

**MTP International Review of Science**

**Physical Chemistry  
Series One**

**Consultant Editor  
A. D. Buckingham**

**Volume 11**

**Chemical Crystallography**

**Edited by J. Monteath Robertson, F.R.S.**

**MTP International Review of Science**

**Volume 11**

# **Chemical Crystallography**

**Edited by J. Monteath Robertson, F.R.S.**  
**University of Glasgow**

**Butterworths · London**  
**University Park Press · Baltimore**

## THE BUTTERWORTH GROUP

### ENGLAND

Butterworth & Co (Publishers) Ltd  
London: 88 Kingsway, WC2B 6AB

### AUSTRALIA

Butterworth & Co (Australia) Ltd  
Sydney: 586 Pacific Highway 2067  
Melbourne: 343 Little Collins Street, 3000  
Brisbane: 240 Queen Street, 4000

### NEW ZEALAND

Butterworth & Co (New Zealand) Ltd  
Wellington: 26-28 Waring Taylor Street, 1

### SOUTH AFRICA

Butterworth & Co (South Africa) (Pty) Ltd  
Durban: 152-154 Gale Street

ISBN 0 408 70272 9

## UNIVERSITY PARK PRESS

### U.S.A. and CANADA

University Park Press Inc  
Chamber of Commerce Building  
Baltimore, Maryland, 21202

#### Library of Congress Cataloging in Publication Data

Robertson, John Monteath.

Chemical crystallography.

(Physical chemistry, series one, v. 11) (MTP  
international review of science)

Includes bibliographies.

1. Crystallography. I. Title.

QD453.2.P58 vol. 11 [QD951] 541'.3'08s [548'.3]

ISBN 0-8391-1025-1 72-2328

First Published 1972 and © 1972

MTP MEDICAL AND TECHNICAL PUBLISHING CO. LTD.

Seacourt Tower

West Way

Oxford, OX2 0JW

and

BUTTERWORTH & CO. (PUBLISHERS) LTD.

Filmset by Photoprint Plates Ltd., Rayleigh, Essex  
Printed in England by Redwood Press Ltd., Trowbridge, Wilts  
and bound by R. J. Acford Ltd., Chichester, Sussex

MTP International Review of Science

## **Chemical Crystallography**

## MTP International Review of Science

### Publisher's Note

The MTP International Review of Science is an important new venture in scientific publishing, which we present in association with MTP Medical and Technical Publishing Co. Ltd. and University Park Press, Baltimore. The basic concept of the Review is to provide regular authoritative reviews of entire disciplines. We are starting with chemistry because the problems of literature survey are probably more acute in this subject than in any other. As a matter of policy, the authorship of the MTP Review of Chemistry is international and distinguished; the subject coverage is extensive, systematic and critical; and most important of all, new issues of the Review will be published every two years.

In the MTP Review of Chemistry (Series One), Inorganic, Physical and Organic Chemistry are comprehensively reviewed in 33 text volumes and 3 index volumes, details of which are shown opposite. In general, the reviews cover the period 1967 to 1971. In 1974, it is planned to issue the MTP Review of Chemistry (Series Two), consisting of a similar set of volumes covering the period 1971 to 1973. Series Three is planned for 1976, and so on.

The MTP Review of Chemistry has been conceived within a carefully organised editorial framework. The over-all plan was drawn up, and the volume editors were appointed, by three consultant editors. In turn, each volume editor planned the coverage of his field and appointed authors to write on subjects which were within the area of their own research experience. No geographical restriction was imposed. Hence, the 300 or so contributions to the MTP Review of Chemistry come from many countries of the world and provide an authoritative account of progress in chemistry.

To facilitate rapid production, individual volumes do not have an index. Instead, each chapter has been prefaced with a detailed list of contents, and an index to the 13 volumes of the MTP Review of Physical Chemistry (Series One) will appear, as a separate volume, after publication of the final volume. Similar arrangements will apply to the MTP Review of Organic Chemistry (Series One) and to subsequent series.

Butterworth & Co. (Publishers) Ltd.

