CLRC
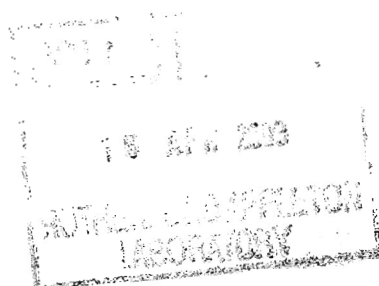
Quantum Correlations Between Protons in Potassium Bicarbonate

D A Keen   S W Lovesey

8th April 2003

COUNCIL FOR THE CENTRAL LABORATORY OF THE RESEARCH COUNCILS

Quantum correlations between protons
in potassium bicarbonate

D.A. Keen[1,2] and S.W. Lovesey[2]

1. Physics Department, Oxford University, Clarendon Laboratory,
Parks Road, Oxford, OX1 3PU, UK

2. ISIS Facility, Rutherford Appleton Laboratory,
Oxfordshire OX11 0QX, UK

Abstract

It is shown that a contribution to the total scattering of neutrons by a single crystal of $KHCO_3$ held at 15K arises from a purely quantum-mechanical and diffuse addition to scattering from identical particles which, in this instance, are protons in small dimers in a configuration described by a monoclinic crystal structure. The addition to scattering engages the total single-atom cross-section, and this feature explains why it is not visible in deuterated crystals where the relevant cross-section is down by an order of magnitude. Moreover, two other features of $KHCO_3$ make it a favourable case in which to observe the quantum-mechanical addition to scattering. First, the addition increases with decreasing nuclear spin I and $I = \frac{1}{2}$ for protons. Secondly, there are two dimer orientations in $KHCO_3$ and their contributions to scattering overlap in reciprocal space and produce high intensity in the form of rods. Our successful model of the observed scattering represents the protons as an ensemble of independent dimers with the appropriate crystal arrangement. Scattering from a dimer is calculated including quantum-mechanical correlations of the nuclei (protons) that in a homonuclear diatomic molecule produce ortho- and para-states.

1. Introduction

Protons in potassium bicarbonate have particularly interesting properties because they are found in small dimers that are well separated [1]. Properties in question include correlations between protons induced by the quantum mechanical treatment of indistinguishable nuclei [2,3]. In the case of a hydrogen molecule the ortho- and para-states are a manifestation of quantum correlations. We present a case for quantum correlations of this type creating a diffuse contributions to the total scattering of neutrons by a single crystal of $KHCO_3$ held at 15K [4]. The diffuse contribution is absent in the spectrum of neutrons scattered by a deuterated sample [4]. Our model successfully accounts for this finding, and applied to $KHCO_3$ (also known as algicidal soap) our model accounts for the high visibility of the diffuse contribution and its spatial distribution.

The essential components of our model are described in the next three sections. First, the established crystal structure which is represented by the monoclinic space-group $P2_1/a$. Secondly, the treatment by quantum mechanics of neutron scattering by two indistinguishable nuclei is described in sections 3 and 4. The total cross-section contains a diffuse contribution that is purely quantum-mechanical in origin. Section 5 describes a plausible calculation of the diffuse contribution by means of simple one-particle orbitals for a dimer. Thereafter, in section 6, our complete model is shown to account for all prominent features of the observed neutron spectrum. A discussion of our findings is provided in Section 7.

2. Crystal structure

The crystal structure of $KHCO_3$ at 14K has been determined previously using single crystal neutron diffraction [4]. Here we describe its pertinent features with reference to the two orthogonal projections in Figure 1. There are four formula units per monoclinic unit cell in space group $P2_1/a$, with $a=15.06(2)$Å, $b=5.570(15)$Å, $c=3.650(8)$Å and $\beta=103.97(15)°$. Pairs of CO_3 groups are joined by two nearly parallel O-H...O bonds to form approximately planar centrosymmetric $(HCO_3)_2$ dimers parallel to the $30\bar{1}$ planes and with their long O-C...C-O axis approximately along the 103 direction. All protons are crystallographically equivalent and no hydrogen bond disorder was observed at 14K. In addition, their thermal motion is decoupled from that of the CO_3

units in the dimer. The crystal structure therefore contains two short intra-dimer H-H contacts, with the protons separated by $|\mathbf{d}|$=2.22Å, and lying principally along $\mathbf{b}$, but inclined in opposite senses within dimers of type I or II. The vectors joining the two protons within the dimer (given by the dot - dashed lines in Figure 1a) are $\mathbf{d_1}$=(–0.030,0.389,–0.094) and $\mathbf{d_2}$=(0.030,0.389,0.094) for dimers I and II, respectively (in lattice units). $\mathbf{d_1}$ and $\mathbf{d_2}$ therefore define the two shortest proton dimers within the crystal structure and are the dimers referred to in subsequent sections. The projections of $\mathbf{d_1}$ and $\mathbf{d_2}$ onto the $\mathbf{a}$-$\mathbf{c}$ lattice plane are also approximately along $\overline{1}0\overline{3}$ and 103 real space directions, respectively.

