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## A MODEL FOR THE HOH BENDING VIBRATIONS IN SOME CRYSTALLOHYDRATES

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### INTRODUCTION

It is generally believed that the HOH bending frequency increases on going from a "free" H<sub>2</sub>O molecule in the gas-phase to a water molecule in a crystallohydrate [1]. Thus, both the normal-coordinate treatment [2] and the recent results of some SCF calculations [3] seem to indicate that the frequency of the HOH bending should *increase in all cases* of water molecules found in crystallohydrates. However there are few cases (KMgPO<sub>4</sub>·H<sub>2</sub>O and its nickel analogue being the most striking examples) in which it has been shown (cf. Ref. [4] and the references therein) that the HOH bending vibrations appear appreciably *lower* than 1595 cm<sup>-1</sup> (the value of HOH bending frequency in the gas-phase). In the present paper an attempt will be made to reveal some of the possible reasons for the lowering of the HOH bending frequency, using a simple model for water molecules undergoing bending vibrations.

### THE MODEL

Let us consider a water molecule in which the bending coordinate is the only normal coordinate and the amplitudes of the atoms during the vibration are reasonably small. The Lagrange function for such a water molecule (see. Fig. 1a) may be written as :

$$L_1 = m_1(\dot{u}_1^2 + \dot{u}_3^2)/2 + m_2\dot{u}_2^2/2 - k\delta^2/2 \quad (1)$$

where  $m_1$  and  $m_2$  are the masses of the H and O atom respectively,  $u_1$ ,  $u_2$  and  $u_3$  are the displacements of atoms 1, 2 and 3,  $k$  is the force constant and  $\delta$  is the bending internal coordinate.

Let us now consider a water molecule in a crystallohydrate (see Fig. 2b). We assume that the only interaction of the hydrogen atom 1 and its surrounding is the shielded electrostatic one with the proton-acceptor 4 (the same holds for atoms 3 and 5) and that this interaction may be treated as a small perturbation to the energy spectrum of the vibrating water molecule (the distance  $r$  is about twice the distance  $l$ ). We also assume that

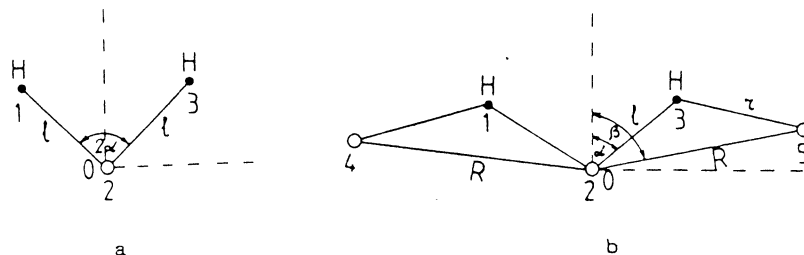


Fig 1 : a) "Free" water molecule ; b) Water molecule in a crystallohydrate

the values for the HOH angle and the distance  $l$  are the same as in the "free" water molecule (in fact, there are small changes in these quantities, but we feel that this simplification will not affect appreciably the final results in this qualitative approach). The mass of the proton-acceptor 4 (5) is, as usually, large enough and so the distance  $R$  is essentially unchanged during the water bending vibration.

Starting with these assumptions, the Lagrange function  $L$  of the system schematically presented in Fig. 1b, may be written as :

$$L = L_1 - 2V(r) \quad (2)$$

where  $V(r)$  is the potential energy of the interaction between atoms 1 (3) and 4 (5), the quantity  $r$  being :

$$r = [R^2 + l^2 - 2lR\cos(\gamma - \delta)]^{1/2} \quad ; \quad \gamma = \beta - \alpha \quad (3)$$

When  $\delta = 0$ ,  $r = r_0$  ( $r_0$  being the equilibrium distance).

If  $\gamma = 0$  (i.e. the hydrogen bonds are linear)  $r$  is always greater than  $r_0$  and the attractive part in the potential  $V(r)$  becomes dominant. On the other hand, if  $\gamma \neq 0$  then  $r > r_0$  for  $\gamma - \delta > \gamma$  and the potential is attractive, whilst  $r < r_0$  for  $\gamma - \delta < \gamma$  and the potential is, mainly, a repulsive one. To summarize, the potential energy may, in general, be presented as consisting of two terms :

$$V(r) = -K_1/r^n + K_2/r^m \quad (4)$$

the first being the attractive and the second - the repulsive one. The quantities  $K_1$ ,  $K_2$ ,  $m$  and  $n$  are some empirical non-negative constants.

