Movement of channel H$_2$O in cordierite observed with quasi-elastic neutron scattering

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Abstract

Quasi-elastic neutron scattering experiments have been performed on natural and synthetic, hydrous and anhydrous, powder samples of cordierite to elucidate the dynamics of the H$_2$O molecules incorporated in the cavities of the cordierite structure. At room temperature, all protons are dynamically disordered. A simple jump model yields residence times at room temperature of about 6 ps. These measurements show that a static description of the orientation of the H$_2$O molecules is inappropriate, which is in agreement with earlier NMR measurements. A model is proposed in which the H$_2$O molecules in alkali-free cordierite, where ideally all the proton-proton vectors are aligned \( \parallel [001] \), revolve around their center of gravity while maintaining their orientation. This model is based on the wave-vector dependence of the elastic incoherent structure factor, which leads to a very small radius of gyration \( (\approx 0.4 \text{ Å}) \). The proposed model is compatible with earlier infrared experiments, in which no disorder of the orientation of the proton-proton vector was observed at room temperature. It is also consonant with the large anisotropic atomic displacement parameters observed for the O in H$_2$O in earlier structural studies. In agreement with a recent theoretical study, the model proposed here implies that it is not the O in H$_2$O that is located at the center of the cavity but rather the center of mass of the molecule. Within the resolution of the current experiments, the time scale of the dynamic behavior of the protons in natural or synthetic samples is similar.

Introduction

The dynamics of H$_2$O molecules in structural cavities of silicates is of great interest, as it is the manifestation of the generally poorly understood interaction between the incorporated "guest" and the framework. These interactions are not only responsible for a variety of fascinating crystallographic phenomena, such as the ordering of the guest molecules and structural phase transitions leading to pseudosymmetric structures, but they also contribute to the thermodynamic properties of these compounds. The dynamics of H$_2$O molecules can be investigated by a number of techniques, such as nuclear magnetic resonance spectroscopy (NMR), vibrational spectroscopy (infrared and Raman), and quasi-elastic neutron scattering. Although quasi-elastic neutron scattering is a unique technique for the investigation of dynamic and geometric aspects of the movement of protons on very short time scales (in the picosecond regime, \( 1 \text{ ps} = 10^{-12} \text{ s} \)), it has only rarely been used in the investigation of the dynamics of H$_2$O molecules in minerals. Typical examples of such earlier studies are those on the zeolites, especially harnotome (Fuess and Stuckenschmidt, 1988; Stuckenschmidt et al., 1988) and clays (Olejnik and White, 1972; Poinssignon et al., 1989). As part of a continuing project in which the dynamics of H$_2$O molecules in minerals are investigated by neutron scattering techniques, we have begun to study the dynamics of H$_2$O molecules in cordierite using incoherent quasi-elastic neutron scattering.

Cordierite, (Mg,Fe)$_x$[(Al$_x$Si$_{2-x}$)O$_{18}$]$_{14}$·nH$_2$O, has an orthorhombic framework structure (space group \( \text{Cccm} \)), with cavities (about 6 Å in diameter) that are linked to form channels parallel to \( [001] \) (Gibbs, 1966). A variety of atoms, ions, and molecules can be incorporated into the cavities, and in natural cordierite the channels are commonly occupied by H$_2$O, CO$_2$, and alkali ions (Armbruster and Bloss, 1982). The channels can be evacuated by heating and refilled under pressure (Johannes and Schreyer, 1981; Armbruster, 1985). Langer and Schreyer (1976) deduced from geometric considerations that, because of the relatively small size of the cavities, it is unlikely that more than one molecule can be incorporated into a single cavity, and that the H$_2$O-framework interaction was very weak. There have also been suggestions that there might be two H$_2$O molecules side by side in a single cavity (Mirwald, 1982), but no such double occupation has ever been detected in structural studies of either synthetic or natural cordierite, to the best of our knowledge. Structural studies based on diffraction experiments gave contradictory results. From diffraction experiments, Cohen...
et al. (1977) concluded that in natural Mg-rich samples the H$_2$O was oriented with its molecular plane parallel to (001), and they inferred from their structure refinements that the H$_2$O molecule was strongly asymmetric. Cohen et al. (1977) assumed disorder over four positions. Hochella et al. (1979) proposed that the O in H$_2$O was located at $\pm 0.027,a,$ $0.97,b,$ and that the H1-o-H2 plane was inclined by $\pm 29^\circ$ from (100), with the H-H vector inclined $19^\circ$ from [001]. Hochella et al. (1979) also concluded that the H$_2$O molecule was asymmetric. These studies pose the question why a very loosely bonded H$_2$O molecule should be distorted. Also, in the work of Cohen et al. (1977), the weaker H bond leads to a shortening of the O-H distance of the H$_2$O molecule, although increasing H bonding leads to a shortening of the O-H distance. Recent ab-initio calculations (Winkler et al., 1994) show that the H$_2$O molecule is undistorted, in agreement with spectroscopic experiments mentioned below.