3. Nuclear correlations

Let us consider scattering by two non-equivalent and identical nuclei. The nuclei, labelled α and β, are separated by a distance $\mathbf{d}$, and they are at positions $\mathbf{R}_\alpha$ and $\mathbf{R}_\beta$. Impinging neutrons are scattered by the potential [5],

$$V(\alpha,\beta) = b_\alpha \exp(i\mathbf{k}.\mathbf{R}_\alpha) + b_\beta \exp(i\mathbf{k}.\mathbf{R}_\beta) ,\qquad (3.1)$$

where b is the scattering length operator and $\mathbf{k}$ is the change in wavevector of the neutrons.

The scattering length operator is expressed in terms of the spin of a neutron, $\mathbf{s}$, and the spin of a nucleus, $\mathbf{I}$. One has,

$$b_\alpha = A + B\mathbf{s}.\mathbf{I}_\alpha ,\qquad (3.2)$$

and a similar expression for b_β in terms of $\mathbf{I}_\beta$. The nuclear spin operators satisfy $\mathbf{I}_\alpha.\mathbf{I}_\alpha = \mathbf{I}_\beta.\mathbf{I}_\beta = I(I+1)$ where I is the spin magnitude (I = ½ (1) for a proton (deuteron)). A and B in (3.2) are related to the coherent, σ_c, and total, σ, cross-sections;

$$\sigma_c = 4\pi A^2, \quad \sigma = 4\pi\left\{ A^2 + \frac{1}{4}B^2 I(I+1) \right\} .\qquad (3.3)$$

By way of orientation to the origin of the quantum effect in scattering by identical particles we hold responsible for the observed intensity, let us examine diffuse scattering by a dimer in the forward direction $\mathbf{k} = 0$. The intensity in question is,

$$T = \left\langle |V(\alpha,\beta)|^2 \right\rangle - \left| \langle V(\alpha,\beta) \rangle \right|^2 ,\qquad (3.4)$$

where angular brackets denote a mean value. Setting $\mathbf{k} = 0$ in (3.1) leads to,

- 3 -

$$\langle V(\alpha,\beta)\rangle = \langle b_\alpha \rangle + \langle b_\beta \rangle = 2\langle b_\alpha \rangle \ , \tag{3.5}$$

where the second equality follows because the two nuclei are identical. If $\mathbf{I}_\alpha$ is randomly orientated $\langle \mathbf{I}_\alpha \rangle = 0$, and, $\langle b_\alpha \rangle = A$ from which it follows that,

$$4\pi |\langle V(\alpha,\beta)\rangle|^2 = 4\sigma_c \ . \tag{3.6}$$

Turning to the other factor in T,

$$\langle |V(\alpha,\beta)|^2 \rangle = \langle b_\alpha^2 \rangle + \langle b_\beta^2 \rangle + 2\langle b_\alpha b_\beta \rangle = 2(\sigma/4\pi) + 2\langle b_\alpha b_\beta \rangle \ . \tag{3.7}$$

Here we have used the fact that the nuclei are non-equivalent and b_α and b_β commute. Additionally, $b_\alpha^2 = A^2 + 2AB\mathbf{s}.\mathbf{I}_\alpha + B^2 \{\mathbf{s}.\mathbf{I}_\alpha\}^2$, together with the identity,

$$\{\mathbf{s}.\mathbf{I}_\alpha\}^2 = \frac{1}{4}\{I(I+1) + 2i\mathbf{s}.\mathbf{I}_\alpha \times \mathbf{I}_\alpha\} \ , \tag{3.8}$$

lead to $\langle b_\alpha^2 \rangle = \sigma/4\pi$.

(a) Distinguishable nuclei

For distinguishable nuclei $\langle b_\alpha b_\beta \rangle = \langle b_\alpha \rangle \langle b_\beta \rangle = A^2$. Hence, in this instance, $4\pi T = 2\sigma + 2\sigma_c - 4\sigma_c = 2\sigma_i$ where $\sigma_i = \sigma - \sigma_c = B^2 I(I+1)/4$ is the incoherent cross-section. We then arrive at the expected result that, the diffuse intensity is equal to the incoherent cross-section multiplied by the number of nuclei.

(b) Indistinguishable nuclei

To obtain $\langle b_\alpha b_\beta \rangle$ in the presence of quantum correlations we use the obvious identity,

$$2b_\alpha b_\beta = b_\alpha^2 + b_\beta^2 - (b_\alpha - b_\beta)^2 \ . \tag{3.9}$$

The total spin $\mathbf{J} = \mathbf{I}_\alpha + \mathbf{I}_\beta$ yields, $\mathbf{J}.\mathbf{J} = J(J+1) = 2I(I+1) + 2\mathbf{I}_\alpha.\mathbf{I}_\beta$. Using the value of $2\mathbf{I}_\alpha.\mathbf{I}_\beta$ from this expression leads immediately to the result,

$$\langle (b_\alpha - b_\beta)^2 \rangle = B^2 I(I+1)\left\{1 - \frac{J(J+1)}{4I(I+1)}\right\} = B^2 I(I+1)R(J) \ , \tag{3.10}$$

where the second equality defines $R(J)$. Assembling the pieces from (3.9) gives,

$$\langle b_\alpha b_\beta \rangle = \langle b_\alpha^2 \rangle - \frac{1}{2} B^2 I(I+1) R(J) ,\qquad (3.11)$$

or, $4\pi \langle b_\alpha b_\beta \rangle = \sigma - 2\sigma_i R(J)$, and we conclude that for indistinguishable nuclei $\langle b_\alpha b_\beta \rangle$ depends on the magnitude, J, of the total spin. It can be shown that an average over J reduces $R(J)$ to ½, and the corresponding value of $\langle b_\alpha b_\beta \rangle$ is identical to its value A^2 for distinguishable nuclei. However, in general $\langle b_\alpha b_\beta \rangle$ depends on J, it is not equal to A^2, and the result leads to specific features in the diffuse intensity for scattering by correlated nuclei.