## Physical Chemistry

### Series One

Consultant Editor

A. D. Buckingham

*Department of Chemistry*

*University of Cambridge*

### Volume titles and Editors

#### 1 THEORETICAL CHEMISTRY

Professor W. Byers Brown, *University of Manchester*

#### 2 MOLECULAR STRUCTURE AND PROPERTIES

Professor G. Allen, *University of Manchester*

#### 3 SPECTROSCOPY

Dr. D. A. Ramsay, F.R.S.C.,  
*National Research Council of Canada*

#### 4 MAGNETIC RESONANCE

Professor C. A. McDowell, *University of British Columbia*

#### 5 MASS SPECTROMETRY

Professor A. Maccoll, *University College, University of London*

#### 6 ELECTROCHEMISTRY

Professor J. O'M Bockris, *University of Pennsylvania*

#### 7 SURFACE CHEMISTRY AND COLLOIDS

Professor M. Kerker, *Clarkson College of Technology, New York*

#### 8 MACROMOLECULAR SCIENCE

Professor C. E. H. Bawn, F.R.S.,  
*University of Liverpool*

#### 9 CHEMICAL KINETICS

Professor J. C. Polanyi, F.R.S.,  
*University of Toronto*

#### 10 THERMOCHEMISTRY AND THERMODYNAMICS

Dr. H. A. Skinner, *University of Manchester*

#### 11 CHEMICAL CRYSTALLOGRAPHY

Professor J. Monteath Robertson, F.R.S.,  
*University of Glasgow*

#### 12 ANALYTICAL CHEMISTRY - PART 1

Professor T. S. West, *Imperial College, University of London*

#### 13 ANALYTICAL CHEMISTRY - PART 2

Professor T. S. West, *Imperial College, University of London*

### INDEX VOLUME

**Inorganic Chemistry  
Series One**

Consultant Editor

H. J. Emeléus, F.R.S.

*Department of Chemistry  
University of Cambridge*

*Volume titles and Editors*

- 1 MAIN GROUP ELEMENTS—  
HYDROGEN AND GROUPS I–IV**  
Professor M. F. Lappert, *University of Sussex*
- 2 MAIN GROUP ELEMENTS—  
GROUPS V AND VI**  
Professor C. C. Addison, F.R.S. and  
Dr. D. B. Sowerby, *University of Nottingham*
- 3 MAIN GROUP ELEMENTS—  
GROUP VII AND NOBLE GASES**  
Professor Viktor Gutmann, *Technical University of Vienna*
- 4 ORGANOMETALLIC DERIVATIVES  
OF THE MAIN GROUP  
ELEMENTS**  
Dr. B. J. Aylett, *Westfield College,  
University of London*
- 5 TRANSITION METALS—PART 1**  
Professor D. W. A. Sharp, *University of Glasgow*
- 6 TRANSITION METALS—PART 2**  
Dr. M. J. Mays, *University of Cambridge*
- 7 LANTHANIDES AND ACTINIDES**  
Professor K. W. Bagnall, *University of Manchester*
- 8 RADIOCHEMISTRY**  
Dr. A. G. Maddock, *University of Cambridge*
- 9 REACTION MECHANISMS IN  
INORGANIC CHEMISTRY**  
Professor M. L. Tobe, *University College,  
University of London*
- 10 SOLID STATE CHEMISTRY**  
Dr. L. E. J. Roberts, *Atomic Energy  
Research Establishment, Harwell*