It was Smith and Schreyer (1962) who first suggested that H$_2$O in cordierite is "not rigidly fixed in the centers of the cavities." Subsequently, the orientation and the dynamics of the H$_2$O molecules in cordierite have been the subject of several spectroscopic studies. Vibrational spectroscopic data (Farrell and Newnham, 1967; Goldman et al., 1977; Aines and Rossman, 1984) have been interpreted as showing that, for alkali-poor cordierite, the proton-proton vector is aligned parallel to [001], with the molecular plane lying in (010) in the crystal setting of Farrell and Newnham (1967), which has interchanged $a$ and $b$ axes relative to that of Goldman et al. (1977). In this paper, the former setting will be used. H$_2$O molecules with their proton-proton vector parallel to [001] have been termed type I; if the proton-proton vector is perpendicular to [001], the H$_2$O is said to be of type II. Aines and Rossman (1984) investigated the changes in the infrared spectrum of beryl and cordierite over a large temperature interval and deduced that above 473 K bound H$_2$O changes into an unbound state, that the temperature at which H$_2$O leaves the cordierite structure is 873 K, and that just below this temperature the ratio of bound to unbound H$_2$O is 3:1. Proton NMR measurements on natural alkali-bearing samples (Tsang and Ghose, 1972; Carson et al., 1982), however, showed that the H$_2$O molecules are dynamically disordered at room temperature. Carson et al. (1982) came to the conclusion that their NMR data were in agreement with infrared data of Goldman et al. (1977), who had observed type I and type II H$_2$O in their natural samples, under the assumption that, relative to the time scale of the NMR experiment (milliseconds), the H$_2$O changes its position rapidly, but that it changes position slowly with respect to the time scale of the infrared experiment (picoseconds).

In the present study, the time scale on which the H$_2$O molecules move has been investigated. Here, direct evidence of the motion of the H$_2$O in cordierite is presented, obtained from quasi-elastic neutron scattering on a significantly shorter time scale than in the NMR experiments. Experimental aspects and methods for the evaluation of quasi-elastic neutron scattering studies have been summarized by Bee (1988). The principles and use of this method for mineralogical problems have been summarized by Line et al. (in preparation). Because of the very large incoherent scattering cross section of H, it is possible to observe the motion of H$_2$O molecules even at low concentration (on the order of 1 wt%), which is common in a variety of minerals. During the experiments using natural samples, we realized that we could not properly correct for elastic incoherent scattering by non-H elements. Because of the low H$_2$O concentration, the elastic incoherent scattering by other elements, especially Na in the channel, cannot be neglected; it prevents the determination of the elastic incoherent structure factor (EISF). Therefore, additional quasi-elastic neutron scattering experiments were performed with hydrous and anhydrous synthetic powder samples on a triple-axis spectrometer, albeit with a lower energy resolution. During the time-of-flight (t-o-f) experiments, we observed some unexpected low-frequency inelastic peaks. These were further investigated using single crystals, and a tentative assignment is presented.