With $\mathbf{k}$ different from zero there is an additional dependence in T on J that comes in the form of the phase factor $(-1)^J$, as shown in the next section. In consequence, we will be faced with averaging the intensity over even and odd J. The weight factor in the averaging $w(J) = (2J+1) / (2I+1)^2$ satisfies,

$$\sum_{J=0}^{2I} w(J) = 1 .\qquad (3.12)$$

Restricting J to odd integers yields:

I = integer,

$$\sum_{J(\text{odd})} w(J) = I/(2I+1) .\qquad (3.13)$$

I = half integer,

$$\sum_{J(\text{odd})} w(J) = (I+1)/(2I+1).\qquad (3.14)$$

Slightly more algebra is required to find average values of $R(J)$. For all I,

$$\sum_{J=0}^{2I} w(J) R(J) = \frac{1}{2} , \quad \text{and} \quad \sum_{J(\text{odd})} w(J) R(J) = \frac{1}{4} ,\qquad (3.15)$$

and the first finding has been used in the preceding discussion.

4.   Diffuse scattering from a dimer

In this section we calculate the diffuse scattering by a dimer including the quantum correlations described in the previous section. The correlations stem from the

identity of the nuclei, and the requirement in quantum mechanics that their wave function $\Psi(\alpha,\beta)$ satisfies $\Psi(\beta,\alpha) = (-1)^{2I} \Psi(\alpha,\beta)$ [6]. The wave function is the product of a spinor $X_M^J(\beta,\alpha) = (-1)^{2I+J} X_M^J(\alpha,\beta)$ and an orbital $\Phi(\alpha,\beta)$. We adopt an independent-particle ansatz in which,

$$\Phi(\alpha,\beta) = \frac{1}{\sqrt{2}}\left\{\varphi_1(\mathbf{R}_\alpha)\varphi_2(\mathbf{R}_\beta) + (-1)^J \varphi_1(\mathbf{R}_\beta)\varphi_2(\mathbf{R}_\alpha)\right\}, \qquad (4.1)$$

where $\varphi_1(\mathbf{R})$ and $\varphi_2(\mathbf{R})$ are one-particle orbital wave functions. Since J is an integer $(-1)^{2J} = 1$ and $\Psi(\alpha,\beta) = X_M^J(\alpha,\beta)\Phi(\alpha,\beta)$ behaves in the correct way to an exchange of the two nuclei. The one-particle orbitals will be taken to be purely real, normalized to unity, and orthogonal.

The quantity of interest in the calculation of diffuse scattering is,

$$\left\langle |V(\alpha,\beta)|^2 \right\rangle = \frac{1}{(2J+1)}\sum_M \int d\mathbf{R}_\alpha \int d\mathbf{R}_\beta \Psi^*(\alpha,\beta)|V(\alpha,\beta)|^2 \Psi(\alpha,\beta)$$

$$= 2\left\langle b_\alpha^2 \right\rangle + 2\left\langle b_\alpha b_\beta \right\rangle\left\{P(\mathbf{k}) + (-1)^J Q(\mathbf{k})\right\} . \qquad (4.2)$$

Here the mean value of $b_\alpha b_\beta$ is $\left\langle b_\alpha b_\beta \right\rangle = \sum_M \left\{X_M^J(\alpha,\beta)\right\}^+ b_\alpha b_\beta X_M^J(\alpha,\beta)/(2J+1)$ with a similar definition of $\left\langle b_\alpha^2 \right\rangle$. Values of $\left\langle b_\alpha b_\beta \right\rangle$ and $\left\langle b_\alpha^2 \right\rangle$ are quoted in the previous section. The quantities $P(\mathbf{k})$ and $Q(\mathbf{k})$ are defined through,

$$2\left\{P(\mathbf{k}) + (-1)^J Q(\mathbf{k})\right\} = \int d\mathbf{R}_\alpha \int d\mathbf{R}_\beta \Phi^2(\alpha,\beta)\left\{Z^*(\mathbf{R}_\alpha)Z(\mathbf{R}_\beta) + Z(\mathbf{R}_\alpha)Z^*(\mathbf{R}_\beta)\right\},$$

$$(4.3)$$

where the dependence on J on the right-hand side is in $\Phi(\alpha,\beta)$ defined in (4.1). For convenience we write $Z(\mathbf{R}) = \exp(i\mathbf{k}.\mathbf{R})$. By inspection of $\Phi(\alpha,\beta)$ it is evident that $Q(\mathbf{k})$ is determined by integrals of $Z(\mathbf{R})$, $\varphi_1(\mathbf{R})$ and $\varphi_2(\mathbf{R})$, and with $Z(\mathbf{R})=1$ at $\mathbf{k}=0$ it follows from the orthogonality of $\varphi_1(\mathbf{R})$ and $\varphi_2(\mathbf{R})$ that $Q(0)=0$. In contrast, $P(\mathbf{k})$ is determined by diagonal matrix elements of $Z(\mathbf{R})$ and it does not vanish at $\mathbf{k} = 0$.