**INDEX VOLUME**

**Organic Chemistry  
Series One**

Consultant Editor

D. H. Hey, F.R.S.

*Department of Chemistry  
King's College, University of London*

*Volume titles and Editors*

- 1 STRUCTURE DETERMINATION  
IN ORGANIC CHEMISTRY**  
Professor W. D. Ollis, F.R.S., *University of Sheffield*
- 2 ALIPHATIC COMPOUNDS**  
Professor N. B. Chapman,  
*Hull University*
- 3 AROMATIC COMPOUNDS**  
Professor H. Zollinger, *Swiss Federal  
Institute of Technology*
- 4 HETEROCYCLIC COMPOUNDS**  
Dr. K. Schofield, *University of Exeter*
- 5 ALICYCLIC COMPOUNDS**  
Professor W. Parker, *University of Stirling*
- 6 AMINO ACIDS, PEPTIDES AND  
RELATED COMPOUNDS**  
Professor D. H. Hey, F.R.S. and  
Dr. D. I. John,  
*King's College, University of London*
- 7 CARBOHYDRATES**  
Professor G. O. Aspinall, *University of Trent, Ontario*
- 8 STEROIDS**  
Dr. W. D. Johns, *G. D. Searle & Co.,  
Chicago*
- 9 ALKALOIDS**  
Professor K. F. Wiesner, F.R.S.,  
*University of New Brunswick*
- 10 FREE RADICAL REACTIONS**  
Professor W. A. Waters, F.R.S.,  
*University of Oxford*

**INDEX VOLUME**

# **Physical Chemistry**

## **Series One**

Consultant Editor

**A. D. Buckingham**

## Consultant Editor's Note

The MTP International Review of Science is designed to provide a comprehensive, critical and continuing survey of progress in research. The difficult problem of keeping up with advances on a reasonably broad front makes the idea of the Review especially appealing, and I was grateful to be given the opportunity of helping to plan it.

This particular 13-volume section is concerned with Physical Chemistry, Chemical Crystallography and Analytical Chemistry. The subdivision of Physical Chemistry adopted is not completely conventional, but it has been designed to reflect current research trends and it is hoped that it will appeal to the reader. Each volume has been edited by a distinguished chemist and has been written by a team of authoritative scientists. Each author has assessed and interpreted research progress in a specialised topic in terms of his own experience. I believe that their efforts have produced very useful and timely accounts of progress in these branches of chemistry, and that the volumes will make a valuable contribution towards the solution of our problem of keeping abreast of progress in research.

It is my pleasure to thank all those who have collaborated in making this venture possible — the volume editors, the chapter authors and the publishers.

Cambridge

A. D. Buckingham



## Preface

The greater part of chemistry is concerned with structure in some sense, and the science of crystallography gives structure by providing the means for mapping out accurately the positions of atoms in space. The importance of this metrical aspect of structure will be clearly evident to anyone who glances through the various volumes on inorganic, physical and organic chemistry in this series. Many structures and much structural data are described and applied to chemical problems.

This volume is devoted specifically to chemical crystallography, but it was apparent from the outset that only selected aspects of this very large subject could be included. During the four or five years covered by this review there has been an enormous expansion of the literature dealing with chemical crystallography. Hardly a week passes without one or more new structures being described. This explosion of information is due in large measure to the increasing availability of large and very efficient computers, automatic diffractometers, and so on, which speed up the collection and handling of data and remove the computational burden. An average structure can now be solved in weeks instead of months, and even the very large structures of biological molecules may sometimes be solved in months instead of years. With this speeding up, accuracy has also been increased by a large factor, and so the results become much more significant.

All this has created great difficulties in compiling this volume, and many chapters have had to be drastically shortened and some omitted. No attempt has been made to describe methods of analysis. The heavy atom and isomorphous replacement methods for phase determination are still probably the most important, and indeed they are the only methods so far available for the determination of large protein and enzyme structures. A feature of recent work, however, has been the increasing power and application of the so-called direct methods, which depend on mathematical relations between the structure factors and do not require a heavy atom derivative. A chapter is devoted to recent applications of this method.

Crystallography is a big subject, but we hope this volume will give some indication of the generality of the method and of the more important advances that are being made in its chemical applications.

