

pumping a Rhodamin-6G dye laser with a repetition rate of  $3 \text{ sec}^{-1}$ . The laser wavelength was 590 nm, the energy per pulse 800  $\mu\text{J}$ , the pulse length 10 nsec. Data were accumulated during about 1000 repetitions. An exponential time dependence corresponding to a lifetime of 5 msec has been observed for certain reflections. The figure shows an example for the time course of an integrated reflection intensity. Such a time behaviour would be in agreement with optical results obtained for CO-Myoglobin in solution at room temperature (Austin, Beeson, Eisenstein, Frauenfelder and Gunsalus, *Biochem.* (1975) **14**, 5355). It is, however, at present not yet clear whether the observed intensity changes entirely reflect structural changes accompanying debinding of the ligand, or whether lattice effects may contribute.

Even higher time resolution on a subnanosecond time scale may eventually be achieved by using the pulsed time structure of S.R. and by varying the time lag between the stimulating laser pulse and the S.R. pulse. A test application of this technique is in progress.

**02.8-01** CIRCULAR HYDROGEN BONDS. By Wolfram Saenger, Abteilung Chemie, Max-Planck-Institut für Experimentelle Medizin, Hermann-Rein-Straße 3, D-3400-Göttingen, Germany.

$\alpha$ -Cyclodextrin ( $\alpha$ -CD) is a circular molecule composed of six glucoses and exhibiting six primary as well as 12 secondary hydroxyl groups. It crystallizes as hexahydrate or, in the form of its methanol complex, as pentahydrate. X-ray and neutron diffraction structure analyses allowed to locate water and hydroxyl hydrogens and to derive the hydrogen bonding scheme. In essence, circular structures are formed with four, five or six O-H groups arranged such as to point all in the same direction (homodromic; Saenger, *Nature* (1979) **279**, 343) or to emanate from one  $\text{H}_2\text{O}$  molecule, and the two branches ending at one oxygen<sup>2</sup> (antidromic). It is proposed that such circular hydrogen bonds play a role in water clusters and, in general, in hydration of biological macromolecules.

**02.8-02** WATER MOLECULE- $\beta$ -CYCLODEXTRIN INTERACTIONS. By Kurt H. Jogun, John M. MacLennan and John J. Stezowski, Institut für Organische Chemie, Biochemie und Isotopenforschung der Universität Stuttgart, Pfaffenwaldring 55, Stuttgart, Federal Republic of Germany.

$\beta$ -Cyclodextrin ( $\beta$ -CD), cycloheptaamylose, is a medium molecular weight (1135 daltons) cyclic oligosaccharide that mimics biologically important macromolecules in several ways. Among them are its ability to form host:substrate complexes (in some cases catalytic activity is observed) and its ability to associate to form dimers that display good structural integrity in the crystalline state and very likely exist in aqueous solution, particularly at high concentrations.

Crystalline  $\beta$ -CD and many of its host:substrate complexes are highly hydrated. We have found that, in several cases, the crystals can be cooled to ca. 120 K and that high resolution data sets (typically  $2\theta_{\text{max}} = 60 \text{ deg.}$ , Mo radiation) can be collected which support extensive refinement of the crystallographic model.

A series of structure determinations of  $\beta$ -CD and host:substrate complexes have been carried out that we feel contribute to an understanding of the interaction of water with biological molecules. Aspects of the interaction of water with hydrophilic functional groups and with hydrophobic regions in the crystals will be examined.

**02.8-03** NEUTRON DIFFRACTION OF  $\beta$ -CYCLODEXTRIN WATER INCLUSION COMPLEX: AN ANALYSIS OF H-BONDS AND WATER STRUCTURE IN A HYDROPHOBIC CAVITY. By B. Hingerty<sup>1</sup>, Biol. Div., ORNL, Oak Ridge, TN 37830, USA; G. M. Brown<sup>2</sup>, Chem. Div., ORNL, Oak Ridge, TN 37830, USA; K. Lindner and W. Saenger, Max Planck Inst. für Experimentelle Med., Göttingen, West Germany.

Cyclodextrins (CD; cycloamyloses) have been used successfully as model structures in the study of non-covalent intermolecular interactions and enzyme mechanisms. These molecules have catalytic activity toward hydrolysis reactions. In order to better understand this activity it is necessary to know the H-bond interactions which are present. While X-ray structures can give the main features of the structure, it is not possible to sort out disordered H-bond networks. To do this we have collected neutron diffraction data for a  $\text{D}_2\text{O}$  exchanged  $\beta$ -CD crystal at the High Flux Isotope Reactor (HFIR) at Oak Ridge. The unit cell is:  $a = 21.261(6)$ ,  $b = 10.306(3)$ ,  $c = 15.124(4) \text{ \AA}$ ,  $\beta = 112.47(3)^\circ$ ,  $Z = 2$ , space group  $P2_1$ . Monochromatized radiation at  $\lambda = 1.015 \text{ \AA}$  was used initially to collect 3380 reflections with  $I/\sigma > 1$  to  $2\theta = 65^\circ$  (.94  $\text{ \AA}$  resolution). Longer counting times were used at higher angles. From these data all missing deuteriums were located, including some water deuteriums with temperature factors of up to  $60 \text{ \AA}^2$ . The structure was refined to an R-factor of .053 using bond length and angle constraints to retain proper stereochemistry, as is done in protein structures. A complicated H-bond network was revealed with an ice-like water structure. Chains of H-bonded  $\beta$ -CD hydroxyls have two alternate sets of H positions, so that for a given chain direction, all H bonds are  $\text{OH}\cdots\text{O}$ , or alternatively,  $\text{O}\cdots\text{HO}$ . Either a dynamic equilibrium, spatial disorder, or a combination of the two are indicated. More data have since been collected. By means of a structure factor calculation using the coordinates at  $R = .062$ , all the