**Experimental methods**

High-energy-resolution quasi-elastic neutron-scattering experiments using natural samples were performed on the six-chopper t-o-f spectrometer, Mibemol, situated at a cold neutron guide at the Orphee reactor of the Laboratoire Leon Brillouin at Saclay, France. One needs to appreciate that neutron beam time for high-resolution quasi-elastic experiments is at present in such short supply that only the minimum length of time necessary was made available for the experiments described here. The cordierite from Origaervi, Finland, was kindly provided by T. Armbruster (University of Bern, Switzerland). The sample was briefly ground, so that the largest grains were smaller than about 0.5 mm$^3$. The sample was put in a Nb container with thin walls (0.1 mm), which was mounted in a radiation furnace. The tank in which the furnace was mounted was evacuated to $10^{-4}$ to $10^{-5}$ mbar. The sample was initially heated to 373 K, and during this period a noticeable degassing occurred, as could be observed by a sudden increase of pressure. After a few minutes, the degassing desisted; degassing also desisted after a few minutes when the sample was subsequently heated to 750 K or, at a later stage, when it was kept exposed to air for 1 d at room temperature and then reheated to 400 K. We therefore conclude, that H$_2$O that was adsorbed on the sample surface and on channel alkalis close to the surface had been driven off during the first heat treatment. The dehydration temperature of the sample used here is comparatively high, first, because the sample fragments were large, and hence, the diffusion distances very long, and second, because of the alkali ions, which are always pres-
g of cordierite were loaded into a cylindrical Al container, with a height of 50 mm and an inner diameter of 10 mm. Twenty percent of H$_2$O had been incorporated (Fig. 1).

Energy transfers were between -1 and 1 meV, and momentum transfers were between 0.25 and 2.25 Å$^{-1}$. Also, several measurements at larger energy transfers and several momentum transfers were performed at room temperature and 150 K during the search for the inelastic peaks seen in the t-o-f spectra on the natural sample. For all of these measurements, the instrumental conditions were similar to those described below for the single-crystal measurements.

Powder measurements on the same natural sample that had been used in the t-o-f experiments were also performed on the TAS to allow a comparison between the two techniques. The agreement was excellent. To investigate if the inelastic peaks were due to volatiles in the channels, the sample was heated under vacuum to 1123 K and kept there until no further degassing could be observed. Then the inelastic measurements were repeated.

To obtain a more complete description of the inelastic peaks observed in both the t-o-f and the TAS experiment on the natural sample, single-crystal measurements were performed. Natural, gem-quality crystals were kindly provided by T. Armbruster of the University of Bern and S. Herting-Agthe of the Technical University of Berlin. The Swiss sample was cut and had a size of about 400 mm$^3$, the Berlin sample was uncut and had a size of about 800 mm$^3$. Both samples were strongly pleochroic, with colors ranging from an intense purple-blue to a light brownish gray. Measurements were performed along all three basic reciprocal translation vectors for a variety of momentum transfers and temperatures. Typically, energy transfers ranged from about -1.4 to 3 meV. For some measurements, the incident wave vector, $k_i$, was fixed to 1.64 Å$^{-1}$ ($\lambda = 3.83$ Å), but, for the measurements aimed at determining the inelastic peaks at higher energy transfers, the measurements were performed with a fixed, final wave vector, $k_f$. Depending on the measurement conditions, either a pyrolytic graphite filter was used to suppress higher-order contaminations to $<3\%$, or a Be filter cooled by liquid N$_2$ was employed. No collimators were used, but, because of the horizontally curved ana-
The time-of-flight spectra of cordierite obtained at several temperatures. The elastic peak is near channel 400; the first inelastic peak mentioned in the text is at approximately channel 300.

RESULTS

The background-corrected and normalized t-o-f spectra, averaged over all scattering angles, are shown in Figure 2. Channel 0 corresponds to the arrival time of the neutrons at the sample. The maximum in the intensity, approximately t-o-f channel 390, is the elastic peak due to neutrons that were scattered by the sample without a change in energy. Its FWHM of 50 μeV is due to the convolution of a Dirac δ, with the triangular resolution function of the instrument. A second component, much broader and of less intensity, centered at the same t-o-f channel as the elastic peak, is the quasi-elastic contribution due to the motion of the protons. The very strong signal at t-o-f channels at short flight times and the sloping background around the elastic peak are due to phonons. Superimposed on this effective phonon density of states are a number of peaks, which we call the inelastic peaks. The high-temperature experiments at 573 and 748 K were conducted first, followed by the room-temperature measurement and, finally, the experiments at intermediate temperatures. All observed changes in the spectra were reversible.

The normalized and background-corrected data around the elastic peak were analyzed by fitting them with the convolution product:

\[
A(Q) = A(Q)\frac{\Gamma}{\pi(\omega^2 + \Gamma^2)} + C_1(Q)\omega + C_2(Q) \otimes R(\omega, Q).
\]

The first term within the bracket describes the elastic, and the second term the quasi-elastic scattering originating from the motion of the protons. The third and fourth terms describe the background. \(R\) is the instrumental resolution function obtained from a V experiment. Details of the numerical treatment of quasi-elastic spectra may be found in Bee (1988) or Line et al. (in preparation).