# Contents

<b>Hydrogen bonding, with special reference to O . . H . . O</b> J. C. Speakman, <i>University of Glasgow</i>	1
<b>Structural chemistry of transition metal complexes:</b> <b>(1) 5-coordination, (2) nitrosyl complexes</b> Bertram A. Frenz and James A. Ibers, <i>Northwestern University,</i> <i>Evanston, Illinois</i>	33
<b>Investigations of crystal structures in the U.S.S.R.</b> B. K. Vainshtein and G. N. Tischenko, <i>Institute of</i> <i>Crystallography, Moscow, U.S.S.R.</i>	73
<b>Co-operative phenomena in inorganic materials</b> S. C. Abrahams, <i>Bell Telephone Laboratories Inc.,</i> <i>Murray Hill, New Jersey</i>	139
<b>Structural studies of large molecules of biological importance</b> Marjorie M. Harding, <i>University of Edinburgh</i>	169
<b>Protein crystallography</b> T. L. Blundell and Louise N. Johnson, <i>University of Oxford</i>	199
<b>Application of direct methods in x-ray crystallography</b> J. Karle and Isabella L. Karle, <i>U.S. Naval Research Laboratory,</i> <i>Washington</i>	247
<b>Structures of natural products</b> A. McL. Mathieson, <i>Division of Chemical Physics, CSIRO,</i> <i>Clayton, Victoria, Australia</i>	311

# 1

## Hydrogen Bonding, with Special Reference to $O \cdots H \cdots O$

J. C. SPEAKMAN

University of Glasgow

---

1.1	INTRODUCTION AND BACKGROUND	2
1.1.1	<i>Origins</i>	2
1.1.2	<i>A note on the mechanism of hydrogen bonding</i>	3
1.1.3	<i>Infrared spectra and hydrogen bonding</i>	4
1.2	CRYSTAL-STRUCTURE ANALYSIS AND HYDROGEN BONDING	6
1.2.1	<i>x-Ray study of hydrogen bonds</i>	6
1.2.2	<i>The study of hydrogen bonds by neutron diffraction</i>	7
1.2.3	<i>Errors in hydrogen positions determined by x-rays</i>	9
1.3	THE GEOMETRY OF $O \cdots H \cdots O$ BONDING	10
1.3.1	<i>The Nakamoto–Margoshes–Rundle curve</i>	10
1.3.2	<i>The potential-energy diagram for <math>O \cdots H \cdots O</math> bonds</i>	12
1.4	CRYSTALLOGRAPHICALLY SYMMETRICAL HYDROGEN BONDS	13
1.4.1	<i>Acid salts of monobasic acids</i>	13
1.4.2	<i>Acid salts of symmetrical dicarboxylic acids</i>	15
1.4.3	<i>Some chelated <math>O \cdots H \cdots O</math> bonds</i>	17
1.4.4	<i>Some basic salts and the <math>H_5O_2^+</math> ion</i>	18
1.5	THE BIFLUORIDE ANION	20
1.6	THE ANALYSIS OF ATOMIC VIBRATIONS IN CRYSTALS	21
1.6.1	<i>General</i>	21
1.6.2	<i>The bifluoride anion</i>	22
1.6.3	<i>Potassium hydrogen di-trifluoroacetate</i>	22
1.6.4	<i>Vibrational correction of bond lengths: a note</i>	23
1.7	PROBLEMS OF VERY SHORT $O \cdots H \cdots O$ BONDS	23
1.7.1	<i>The symmetry problem</i>	23
1.7.2	<i>The isotope effect</i>	25
1.7.3	<i>The Kroon–Kanters–McAdam effect</i>	25

2	CHEMICAL CRYSTALLOGRAPHY	
1.8	THE POLYMORPHS OF ICE	27
1.9	CONCLUSION	29
	ACKNOWLEDGEMENTS	30
	NOTE ADDED IN PROOF	30

'One of the difficulties attending investigations of the hydrogen bond is that reliable determinations of the position of the hydrogen atom are difficult to make.'

(J. M. Robertson, *Organic Crystals and Molecules*, 1953)

## 1.1 INTRODUCTION AND BACKGROUND

### 1.1.1 Origins

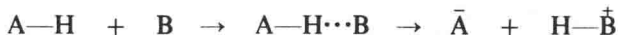
Hydrogen bonding is used to describe a situation resulting from the process



whereby the entities AH and B become attached to one another. It is a weak form of valency bonding, with an energy usually less than 10% of that associated with ordinary covalency. A and B, whether they be isolated atoms or parts of larger molecules, must be electronegative. Relatively strong hydrogen bonding is largely confined to cases where A and B are atoms of the three most electronegative elements—fluorine, oxygen and nitrogen. Though weak bonding sometimes occurs with chlorine, or bromine, or sulphur—even with carbon, when it is attached to very electronegative atoms—the interaction is then feeble and hard to distinguish from the general dispersion forces that operate between contiguous molecules.

