At the Columbus Symposium in June it was evident that a number of independent groups were actively engaged in the calculation of force constants and normal coordinates on digital computers. At this meeting an informal discussion was held (those present were Drs. Scherer, Califano, Miyazawa, Nakagawa, Smith and Overend) and it was generally agreed that a periodic News Letter reporting recent developments in the field in an informal way would allow these groups to keep in close touch; this being particularly important in view of the rapid advances in computational techniques.

At Dr. N. Wright's suggestion we are launching this News Letter under the auspices of the Coblentz Society, although membership in the Society is not mandatory for participants in the News-Letter scheme, and we do not intend to distribute the News Letter to all members of the Society but only to those who specifically request copies.

The nature of this News Letter should encourage workers to use it as a vehicle for informal comments, preliminary results and tentative conclusions which might interest or amuse fellow workers. Consequently, any contributor will be entitled to modify (or even disown) his statements and opinions without blush or apology.

FORCE CONSTANTS OF CYCLOPROPAE

by S. J. Cyvin

In the course of the computations of the mean amplitudes of vibration 1) in cyclopropane 2) from spectroscopic data, it was needed to recalculate the force constants of this molecule 3) The calculations were based on a set of normal frequencies estimated from the fundamentals of C3H6 and C3D6, partially taken from Ref. 4) (infrared data for the gaseous state and some Raman data for the liquid phase), and from Ref. 5) (Raman data for the gaseous state). For the equilibrium parameters the following recent electron-diffraction data 6) have been adopted: C-H = 1.089 Å, C-C = 1.509 Å, CCH = 113.64°. Some of the results (in mdyn/Å units) are given in the following.

<table>
<thead>
<tr>
<th>Type of Motion</th>
<th>Force Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH stretching</td>
<td>5.6979</td>
</tr>
<tr>
<td>CH-CH interaction</td>
<td>0.28580</td>
</tr>
<tr>
<td>CC stretching</td>
<td>4.2208</td>
</tr>
<tr>
<td>CC-CC interaction</td>
<td>-0.13542</td>
</tr>
<tr>
<td>CH2 deformation; K(A1)</td>
<td>0.61504</td>
</tr>
<tr>
<td>CH2 wagging; K(B2)</td>
<td>0.63555</td>
</tr>
<tr>
<td>CH2 twisting; K(A2)</td>
<td>0.95183</td>
</tr>
<tr>
<td>CH2 rocking; K(B1)</td>
<td>0.16157</td>
</tr>
</tbody>
</table>
The angle-deformation displacement coordinates $K(A_1),...$ are identical with those given by Wilson, Decius and Cross, but have been multiplied by the constant $(RD)^{1/2}$. Here $R$ and $D$ denote the equilibrium values of the C-H and C-C bond lengths, respectively.

A detailed report of these calculations will appear elsewhere.

6) A. Almenningen, O. Bastiansen, L. Fernholt and P. Skancke (unpublished).

S. J. Cyvin
Institute of Theoretical Chemistry
Technical University of Norway,
Trondheim, Norway.

STUDY OF FORCE CONSTANTS MADE BY THE TOKYO GROUP
by T. Shimanouchi

(1) We are trying to explain vibration frequencies of many polyatomic molecules by the method of Modified Urey-Bradley Force Field. 180 molecules has been dealt with. All the force constants so far obtained are given in an appendix table of 11 pages of the following book:

S. Mizushima and T. Shimanouchi: Sekigaisen Kyūshū to Raman Kōka (Infrared Spectra and Raman Effect, 1958)
Publisher: Kyoritsu Shuppan Ltd.
9, Surugadai 3, Kanda, Chiyoda, Tokyo, Japan ($1.40$

(2) These results show that the U-B force field works well for most of the molecules. However, the following two facts were found:
(a) In the case of ethane and in-plane vibrations of ethylene, we have to consider the flexibility of the central C-C bond.

(b) When there is considerable contribution of resonance structures such as in the case of -CO-NH- or -CO$, one of the repulsive force constants is much larger than we expect.

(3) Recently we have made a complete program for the calculation of normal vibrations by a digital computer, PC-1. The program includes also the least square procedure for the calculation of force constants.

(4) Trials have been made for the Duncan-Collar Method for the symmetric and asymmetric matrix and for a modified Jacobs Method. The last method was the fastest and the most convenient. Even if the matrix has characteristic values very close to each other as in the case of CHCl$_2$Cl$_3$, the last program works very well.

(5) The automatic calculation of elements of G and F matrix has also been made for methane derivatives. A project is now going on for the elucidation of force constants and the calculation of L-matrix, P.E.D and Jacobian matrix for very many kinds of methane derivative molecules.

Takehiko Shimanouchi
Department of Chemistry
Faculty of Science
University of Tokyo
Tokyo, Japan

-------------
THE CALCULATION OF ACCURATE NORMAL COORDINATES
by Ian M. Mills

(Abstracted from a paper presented at the meeting of the European Spectroscopy Group, Bologna, 1959)

A program has been written for the Ferranti Mercury computer by which a complete set of frequencies, coriolis coefficients and centrifugal stretching constants may be calculated from an assumed set of force constants and appropriate G(1) and C(2) matrices. This program has been used to calculate a set of quadratic force constants for methane which reproduce fairly faithfully the observed frequencies, Coriolis coefficients and stretching force constants (where these are known) of CH$_4$, CD$_4$, CT$_4$, CH$_3$D, CD$_3$H, CT$_3$H, and CH$_2$D$_2$. The finally-accepted values of the symmetry force constants are

\[
\begin{align*}
F_{11} &= 5.8420 \pm 0.02 \\
F_{22} &= 0.4860 \pm 0.002 \\
F_{33} &= 5.3825 \pm 0.02 \\
F_{34} &= -0.2060 \pm 0.02 \\
F_{44} &= 0.4581 \pm 0.002
\end{align*}
\]
the symmetry coordinates being defined as:

\[
S_1 = \frac{1}{2}(r_1 + r_2 + r_3 + r_4) \\
S_2 = \frac{R}{2}(\alpha_{13} - \alpha_{32} + \alpha_{24} - \alpha_{41}) \\
S_3 = \frac{1}{2}(r_1 + r_4 - r_2 - r_3) \\
S_4 = \frac{R}{2}(\alpha_{23} - \alpha_{14})
\]

(1) Wilson, Decius and Cross, Molecular Vibrations, McGraw Hill, 1955


Ian M. Mills  
Department of Chemistry  
University of Reading  
Reading, England