Mean Amplitudes of Vibration of *Cyclo*propane from Electron Diffraction and Spectroscopic Calculations

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Table 1. Mean amplitudes of vibration (*u*) in Å units.

Atom pair	u spectroscopic $T = 0$	298°K	u electr. diff.	
C—H	0.0750	0.0750	0.0753	±0.0030
C...H	0.1082	0.1090	0.108	±0.0030
C—C	0.0510	0.0514	0.0497	±0.0015
$H_1...H_1'$	0.1180	0.1181		
$H_1...H_2$	0.1758	0.1783		
$H_1...H_2'$	0.1316	0.1320		

In a previous work [1] values for the mean amplitudes of vibration (*u*) for the bond distances of *cyclo*propane were reported. The values were obtained a) from electron diffraction studies of the molecule in the gaseous state and b) from theoretical computations based upon spectroscopic data. The values reported were obtained using approximation calculations. In the present work a more rigorous calculation has been carried out using the same two methods.

Electron diffraction calculations. New *u* values for the bond distances and for the non-bonded C—H distance have been calculated. The following procedures were used: 1. Approximating the radial distribution curves with sums of Gaussian peaks. 2. Using least squares calculations on the intensity curve. 3. Studying the areas under the sinusoidal curve for the outer part of the intensity curve. The last procedure leads to the determination of the *u* value for the C—C distance. It was found advisable to study the *u* value for the C—H distances after the subtraction of the contribution from the C—C distance. Attempts were made to determine the error limits of the *u* value determination. The results of these studies are presented in the last column of Table 1. The resulting *u* value for C—C is a trifle larger than that obtained earlier. The error estimations indicate that the earlier rough evaluation of the accuracy of the *u* value for the C—H bond was a little too optimistic.

Spectroscopic calculations. While an electron diffraction study is unable to determine the *u* values of the H—H distances with any reasonable accuracy, calculations from spectroscopic data yield useful values for all six amplitudes of vibration associated with the various interatomic distances of the *cyclo*propane molecule. The results of the spectroscopic calculations are given

in Table 1 computed both for the zero point and for 298°K.

The spectroscopic computation is summarized in the following: (For further details of the theory, see *e. g.* Morino *et al.*[2] and Cyvin [3].)

Let Δr_i represent the interatomic displacements for the six types of (bonded and non-bonded) atom pairs ($i = 1, 2, ..., 6$). If the matrix P is formed according to $P_{ij} = \langle \Delta r_i \Delta r_j \rangle$, the mean-square amplitudes of vibration (u^2) will appear on its main diagonal. One has

$$P = K \langle Q^2 \rangle \widetilde{K} \qquad (1)$$

where $\langle Q^2 \rangle$ is a diagonal matrix with the elements $\langle Q^2 \rangle_k = (h/8\pi^2 \nu_k) \coth (h\nu_k/2kT)$,[2] and K is the transformation matrix given by $r = KQ$. Here r represents the Δr_i coordinates and Q the vibrational normal coordinates. The K matrix may be computed according to

$$K = VL \qquad (2)$$

The L matrix ($S = LQ$, where S denotes a set of symmetry coordinates) is obtainable by a normal coordinate analysis [4] if the force constants and the equilibrium parameters are known. The V matrix is defined by $r = VS$ and may be obtained from geometrical considerations.

The mean-square amplitude matrix Σ is defined by $\Sigma_{ij} = \langle S_i S_j \rangle$, where S_i and S_j are symmetry coordinates. For this matrix one has

$$\Sigma = L \langle Q^2 \rangle \widetilde{L} \qquad (3)$$

An alternative method of computing the u^2 values may be applied, according to the relation

$$P = V \Sigma \widetilde{V} \qquad (4)$$

from which the u^2 quantities may be expressed in terms of the a matrix elements. The relation (4) is deducible from eqns. (1)—(3).

In the present case a set of force constants for *cyclo*propane has been established [5] by means of vibrational frequencies taken from literature [6] for both C_3H_6 and C_3D_6. For the numerical L matrix elements, see Ref.[5] One of the writers (S. J. Cyvin) intends to give some details of the theory of mean-square amplitude matrices applied to the *cyclo*propane molecule in a coming publication.

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A Note on the Crystal Structure of Sodium Dimolybdate

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About ten years ago the present author carried out a series of structure determinations of polymolybdates, polytungstates, polyniobates and polytantalates. In most cases the proposed oxygen co-ordination around the heavy atoms was supported by some evidence of vectors in the three-dimensional Patterson functions. There were, however, two exceptional cases with very weak or no evidence at all for the oxygen positions which were assumed from spatial discussions. In one of these cases, $MoO_3 \cdot 2 H_2O$, the presence of a complicated superstructure has later been shown [1].

The other case is sodium dimolybdate [2]. The molybdenum positions were conclu-

sively derived but the oxygen co-ordination proposed was based on the assumption that the co-ordination around the molybdenum atoms should be either tetrahedral or octahedral. As the resulting structure exhibited an interesting mixed co-ordination an attempt has been made to derive the oxygen positions directly from the three-dimensional Patterson function using the Buerger minimum function [3].

This derivation has confirmed the structural suggestion of the earlier paper. The positions of the oxygen and sodium atoms are, however, shifted to some extent. The old data do not permit a refinement with modern methods and the atomic positions are therefore still very uncertain. The following rough parameters give a R value of 0.17 (the old parameters within brackets):

8	Mo_I	in	8	(e)	:	$x = 0.25$
8	Mo_{II}	in	8	(f)	:	$x = 0.00$
8	Na_1	in	8	(d)	:	$x = 0.25$
8	Na_{II}	in	8	(f)	:	$x = 0.00$
16	O_I	in	16	(g)	:	$x = 0.18$ (0.21)
16	O_{II}	in	16	(g)	:	$x = 0.18$ (0.21)
8	O_{III}	in	8	(f)	:	$x = 0.00$
8	O_{IV}	in	8	(f)	:	$x = 0.00$
8	O_V	in	8	(f)	:	$x = 0.00$

$y = 0.08$	$z = 0.25$
$y = 0.25$	$z = 0.08$
$y = 0.00$	$z = 0.00$
$y = 0.31$ (0.36)	$z = 0.36$ (0.30)
$y = 0.22$ (0.21)	$z = 0.17$ (0.16)
$y = 0.48$ (0.49)	$z = 0.33$ (0.34)
$y = 0.11$ (0.08)	$z = 0.28$ (0.27)
$y = 0.38$ (0.41)	$z = 0.02$ (0.13)
$y = 0.37$ (0.35)	$z = 0.52$ (0.49)

The proposed mixed tetrahedral and octahedral co-ordination around the molybdenum atoms can be considered as strongly supported by this result. The relatively low R value by no means proves, however, that the atomic positions are well determined, as the contributions from the Mo atoms are too dominating. A further discussion of the bond lengths on the basis of these rough parameters therefore cannot be recommended.

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