The experiment of interest to us measures the total scattering of neutrons by $KHCO_3$ [4]. For this situation, the intensity is proportional to $\left\langle |V|^2 \right\rangle$ and the mean value

of $|V|^2$ is taken to include an average over the allowed values of the total angular momentum J. To this end, the relevant results in section 3 are (3.11) and (3.15).

After averaging over all J the value of $\langle |V|^2 \rangle$ in (4.2) reduces to,

$$4\pi \langle |V(\alpha,\beta)|^2 \rangle = 2\left\{ \sigma + \sigma_c P(\mathbf{k}) + \frac{\sigma}{(2I+1)}(-1)^{2I} Q(\mathbf{k}) \right\}. \tag{4.4}$$

The term in $Q(\mathbf{k})$ survives the averaging because there are different fractions of states with even and odd J. It is evident that the contribution to scattering from $Q(\mathbf{k})$ is purely quantum mechanical and it has no classical analogue. The contribution is particularly large for protons because $I = \frac{1}{2}$, and $\sigma_i = \sigma - \sigma_c$ is very large. Using the values $P(0)=1$ and $Q(0)=0$ we recover at $\mathbf{k} = 0$ the value of $\langle |V(\alpha,\beta)|^2 \rangle$ found in section 3.

In applying our finding to the interpretation of scattering by KHCO3 we will use $\sigma \gg \sigma_c$ and $I = \frac{1}{2}$ and base our discussion on the expression

$$T(\mathbf{k}) \approx 2\sigma\{1 - Q(\mathbf{k})/2\} . \tag{4.5}$$

It remains to derive a plausible result for $Q(\mathbf{k})$ for a proton dimer, and this task is the subject of the next section.

5. One-particle orbitals

Having adopted in section 4 an independent-particle ansatz for the dimer orbital, $\Phi(\alpha,\beta)$, we have arrived at an expression for the diffuse contribution to total scattering, $Q(\mathbf{k})$, which contains matrix elements created with orthogonal one-particle orbitals. At a first level of approximation, designed to capture the essential physics using a simple algebraic expression, one-particle orbitals are represented in terms of a single radial wavefunction. In this instance, we achieve $Q(\mathbf{k})$ expressed in terms of only two parameters, later chosen to give $Q(\mathbf{k})$ in good agreement with the available experimental data.

Let the radial wavefunction be denoted by $\psi(\mathbf{R})$ and elect to use one-particle orbitals,

$$\varphi_1(\mathbf{R}) = N_1\{\psi(\mathbf{R}) + a\psi(\mathbf{r} - \mathbf{R})\} \text{ and, } \varphi_2(\mathbf{R}) = N_2\{\psi(\mathbf{R}) - b\psi(\mathbf{r} - \mathbf{R})\} , \tag{5.1}$$

where one anticipates on physical grounds that $\mathbf{r}$ is very close to the vector $\mathbf{d}$ that joins the two nuclei in the model dimer. Normalization and orthogonality require,

$$N_1^2\left(1+a^2+2aS\right)=1, \quad N_2^2\left(1+b^2-2bS\right)=1, \tag{5.2}$$

and, $1+S(a-b)=ab$ where S is an overlap integral,

$$S=\int d\mathbf{R}\psi(\mathbf{R})\psi(\mathbf{r}-\mathbf{R}). \tag{5.3}$$

The corresponding value of $Q(\mathbf{k})$ is essentially a function of the angle $\xi=(\mathbf{r}.\mathbf{k})/2$. We find,

$$Q(\mathbf{k})=(N_1N_2)^2\cos(2\xi)\exp(-2W_0)\left\{(1+ab)^2\sin^2\xi+(1-ab)^2(1-\cos\xi)^2\right\}, \tag{5.4}$$

where $\exp(-2W_0)$ is a Debye-Waller factor due to zero-point motion of the nuclei.

On comparing our expression for $Q(\mathbf{k})$ with data in the next section we conclude that the diffuse contribution to scattering is well described by the second term in (5.4) that is proportional to $\sin^4(\xi/2)$. Setting $ab=-1$ leads to ,

$$Q(\mathbf{k})=\frac{4S^2}{\left(1-S^2\right)^2}\cos(2\xi)\exp(-2W_0)\sin^4(\xi/2). \tag{5.5}$$

We note that in the limit $S=0$ the one-particle orbitals are $\psi(\mathbf{R})$ and $\psi(\mathbf{r}-\mathbf{R})$, and $Q(\mathbf{k})=0$. (On the other hand, $ab=1$ requires $a=b=1$ and $Q(\mathbf{k})$ does not vanish in the limit $S=0$. Setting $ab=1$ in (5.4) produces in $Q(\mathbf{k})$ a dependance on ξ which is found with a Heitler-London ansatz for the orbital $\Phi(\alpha,\beta)$.)