Although a quasi-elastic component was observed at all temperatures, at temperatures above room temperature, the quasi-elastic contribution gets too broad to be distinguished unambiguously from the background. At room temperature, an extrapolation to a zero wave-vector transfer gives an HWHM, \(\Gamma = 0.1\) meV. The extrapolation is necessary, as the quasi-elastic signal vanishes as \(Q \to 0\). To a first approximation, the residence time, \(t\), of the protons can be obtained from \(t = h/\Gamma \approx 6\) ps. There is no long-range translational diffusion, as this would, according to Fick's law, lead to \(\Gamma \to 0\) for \(Q \to 0\).

For a further analysis of quasi-elastic neutron scattering data, the ratio of the incoherently elastically scattered intensity to the total incoherently scattered intensity as a function of momentum transfer, \(A(Q)\), is calculated to obtain the elastic incoherent structure factor (EISF), whose wave-vector dependence can give insight into the microscopic aspect of the motion of the proton (Bee, 1988, 1992):

\[
A(Q) = \frac{I_e(Q)}{I_e(Q) + I_q(Q)}
\]

where \(I_e\) is an abbreviation for incoherent elastic and \(I_q\) stands for incoherent quasi-elastic. The elastic incoherent peak is due to the localization of the incoherent scatterer, and the quasi-elastic component is due to the characteristic time of the motion of the incoherent scatterer (Bee, 1988, 1992). Hence, in a solid (e.g., V, which has a large incoherent cross section and is therefore used to determine the resolution function of the spectrometer, as has been mentioned above), only the elastic incoherent component can be observed, as all the atoms are fixed at their sites. In contrast to this, the absence of the incoherent elastic peak and the presence of only incoherent quasi-elastic scattering is characteristic for liquids, e.g., water (Bellissent-Funel and Teixera, 1991; Salmon, 1989). In cordierite, both components have been observed, and
hence the protons are dynamically disordered, but they are confined to a small volume.

As has been mentioned above, we could not correct for the incoherent scattering by non-H elements in the initial high-resolution experiments. In the TAS experiments, with the synthetic samples, results obtained with the anhydrous sample were used for a background correction. After the subtraction, the data obtained with the hydrous sample were evaluated using a procedure similar to the one employed in the analysis of the t-o-f data. The EISF is shown in Figure 3. The extrapolation of the EISF to $Q = 0$ shows that $A(Q = 0) \approx 1$. This is the expected value for the EISF, as the time correlation of a position vector associated with the incoherent scatterer at the time origin, $r(0)$, and at time $t$, $r(t)$, is investigated in the limit of $t \rightarrow 0$. This confirms that our observations are not influenced by multiple scattering, as this leads to a decrease in the EISF at $Q = 0$ (Bee, 1988, 1992).

The interpretation of the EISF is model-dependent. In analcime (Line et al., in preparation), similar measurements and results indicated that only a fraction of the H$_2$O molecules were reorienting. Hence the measured EISF was smaller than the EISF corresponding to the motion of the protons. This could, in principle, also be the case in the present measurements. However, the NMR measurements of Carson et al. (1982) indicate that at room temperature there is only one kind of H$_2$O which is undergoing a reorientational anisotropic motion. A qualitative analysis of our high-temperature data supports the conclusions of Carson et al. (1982), as no additional quasi-elastic signal has been observed. Therefore, although the jump geometry and characteristic time of the motion at high temperatures may be very different (which is likely to be the case, as is indicated by the high-temperature data of Aines and Rossman, 1984, and an extrapolation of the data of Carson et al., 1982), the number of protons moving does not seem to increase.