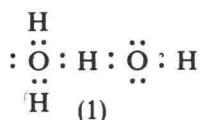
This Review is mainly concerned with systems in which A and B are both oxygen atoms.

From another, though related, point of view AH must be acidic; B must be basic. Within limits, increasing acid and basic strength favours hydrogen bonding. But, if the strengths become too great, an electrovalency will result:



Though the name, hydrogen bond, is more recent, the phenomenon was first explicitly recognised in the first decade of this century. For the roots of the concept we need to go back at least another century to the recognition of water as a remarkably unorthodox chemical compound. The simplest illustration of this is the boiling point, which is strangely high for material of molecular weight 18. No other material with a molecular weight less than 20 is not gaseous at ordinary temperatures. When physical chemistry began to develop, molecular association was recognised as the general cause of the abnormal behaviour of water in particular, and of other liquids in a lesser degree. These were usually compounds whose molecules included hydroxyl or amino groups: ROH, RNH<sub>2</sub>, etc. Association could be correlated with the presence of such polar groups in the molecule.

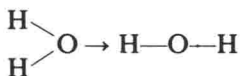
The abnormality disappeared when the hydrogen atoms of the OH or NH<sub>2</sub> groups were replaced by a methyl group, for example. When the hydrogen atoms of water are so replaced, to yield dimethyl ether, the boiling point drops by 124 °C, despite more than a doubling of molecular weight. Many observations of this sort implied that the hydrogen atom is an essential link in the machinery of molecular association. By about 1907 certain chemists were bold enough to write formulae which carried the disturbing implication that hydrogen could behave as if it were bivalent: for instance, F—H···F or H<sub>2</sub>O···H—O—H. The meaning of the dotted line was obscure, though not any more so—at the time—than that of the ordinary chemical bonds. Then in 1920, Latimer and Rodebush wrote the electronic formula (1):



The hydrogen bond was explicit, though this formula could hardly have been taken quite literally even in 1920.

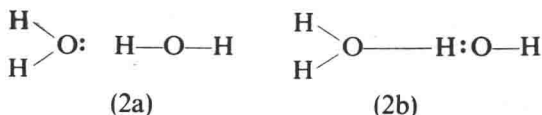
### 1.1.2 A note on the mechanism of hydrogen bonding

The causes of hydrogen bonding came within range of speculation, at the atomic level, after 1927. The first type of explanation, which we may term 'chemical', arose from a formal resemblance between the holding of two atoms or groups together by a hydrogen atom and coordination through a metal atom. Just as the complex [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> was attributed to dative covalency (H<sub>3</sub>N → Co), so a dimerised water molecule might be formulated as



This was quickly rejected because the 1s orbital of hydrogen cannot accommodate two pairs of electrons\*.

Proponents of a chemical mechanism then invoked the concept of resonance which Pauling had popularised. The hydrogen bond between (say) two water molecules might owe its stability to hybridisation between two electronic formulations (2a) and (2b):

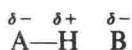


This idea fell into disfavour when it was pointed out that form (b), as we have drawn it, would have a much higher energy than (a). Resonance stabilisation

\*The contingency amendment, that the donated electron pair went into a second-shell orbital, was summarily rejected because this would be at too high an energy level. But Dr. Brian Webster opines that this objection is not necessarily so valid as it appeared to be in 1935.

would be significant only if the proton were centrally placed between the two oxygen atoms, or nearly so. This is certainly not true of most hydrogen bonds. However, in this Review we shall give prominence to some crystals which do have symmetrical, or quasi-symmetrical,  $O\cdots H\cdots O$  bonds. For such bonds, the resonance mechanism—or its more modern counterpart—may be important (see Section 1.7.1).