Useful insight to the nature of the dimer orbital related to (5.5) and the part played by S is found by looking at the corresponding one-particle density $\rho(\mathbf{R})$. The two maxima in $\rho(\mathbf{R})$ indicate the most probable positions of the nuclei and separation of the peaks is a fair measure of the dimer bond-length $d=|\mathbf{d}|$. For the case of $ab=-1$ we find,

$$\rho(\mathbf{R})=\varphi_1^2(\mathbf{R})+\varphi_2^2(\mathbf{R})=\left\{\psi^2(\mathbf{R})+\psi^2(\mathbf{r}-\mathbf{R})-2S\psi(\mathbf{R})\psi(\mathbf{r}-\mathbf{R})\right\}/\left(1-S^2\right). \tag{5.6}$$

From this result for $\rho(\mathbf{R})$ it is evident that $S>0$ leads to a separation between nuclei d which is larger than r. By way of illustration, an isotropic Gaussian function for $\psi(\mathbf{R})$ and $S=\tfrac{1}{2}$ leads to $d=1.24r$, while d/r increases monotonically with S.

6. Confrontation of experimental data and theory

The scattering intensity, $T(k)$, given by (4.5) and (5.5) for a single proton dimer is planar perpendicular to the dimer direction and modulated parallel to the dimer direction. In addition, the Debye-Waller factor causes the intensity to decrease as $|k|$ increases. Along the dimer direction and with increasing k, moderate intensity is observed at $k=0$ which then peaks before dropping to a minimum for $\xi=(r \cdot k)/2= \pi$. The modulation is then repeated in reverse between $\xi=\pi$ and 2π, albeit suppressed by the Debye-Waller factor. At first sight this appears incompatible with the observed one-dimensional rods of diffuse scattering in the a^*-c^* reciprocal lattice plane of $KHCO_3$ [4] (Figure 2). These rods lie along the $30\overline{1}$ direction, at a minimum $|k|$ of 10.25Å^{-1} where they intersect the 701 direction.

The reciprocal lattice plane of calculated scattering, $T(k)$, containing the 701 reciprocal direction (which is parallel to the 103 real space direction and perpendicular to $30\overline{1}$) and b^* is shown in Figure 3. This plane is chosen because it contains the dimers, d_1 and d_2, and is perpendicular to the observed diffuse scattering in the a*-c* plane (see Figure 2). In this calculation, the contributions from each dimer (given by 5.5) have been summed and we have not included a Debye-Waller factor. The vector r in the definition of ξ will be in the same direction as d, the vector joining the protons. The dimer bond-length $|d|$ is larger than the parameter $|r|$ in the one-particle orbitals that are described in the previous section. We have chosen values of $r = 0.7d_1$ and $r = 0.7d_2$ to provide best agreement with the observed data (see below).

Two sets of identical planes of intensities are superimposed, one with planes normal to an axis 13° from b^* and one normal to an axis −13° from b^*. The effect of the superposition of intensity from the two dimers is to give peaks of intensity in Figure 3. These peaks are actually rods of scattering perpendicular to the reciprocal lattice plane plotted in Figure 3 and occur in parts of reciprocal space where the planes with maximum intensity from each dimer contribution overlap. In particular, a rod of scattering is observed for $k = \pm 10.25$ Å^{-1} along 701 when $k=0$ along b^*. This is in the same position and orientation to the ridge of scattering observed in the experimental data (Figure 2). This is seen more clearly in Figure 4, where the calculation of $T(k)$ has been made for the a^*-c^* plane, and introducing an overall isotropic Debye-Waller factor, $\exp(-2W)$. This

Debye-Waller factor reflects the variations of different proton dimers through thermal fluctuations and is distinct from the Debye-Waller factor $\exp(-2W_0)$ in (5.5).

There is only really one significant shortcoming in the calculation, revealed by confronting Figures 2 and 4, and that is an apparent overestimate of the widths of the rods of intensity. An assessment of the physics behind this finding calls for a more sophisticated calculation of the diffuse contribution to scattering $Q(k)$ and additional experimental data for other directions of k. We also have in mind anisotropy in the proton Debye-Waller factor [4], for example.

It has been interesting to find the influence of alternative dimers. Looking at the packing of protons in the unit cell, the next nearest possible candidate dimers, d_1-b and d_2-b, are given by the dotted lines in Figure 1a. Since these dimers only differ from d_1 and d_2 in their components along b, these would add to the intensity of the rods of scattering in the a^*-c^* plane.

7. Discussion

A recently discovered, spatially coherent addition to the total scattering of neutrons by a single crystal of potassium bicarbonate [4] is here attributed to diffuse scattering from proton dimer units. It is shown that the relatively high intensity of the addition and its spatial characteristics stem simply from the actual configuration of dimers in the $P2_1/a$ monoclinic crystal structure. The diffuse scattering in question has no analogue in classical physics and it engages the total single-atom neutron cross-section. These features of the proposed mechanism for the additional scattering will explain why it is not visible in total scattering by a deuterated crystal ($KDCO_3$), for the spin ($I = 1$) and cross-section ($\sigma = 7.6$ barns) of a deuteron are significantly different from the corresponding quantities for a proton ($I = \frac{1}{2}$ and $\sigma = 81.7$ barns). Crucially, the diffuse scattering by a dimer that we call on to explain the data on $KHCO_3$ depends on the change in wavevector of the neutrons scattered by the crystal. Disorder in proton positions in the crystal that is brought about by raising its temperature will destroy the delicate quantum correlations in a dimer.