As mentioned earlier, the amplitudes of the vibration are small. This allows us to expand the  $\cos(\gamma - \delta)$  term of Eqn. (3) into a power series of the small quantity  $\delta$ . Omitting terms of order

higher than 2, the potential  $V(r)$  may be written as

$$V(r) = K_2 r_0^{-m} - K_1 r_0^{-n} - (mK_2 r_0^{-m} - nK_1 r_0^{-n}) lR \cdot \cos \gamma \cdot \delta^2 / (2r_0^2) - \\ - [m(1 + m/2)K_2 r_0^{-m} - n(1 + n/2)K_1 r_0^{-n}] \cdot \sin^2 \gamma \cdot \delta^2 \cdot (lR/r_0^2)^2 + \\ + (mK_2 r_0^{-m} - nK_1 r_0^{-n}) \cdot \sin \gamma \cdot \delta lR/r_0^2 \quad (5)$$

Using the condition  $V'(r) = 0$ , for the equilibrium state, one obtains :

$$(mK_2 r_0^{-m} - nK_1 r_0^{-n}) \cdot \sin \gamma = 0 \quad (6)$$

For nonlinear hydrogen bonds ( $\gamma \neq 0$ ) the Eqn. (6) is fulfilled if and only if :

$$mK_2/nK_1 = r_0^{(m-n)} > 0 \quad (7)$$

Making use of equations (1), (5) and (7), the Lagrange function (2) for the bending water molecule in the crystalline environment may be written as :

$$L = m_1(\dot{u}_1^2 + \dot{u}_3^2)/2 + m_2 \dot{u}_2^2/2 - \\ - [kl^2/2 - 2nK_1(m-n) \cdot (lR/r_0^2)^2 \cdot r_0^{-n} \cdot \sin^2 \gamma] \cdot \delta^2 \quad (8)$$

It is obvious that Eqn. (8) is the Lagrange function for an one-dimensional harmonic oscillator, the frequency of which is :

$$\omega^2 = 2[k - 4nK_1(m-n)R^2 r_0^{-n-2} \cdot \sin^2 \gamma] \cdot (1+2m_1 \cdot \sin^2 \alpha/m_2)/m_1 \quad (9)$$

The vibrational frequency of the "free" water molecule may be obtained from equation (9) if the second term in the square brackets is omitted. It is this term that describes the change of the HOH bending frequency (due to hydrogen bonding), for a water molecule in a crystallohydrate. This term may be either positive (if  $m > n$ ) or negative (if  $m < n$ ). In the first case the condition  $K_2/K_1 < r_0^{m-n}$  has to be satisfied, whilst in the second the ratio  $K_2/K_1$  will be larger than  $r_0^{m-n}$ . From the physical point of view, the existence of both possibilities may be justified by the fact that  $r > 1$ , which ensures that repulsive interaction between atoms 1 (3) and 4 (5) may appear if  $m > n$  as well as if  $m < n$ , depending on the magnitudes of  $K_1$  and  $K_2$ . The values of these constants, namely, may vary for different crystallohydrates and are expected to depend on  $r_0$ .

For  $\gamma = 0$ , an equation analogous to Eqn. (9) may be obtained :

$$\omega^2 = 2[k - (mK_2 r_0^{-m} - nK_1 r_0^{-n}) \cdot R/lr_0^2] \cdot (1+2m_1 \cdot \sin^2 \alpha/m_2)/m_1 \quad (10)$$

In this case (linear hydrogen bonds)  $r > r_0$  during the vibration and the attractive part of the potential dominates over the repulsive one. As a consequence, the second term in the square brackets of Eqn. (10) is negative and the frequency of the vibration increases.

#### CONCLUSION

The model employed in the present paper is admittedly a rather simple and crude one. Nevertheless it shows that conditions leading to a lowering of the HOH bending frequencies could exist. A future goal is to make the model more sophisticated and more in agreement with the experimental findings.

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