The second type of explanation, which may be labelled 'physical', attributes hydrogen bonding to a straightforward, classical electrostatic force. In the  $A-H \cdots B$  system,  $AH$  is necessarily dipolar in the sense symbolised below; and  $B$ , for similar reasons, carries a negative charge—a full charge if it is an anion (as in  $HF_2^-$ ), a partial charge if it is part of a larger molecule. When in the mutual orientation



an attractive force operates between  $A$  and  $B$ . One advantage of this scheme was that it lent itself to simple quantitative calculations. Provided secondary effects were neglected, quite elementary calculations gave bonding energies of correct order of magnitude, at any rate for weak hydrogen bonds.

The theory of hydrogen bonding is surveyed in the standard monographs by Pimentel and McClellan<sup>1</sup> and by Hamilton and Ibers<sup>2</sup>. From a specialist position there is a recent review by Bratož<sup>3</sup>; and Murrell<sup>4</sup> has written a more elementary account for the general reader.

The molecular interactions we classify as hydrogen bonds cover a wide range, from the minimal, or notional, attraction in (say)  $N-H\cdots Cl$ , to the strongest bonding in  $[F-H-F]^-$ . Each exists in a molecular system that is stable in its own right. As Murrell has emphasised, it is artificial to divide the total molecular bonding energy amongst separate bonds, each with a bonding energy resolvable into components due to distinct forces. It is therefore dangerous to think we have clarified the situation when we say that the weak  $N-H\cdots Cl$  bond and the very strong  $F-H-F$  differ merely in the relative participation in them of electrostatic and delocalisation forces. Nevertheless it comes naturally to many chemists to do just this.

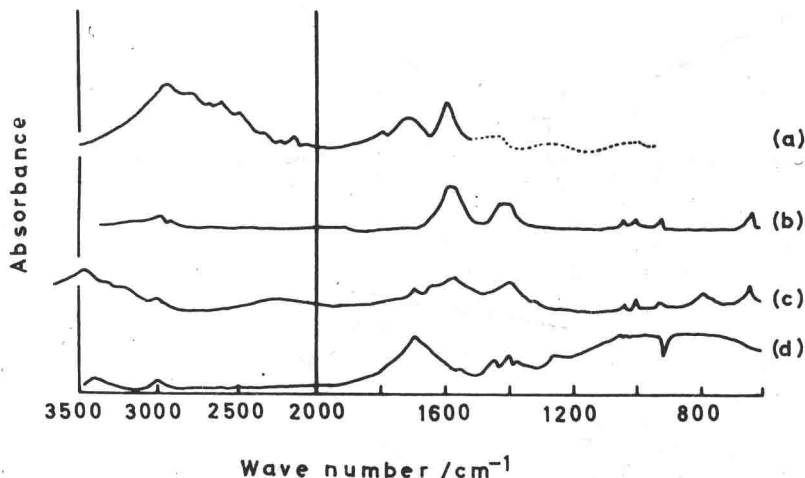
### 1.1.3 Infrared spectra and hydrogen bonding

In this Review we are concerned with hydrogen bonding as it may be studied by crystal-diffraction methods. However, other methods require brief mention, one such being infrared spectroscopy.

An unperturbed hydroxyl group in a gaseous molecule is associated with a stretching frequency, which appears as a sharp absorption band centred near  $3700\text{ cm}^{-1}$  ( $1.1 \times 10^{14}\text{ Hz}$ ). The spectra of solutions of hydroxylic compounds in an inert solvent show a similar peak. When the hydroxyl enters into hydrogen bonding, this feature changes notably. The peak moves to lower frequency; it becomes less sharp; it also becomes broader, with enhancement of its integrated intensity. These changes are progressive with increasing strength of the hydrogen bonding. For instance, there is a smooth, inverse correlation between frequency and strength as indicated by the over-

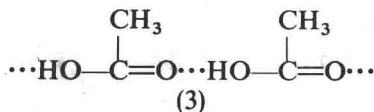
all shortening of the  $\text{O—H}\cdots\text{O}$  distance<sup>1,2</sup>. It can be followed down to frequencies of about  $2000\text{ cm}^{-1}$ .