The main ingredients in the proposed explanation, the crystal structure and the treatment by quantum mechanics of total scattering by a dimer, are indeed surely footed.

To accomplish a comparison with the experimental data we are called upon to model the orbital state of protons in a dimer. We use for the orbital wavefunction a plausible independent-particle ansatz that has the merit of simplicity, and our expression for the diffuse intensity contains only two parameters. Most importantly, the orbital ansatz permits us to correctly identify the essential spatial parameter that we demonstrate to be the projection of the scattering wavevector on the axis of a dimer unit, of which there are two types in the crystal structure. Quantitative agreement between the experimental data and calculated intensity is achieved with values of the two parameters that are shown to be entirely reasonable. The data indicate that the calculated intensity in reciprocal space is too broad. One looks to a future *ab initio*, parameter-free calculation of diffuse scattering by a dimer with correlated nuclei for improvement on this item in the confrontation of data and theory.

Our interpretation of the addition to total scattering by a potassium bicarbonate crystal is different from the one already offered [4], where a special macroscopic state of two-dimensional quantum-mechanical vibrations of the protons is invoked.

References

1. Thomas J.O., Tellgren R. and Olovsson I. (1974) *Acta Cryst.* **B30**, 1155; *ibid* **B30**, 2540.

2. Fillaux F. (1998) *Physica* D **113**, 172.

3. Ikeda S. and Fillaux F. (1999) *Phys. Rev.* B **59**, 4134.

4. Fillaux F., Cousson A. and Keen D.A. (2003) *Phys. Rev.* B **67**, 054301.

5. Lovesey S.W. (1987) Theory of Neutron Scattering by Condensed Matter, Vol.1 Third Edition (Clarendon Press: Oxford).

6. Landau L.D. and Lifshitz E.M. (1977) Quantum Mechanics, Third Edition (Pergamon Press: Oxford).

Figure Captions

Figure 1. Projections of the structure of KHCO$_3$ at 14K using the parameters determined in [4] and including anisotropic temperature factors. The figures show pairs of connected HCO$_3$ groups and separated K atoms. (a) Projection onto the plane, normal to **c** showing the two, symmetry-related (HCO$_3$)$_2$ dimers, I and II, together with the shortest and next shortest proton dimers, given by the dot - dashed and dotted lines, respectively. Note that these (HCO$_3$)$_2$ dimers are actually inclined with respect to the *a-b* plane, as shown in (b). (b) Projection onto the plane normal to **b** (orthogonal to the plane in (a), above and rotated by 14° about **b**), showing the orientation of the planar (HCO$_3$)$_2$ dimers. The reciprocal lattice vectors are shown as dashed lines and are not to scale with respect to the real space unit-cell vectors.

Figure 2. The diffraction pattern from KHCO$_3$ at 15K in the *a*-c** plane (from [4]). Dark spots correspond to Bragg peaks. Strong diffuse scattering is observed centred at $k=0$ and in two ridges (marked by arrows) along $30\overline{1}$ directions, perpendicular to 701 and either side of the origin.

Figure 3. Calculated diffuse scattering, $T(k)$, in the (701)-(010) reciprocal lattice plane from the d_1 and d_2 proton dimers in KHCO$_3$. Dot-dashed lines show the directions of the dimers and dashed lines show the planes perpendicular to the dimers that overlap to produce the rods of intensity in the *a*-c** plane. Contours are in arbitrary units.