The model proposed by Carson et al. (1982) implies the localization of the protons on a sphere or an ellipsoid around the center of the cavity with a radius of $\approx 1$ Å. Our measurements yielded a wave-vector dependence of the EISF that could not be fitted to such a model (Fig. 3). Hence, here we propose an alternative model based on a rigid H$_2$O molecule with a fixed orientation of the proton-proton vector (Fig. 4). The dynamics of this H$_2$O molecule can be derived from the revolution around its center of mass. A fixed orientation of the proton-proton vector implies that the protons would move on a circle, as has been indicated in Figure 4. This may be either a hopping motion between distinct sites or a continuous, diffusive motion. The EISF for a powder average of such a model has been calculated by Bee (1988). Figure 3 shows that a model based on a radius of gyration of $0.4$ Å describes the wave-vector dependence of the EISF well. However, the restricted data set obtained in the present study does not allow a more detailed interpretation. The simplest model would be a two-orientations model, where for each proton two positions, related to each other by a mirror plane in (100), would be energetically most favorable. A rigid H$_2$O molecule would then revolve around its center of mass, and the protons would each move on a circle that is characterized by its radius of gyration. In this model, the proton-proton vector is always parallel to [001].
The time taken for the reorientation is assumed to be negligible; this is virtually always assumed in the interpretation of quasi-elastic neutron scattering data. Experiments on time scales longer than the picosecond regime therefore always give a constant orientation of the molecular plane, which, in the setting used here, is parallel to (010).

Other features in the t-o-f spectra (Fig. 2) are low-energy inelastic peaks. There was no significant change in the intensity or position of the inelastic peaks of the degassed natural sample relative to the same sample before the degassing. No such peaks could be observed under any measuring condition in the synthetic samples. The single-crystal experiments obtained between room temperature and 20 K for several wave vectors along the three basic directions of the reciprocal lattice allowed a more thorough description of the inelastic peaks. A typical result is shown in Figure 5. The peaks at approximately 0.99 (very small) and 1.6 THz (Fig. 5) are contaminations caused by elastic scattering \((3k, = 4k, and 2k, = 3k, \text{contamination})\). At all temperatures, the ratios of the intensities of the inelastic peaks observed in energy gain to those observed in energy loss are related by the detailed balance principle. These excitations are anisotropic and are most probably due to transitions between ground states split by the crystalline electric field experienced by $^{56}$Fe$^{2+}$. We are currently investigating if the excitations can be used as a local probe for the Fe environment, and a full discussion will be given in another study.

**DISCUSSION**

A model that attempts to explain the motion of the H$_2$O molecules must consider previous X-ray, NMR, infrared, and optical data. Here we discuss whether the model derived above, in which a rigid H$_2$O molecule with a fixed orientation of the proton-proton vector relative to [001] revolves around its center of mass, is consistent with all the earlier and present data. In the absence of further data, the discussion is restricted to the simplest model, which is the two orientation model described above.

First, we consider only the case in which there are no alkalis in the channel. The infrared spectroscopic measurements do not necessarily imply that the molecule is bound, as has been inferred by Aines and Rossman (1984), but only show that there is no significant disorder of the orientation of the proton-proton vector relative to [001] on the time scale of the IR experiment and that the molecular plane is parallel to [010] virtually all the time. Hence the two-orientation model proposed here is consistent with these measurements. In their temperature-dependent, infrared spectroscopic study (Aines and Rossman, 1984), the appearance of a broad band at 473 K indicated the free reorientational motion of the H$_2$O molecules. The temperature for the appearance of freely rotating H$_2$O molecules obtained by Aines and Rossman (1984) is in good agreement with an extrapolation of the NMR data of Carson et al. (1982), which implies that all H$_2$O molecules rotate isotropically at about 450 K. However, these two results show that there is a distinct difference between the high-temperature motion and the dynamics at room temperature, which have been investigated in the present study.