To get access to a range of measurable hydrogen bonds, we need to study crystalline solids. The interpretation of the spectra of solids is much more difficult than for gases. But it is clear that shortening of the bond is associated not only with a lowering of frequency, but also with more profound changes of spectrum in very strong bonds. This subject has been extensively studied



**Figure 1.1** Infrared spectra of acetic acid and some salts: (a) crystalline acid; (b) sodium acetate; (c) sodium acetate trihydrate; (d) sodium hydrogen diacetate

by many authors, and reference may be made to recent articles by Hadži<sup>5</sup> and Sheppard<sup>6</sup>. An example is shown in Figure 1.1, which is concerned with acetic acid and its sodium salts. The first spectrum (a) is that of solid acetic acid, in which the molecules are linked into infinite chains by moderately strong hydrogen bonds (3).



The large peak  $\sim 3000\text{ cm}^{-1}$  is attributable to the  $\text{O—H}$  stretching. The  $\sim 700\text{ cm}^{-1}$  lowering of frequency is typical. Figure 1.1(b) gives the spectrum of the anhydrous sodium salt, (c) that of its trihydrate. In (b) there is no peak attributable to  $\text{OH}$ : in (c) there is a broad peak near  $3500\text{ cm}^{-1}$ , due to hydrogen-bonded water molecules. Figure 1.1(d) shows the spectrum of the *acid salt*,  $\text{NaH}(\text{CH}_3\text{CO}_2)_2$ , to which we shall refer later. This is characteristic of the spectra given by systems (particularly, but not necessarily, crystalline) with very strong  $\text{O}\cdots\text{H}\cdots\text{O}$  bonds. They have been classified by Hadži<sup>5</sup> as Type (ii) spectra. Sheppard has described them as 'remarkable spectra by any standards'. Their principal peculiarities are two: there is no peak unambiguously attributable to  $\text{O—H}$  stretching, though the peak

near  $1700\text{ cm}^{-1}$  in this case might possibly involve interaction of this mode with the C—O stretching; instead, there is a vast region of general absorption culminating near  $900\text{ cm}^{-1}$ , sometimes known as the 'D band'. These features of Type (ii) spectra are diagnostic of very strong hydrogen bonding, and have led to successful predictions of unknown crystal structures<sup>7</sup>.

## 1.2 CRYSTAL-STRUCTURE ANALYSIS AND HYDROGEN BONDING

Some of the earliest direct evidence of hydrogen bonding was derived from the x-ray analysis of crystals<sup>8,9</sup>. It is still an important method. In principle it enables us to assign relative positions to all the atoms; when applied to a molecular crystal, it reveals hydrogen bonds *in situ*, whether between different molecules or between different parts of the same molecule.

### 1.2.1 x-Ray study of hydrogen bonds

x-Rays are scattered by the electron-density condensation around an atomic nucleus. Atoms therefore show up more prominently the greater the atomic number. Because the electron density associated with a hydrogen atom is low, hydrogen atoms are more difficult to find. In early x-ray work they were not located at all, and the evidence for hydrogen bonding was to that extent incomplete, though convincing enough. The typical experimental finding was a pair of oxygen atoms too far apart for them to be directly linked by covalency, yet too close together for them to be non-bonded. The Pauling value for the van der Waals radius of oxygen is  $1.40\text{ Å}^*$ , the covalent radius  $0.66\text{ Å}$  (though the O—O distance in the hydrogen peroxide molecule is  $1.50\text{ Å}$ ). Thus any pair of atoms separated by a distance in the range  $1.5\text{--}2.8\text{ Å}$  would be suspected of some form of liaison weaker than normal covalency. In practice distances significantly shorter than  $2.4\text{ Å}$  are unknown. Hydrogen bonding would then be indicated by  $\text{O}\cdots\text{O}$  distances between  $2.4$  and  $2.8\text{ Å}$ .

The upper limit needs some increase to meet the following consideration. If there is to be any bonding, a hydrogen atom must be attached to one of the oxygens. Supposing this to be—as it must—nearly on the  $\text{O}\cdots\text{O}$  line, we must add to the van der Waals radius of the acceptor oxygen atom the O—H distance at the donor, plus the van der Waals radius of the hydrogen; these amount, respectively, to  $\sim 1.0$  and  $\sim 0.9\text{ Å}$ , giving a total  $\text{O}\cdots\text{O}$  distance of  $3.3\text{ Å}$  for the upper limit. (However this has been questioned by Bellamy<sup>10</sup>.)