Figure 4. Calculated diffuse scattering, $T(k)$, in the *a*-c** reciprocal lattice plane from the d_1 and d_2 proton dimers in KHCO$_3$. Contours are in arbitrary units.
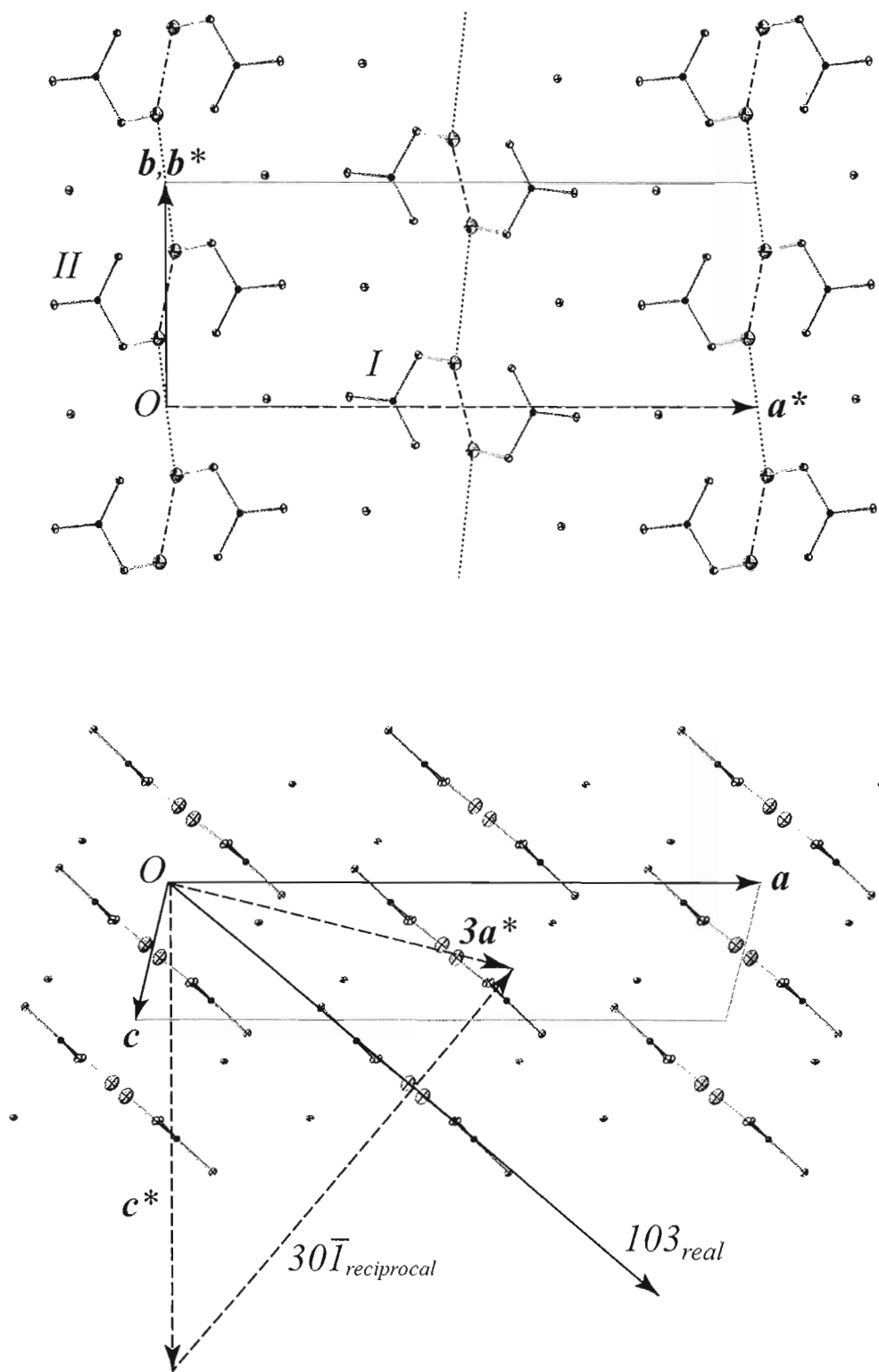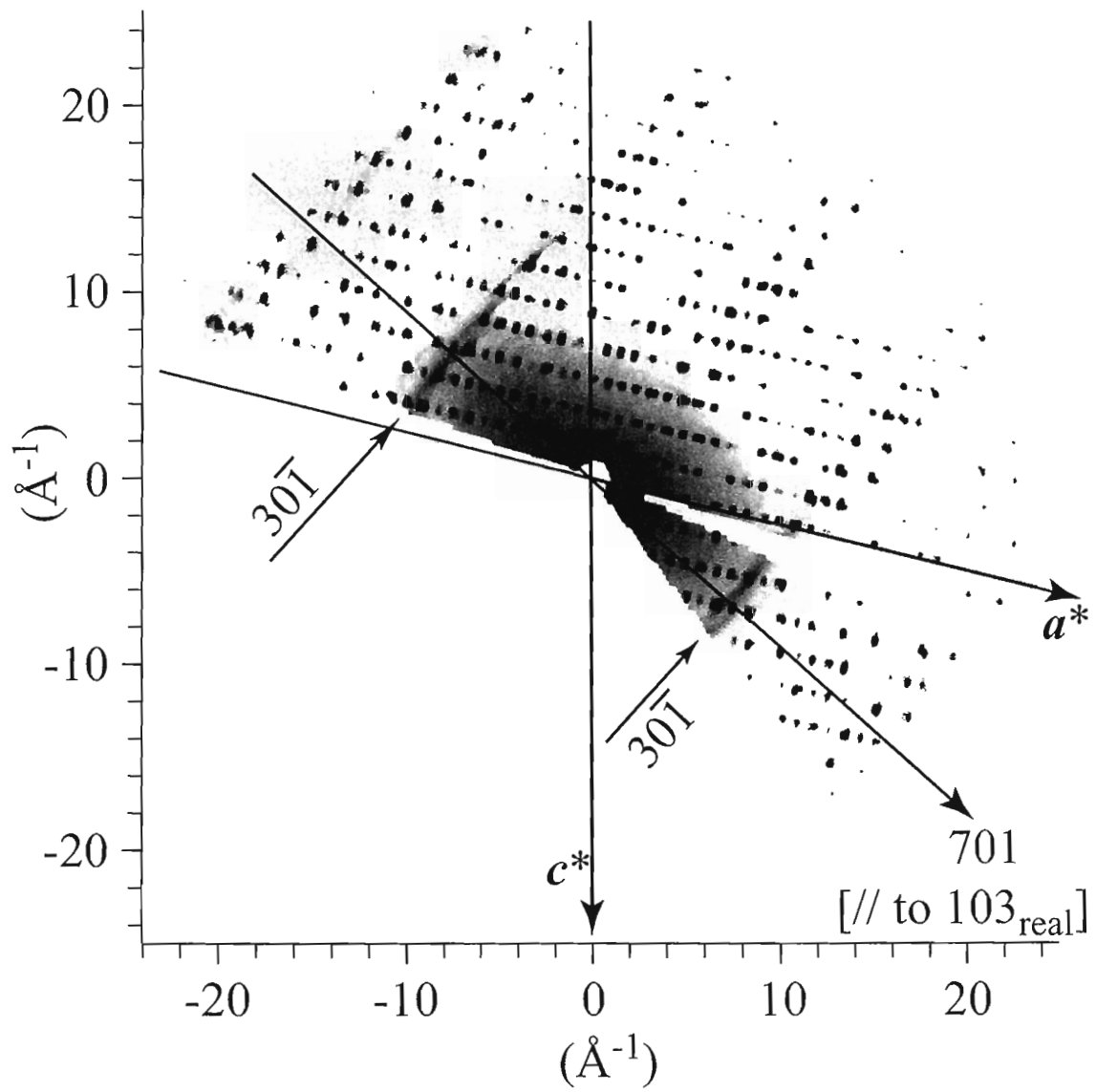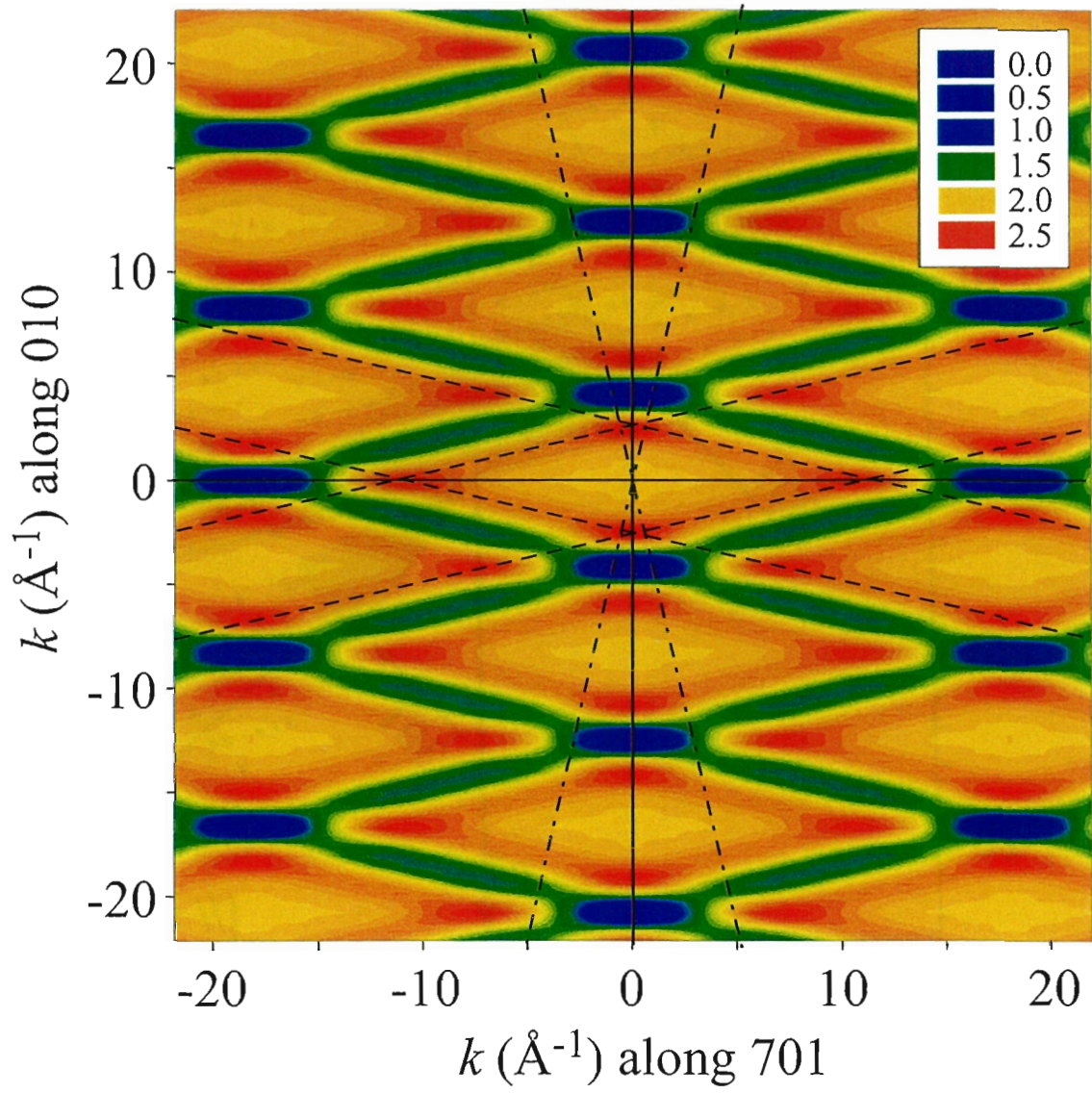
Figure 1.

Figure 2.

Figure 3.

Figure 4.