_d(\mathrm{at})=\varrho_d(\mathrm{at, libration})-\varrho_d(\mathrm{at, vibration})$ we have calculated the dynamic density $\varrho_d(\mathrm{at, libration})$ for the free-atom ethyne structure with $\langle\alpha^2\rangle^{1/2}=\langle\beta^2\rangle^{1/2}=4°$ corresponding to $\langle u^2(\mathrm{C},x)\rangle=\langle u^2(\mathrm{C},y)\rangle=0{\cdot}0063$ a.u.^{2} and $\langle u^2(\mathrm{H},x)\rangle=\langle u^2(\mathrm{H},y)\rangle=0{\cdot}0478$ a.u.^{2} or $B(\mathrm{C})=0{\cdot}14$ and $B(\mathrm{H})=1{\cdot}06$ Å^2. In $\varrho_d(\mathrm{at, vibration})$ the $\langle u^2\rangle$ values of the atoms have been ascribed to linear vibrations. Fig. 3 (curve *a*) shows that the difference in the centre of the C–C bond is positive, as expected, but small. The numerical data show that it amounts to 0·003 e a.u.$^{-3}$=0·02 e Å^{-3}, which is approximately 2·5% of the bonding maximum on C–C. The difference is considerably smaller, however, than the standard deviations obtained for accurate low-temperature X-ray diffraction studies (cyanuric acid, $\sigma=0{\cdot}06$ e Å^{-3}; Verschoor & Keulen, 1971). On the centre of C–H the difference is even smaller.

As is seen in Fig. 3 (curve *a*) a much larger effect is observed at the carbon atom where the difference density shows a considerable slope. It is well known that such a slope when occurring in a difference synthesis during a structure refinement causes the carbon atom to shift towards the centre of C–C, thus resulting in a shortening of C–C. Cruickshank (1956*b*) has pointed out that bond shortening occurs for X-ray refinements, where librations are treated as linear vibrations. According to his formula the shift of C towards the centre of C–C is 0·0029 Å for the librations considered in the present case. We have attempted to eliminate the slope at C in our difference map by applying this shift of 0·0029 Å to C in $\varrho_d(\mathrm{at, vibration})$. The difference map obtained in this way is given by curve *b* in Fig. 3. The difference at the centre of the C–C bond is reduced to 0·001 e a.u.$^{-3}$=0·01 e Å^{-3}. Around the carbon atom there are ripples which may be expected to be smeared out to a large extent by the translational motions. It seems reasonable to assume that positive and negative regions close to the atomic nucleus will compensate each other, but at somewhat larger distances $D_d(\mathrm{at})$ will remain positive for $z<z(\mathrm{C})$ and negative for $z>z(\mathrm{C})$. Owing to translational motions corresponding to $B=1{\cdot}07$ Å^2, the height of the carbon atom in ethyne reduces to 5·4% of its static value. If for $D_d(\mathrm{at})$ the same reduction is assumed to occur for the maximum of 0·24 e a.u.$^{-3}$ at $z\simeq 0{\cdot}97$ a.u. and for the minimum of $-0{\cdot}24$ e a.u.$^{-3}$ at $z\simeq 1{\cdot}33$ a.u., the remaining values are (plus or minus) 0·09 e Å^{-3}. The errors due to treating librations as linear vibrations are thus largely, but not completely, compensated by shifts of the atoms as occurring in normal structure refinements. It is therefore advisable to account for librations in the correct way in accurate studies of bonding effects. Methods have been proposed by Johnson (1969) and Maslen (1969).

The errors in the theoretical dynamic density distribution due to describing librations as linear vibrations are obtained from the map

$$\begin{aligned} &D_d(\mathrm{libration})-D_d(\mathrm{vibration}) \\ &=[\varrho_d(\mathrm{mol, libration})-\varrho_d(\mathrm{at, libration})] \\ &\quad-[\varrho_d(\mathrm{mol, vibration})-\varrho_d(\mathrm{at, vibration})] \\ &=D_d(\mathrm{mol})-D_d(\mathrm{at}) \end{aligned}$$

with

$$D_d(\mathrm{mol})=\varrho_d(\mathrm{mol, libration})-\varrho_d(\mathrm{mol, vibration})$$

and

$$D_d(\mathrm{at})=\varrho_d(\mathrm{at, libration})-\varrho_d(\mathrm{at, vibration}).$$

$D_d(\mathrm{at})$ has been discussed above. For the calculation of $D_d(\mathrm{mol})$ along **z** of the ethyne molecule it was assumed that the vibrational motions of neighbouring C and H atoms in the molecule are in phase, whereas those of the centrosymmetrically related C–H parts are in antiphase. It appears that $D_d(\mathrm{mol})-D_d(\mathrm{at})$ is 0·0035 e a.u.$^{-3}$=0·023 e Å^{-3} on the centre of C–C. At C–H and close to the hydrogen atom the differences are smaller. At the position of the carbon atom $D_d(\mathrm{mol})-D_d(\mathrm{at})$ shows a slope of 0·3 e a.u.$^{-4}$ with maximum and minimum values of approximately 0·018 and $-0{\cdot}018$ e a.u.$^{-3}$ respectively. The sign of the slope is opposite to that in Fig. 3 because the difference density $D_d(\mathbf{r})$ is negative rather than positive at the carbon atom. To a rough approximation the maximum and minimum values may be assumed to be reduced by the same percentage amount as the carbon atom in ethyne because of the presence of translational motions. With this assumption the reduced values are estimated at $0{\cdot}0009$ e a.u.$^{-3}=0{\cdot}006$ e Å^{-3} and $-0{\cdot}006$ e Å^{-3} for $B=1{\cdot}07$ Å^2, which shows that they are negligibly small. From the results obtained it can be concluded that the errors in theoretical dynamic difference densities due to using vibrations instead of librations are small in comparison with the standard deviations of present experimental X-ray studies.

Conclusion

The results of the previous sections show that theoretical dynamic difference densities can be obtained from the static densities by making use of the $\langle u^2\rangle$ values of the atoms determined by X-ray diffraction. To get the coupling of the atoms right for the predominant part of the thermal motions the $\langle u^2\rangle$ values should be interpreted in terms of rigid-body motions as far as possible. For rigid molecules a thermal motion analysis should therefore be carried out for the molecule as a whole, whereas in molecules consisting of rigid fragments the rigid-body motions of these fragments will need to be considered in addition to those of the complete molecule. For the translational motions all atoms have the same amplitude and vibrate in phase. For the librational motions, which can be treated as linear vibrations, the amplitudes of the atoms depend on their distances from the libration axes and parts of the rigid fragment will vibrate in anti-phase. Residual $\langle u^2\rangle$ values are ascribed to independent linear vibrations. Errors may occur in the theoretical dynamic difference density owing to uncertainties in the coupling constants, if it appears to be impossible to obtain separate values for the librational and translational parts of the thermal motion. Cruickshank (1956*a*) has pointed out for which types of molecules this difficulty may arise.

For the experimental $[F_o-F_c]$ maps, which have to be compared with the theoretical maps, systematic errors due to using vibrations instead of librations are expected to exceed the standard deviations of accurate X-ray diffraction studies. Moreover it should be noticed that with the present precision of the X-ray work changes as large as 10 to 20% of the bonding maxima cannot be detected with certainty. It is therefore necessary to improve the experimental accuracy. In such accurate X-ray diffraction studies librational motions must be accounted for in the correct way during the structure refinement.

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