From structure refinements of hydrous cordierite it is well known that the O is localized near or at the center of the cavities. The atomic displacement parameters of the O in H$_2$O show a distinct anisotropy, with $U_{11} \approx U_{22} \approx 2 \times U_{33}$ (Armbuster, 1985). These $U_{ij}$s are one order of magnitude larger than the atomic displacement parameters of the framework atoms, and hence the X-ray data imply that the O in H$_2$O is either statically or dynamically disordered. Both NMR and our quasi-elastic experiments show that the H$_2$O is dynamically disordered; the quasi-elastic neutron scattering experiments indicate that this disorder is on the picosecond time scale. Hence the X-ray data can be interpreted by assuming that the O in H$_2$O is moving in (001) around the center of the cavity at 0,0,$\frac{1}{4}$. If one assumes a rigid H$_2$O molecule, with its proton-proton vector parallel to [001], an O-H distance of 1 Å, and an H-O-H angle of 104.5°, revolving around its center of mass, the protons would move on circles with radii of $\approx 0.54$ Å (Fig. 4). The observed radius of gyration ($\approx 0.4$ Å) is smaller than the value obtained from this simple model. However, the deformation of the H$_2$O molecule due to the host-guest interactions and the actual dynamics of the H$_2$O molecule, which have been approximated only roughly, may explain this relatively small difference. A recent theoretical study by Winkler et al. (1994) also showed unambiguously that an orientation of the proton-proton vector parallel to [001] was energetically most favorable, and that the O in H$_2$O of the undistorted molecule was slightly displaced within (001) from the center of the cavity. The orientation of the molecule obtained in the theoretical study is different from that in the model presented here, as the center of mass...
The proton vector is fixed perpendicular to [001], and that
H₂O. The model proposed here would then lead to the
virtually no shielding between the alkali and the O in
alkali (1991) implies a relatively strong bonding, as there is
the O in H₂O. A model such as described by Sherriff et
of the attractive interaction between the alkali ion and
two orientations of the H₂O molecule, which has not been
observed directly yet, would then depend on the strength
is coordinated by two H₂O molecules in the two adjacent
ions? It has long been recognized that, because of electro-
static interactions, the H₂O molecule could rotate so that
the proton-proton vector is perpendicular to [001]. This
actually seems not to influence the time scale of the dy-
namics of the protons, as the width of the quasi-elastic
component observed in synthetic and natural (alkali-
bearing) samples are indistinguishable. However, the po-
tential in which an H₂O molecule close to an alkali ion
moves is different from that experienced by an H₂O mol-
ecule in Mg end-member cordierite. As the orientation
of the H₂O molecule is not due to H bonding, electro-
static interactions, probably between the O in H₂O and
the framework O atoms, determine the potential in which
the molecule moves. It is currently thought that, similar
to beryll (Sherriff et al., 1991), in an idealized case each
alkali ion located in the center of the six-membered ring
is coordinated by two H₂O molecules in the two adjacent
cavities. The possibility of a flipping motion between the
two orientations of the H₂O molecule, which has not been
observed directly yet, would then depend on the strength
of the attractive interaction between the alkali ion and
the O in H₂O. A model such as described by Sherriff et
al. (1991) implies a relatively strong bonding, as there is
virtually no shielding between the alkali and the O in
H₂O. The model proposed here would then lead to the
suggestion that, in this case, the orientation of the proton-
proton vector is fixed perpendicular to [001], and that
therefore the H atoms would move in (001), thus having
a radius of gyration of 0.8 Å. However, as noted above,
the presence of Na in the channel must be taken into
account when measuring the EISF, which greatly com-
plexes the experiments.

The present data set is too limited to allow an unam-
biguous determination of the geometry of the movement
of the H₂O molecules. The experiments necessary to con-
firm the present model and to determine the jump model
are very demanding but may become feasible with the
advent of new, more powerful neutron sources. The qua-
si-elastic scattering has to be measured up to wave-vector
transfers of 10 Å⁻¹. The resolution (FWHM) for elastic
scattering must be better than about 150 μeV. The min-
umum of the EISF should be at a wave vector transfer of
about 5 Å⁻¹; this would confirm a jump over two sites
on a circle with a radius of 0.4 Å. If the EISF only drops
down to a low value of ≈0.1 without increasing at larger
wave-vector transfers, that would indicate the protons
hop over more than four sites. At higher temperatures,
the radius of gyration should get larger until it reaches a
value of ≈1.2 Å, which would indicate free rotation of
the H₂O molecules.

In summary, the quasi-elastic neutron scattering ex-
periments here have confirmed that the H₂O molecules
are dynamically disordered at room temperature. This
excludes a static description, such as has been proposed
by Hochella et al. (1979). It also implies that the H₂O is
not bound in a conventional sense, as has been deduced
by Aines and Rossman (1984), but rather that the H₂O
is fixed in a certain orientation because of short-range
interactions with the framework and that these interac-
tions do not prohibit a revolving motion. This has been
deduced from the observed small radius of gyration, which
has led to a model with a fixed orientation of the proton-
proton vector. This model is therefore consonant with
atomic displacement parameters derived from earlier
X-ray studies (Armbruster, 1985) and the orientation of
the proton-proton vector and the molecular plane ob-
tained from infrared studies (Farrell and Newnham, 1967;
Goldman et al., 1977; Aines and Rossman, 1984) and a
theoretical study (Winkler et al., 1994). The present study
also confirms some of the findings of a previous NMR
study (Carson et al., 1982), namely, that the dynamics
are indeed faster than what can typically be resolved with
NMR measurements.

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