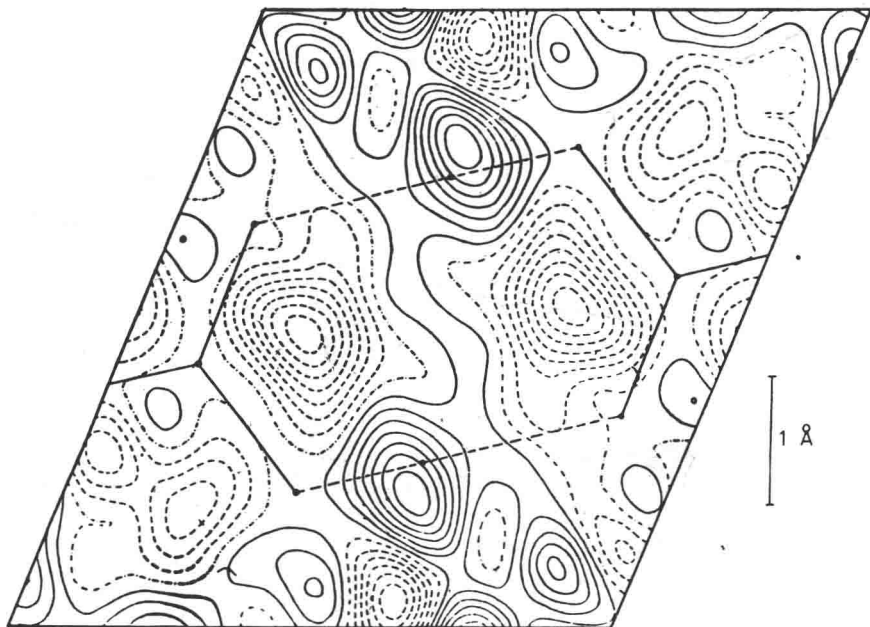
Application of this criterion to the results of x-ray work revealed many examples of  $\text{O—H}\cdots\text{O}$  bonding, overall distances being mainly in the range  $2.5\text{--}3.2\text{ Å}$ . Bonds with  $\text{O}\cdots\text{O} > 2.75\text{ Å}$  came to be called 'long', whilst those between  $2.5$  and  $2.65\text{ Å}$  were 'short'. We now have plenty of examples of bonds with  $\text{O}\cdots\text{O}$  between  $2.4$  and  $2.5\text{ Å}$ . These have had to be termed

\*As is still the almost universal practice amongst crystallographers, we express interatomic distances in ångströms:  $1\text{ Å} = 100\text{ pm}$ .



'very short' hydrogen bonds. They are of particular concern for us in this Review.

At the level of x-ray structure analysis implied above, participation of the hydrogen atom was deduced by inference. As there was always chemical evidence for the presence of hydrogen, and in a stereochemically reasonable position, the inference was strong. Improvements in x-ray methods substantiated the inference. In a modern analysis, based on more accurate intensity measurements, the small electron-density peak due to hydrogen



**Figure 1.2** Electron-density 'difference' synthesis of the region between two carboxyl groups, based on the x-ray study of  $\beta$ -succinic acid (Negative contour lines are broken. The positions of the carbon and oxygen atoms of the carboxyl groups are indicated) (From Robertson, J. M.<sup>9</sup>, by permission of the Royal Society)

can normally be detected, at any rate in crystals without elements of high atomic number. Such peaks show up better in the electron-density 'difference' synthesis—a Fourier series whose coefficients are  $(F_o - F'_c)$ , where  $F_o$  is the observed structure amplitude (suitably phased) and  $F'_c$  is the structure factor calculated for all the heavier atoms, but omitting hydrogens. An example is given in Figure 1.2. With the mountains taken out, the foothills show up more prominently.

### 1.2.2 The study of hydrogen bonds by neutron diffraction

Neutrons are scattered by the atomic nuclei. Though the scattering powers for 'thermal' neutrons ( $\lambda \sim 1.0 \text{ \AA}$ ) show a general increase with rising atomic