Theoret. chim. Acta (Berl.) 9, 116—122 (1967)

The Infrared Spectra of Hydrogen-Bonded Crystals

YVES MARÉCHAL, and ANDRZEJ WITKOWSKI*

Laboratoire de Chimie Organique Physique, Centre d'Etudes Nucléaires, Grenoble, France
Laboratoire de Spectrométrie Physique (associé au C.N.R.S.), Institut Fourier, Grenoble, France

Received July 20, 1967

A theoretical approach is proposed to explain the spectral changes in the X–H stretching region of hydrogen-bonded crystals. The model proposed here is restricted to a one dimensional crystal. The X–H stretching modes are supposed to be coupled to H-bond vibrations of lower frequency, and in general the separation of these modes is no longer possible. The fundamental hamiltonian describing this coupling is derived and formulae for quantities, such as intensity, bandwidth and center of gravity of the infrared line in the X–H stretching mode region are calculated.

Es wird eine theoretische Näherung vorgeschlagen, um die Veränderung im Infrarot-Spektrum von Kristallen mit Wasserstoff-Bindungen im Bereich der X–H-Längsschwingungen zu erklären. Das vorgeschlagene Modell ist eindimensional. Die X–H-Schwingungen sind mit (X–H...Y)-Längsschwingungen geringerer Frequenz gekoppelt; die verschiedenen Schwingungstypen lassen sich i. a. nicht trennen. Der fundamentale Hamiltonoperator, der die Kopplung beschreibt, wird eingeführt, und es werden Größen wie Intensität, Bandbreite und 1. Moment der Spektrallinien der X–H-Schwingungen berechnet.

Nous formulons une proposition théorique afin d'expliquer les changements intervenant dans le spectre infrarouge de cristaux à liaison hydrogène, dans la région des modes de vibration d'élongation X–H. Le modèle proposé est un modèle à une dimension. Les modes d'élongation X–H sont couplés à des modes d'élongation du type X–H...Y de plus basse fréquence; en général, on ne peut plus séparer ces divers modes. Nous établissons l'hamiltonien fondamental qui décrit ce couplage et nous calculons des grandeurs telles que l'intensité, la largeur de bande et le centre de gravité des raies du spectre de vibration d'élongation X–H.

Introduction

The hydrogen-bond formation introduces some marked changes in the spectral properties of systems. In particulier the X–H stretching vibration in the infrared region shows, after hydrogen-bond formation, most characteristic changes: an unusual big increase of the bandwidth and total intensity, a frequency shift and a complicated fine structure [6]. These spectral changes in the X–H stretching region are most characteristic for the hydrogen bond and serve as a principal mean for its detection.

The understanding of these unusual spectral changes is therefore of principal interest but for the time being rather few theoretical approaches have been proposed [6, 3, 7, 2].

---

* Permanent address: Department of Theoretical Chemistry, Jagellonian University, Cracov, Poland.

Many spectral investigations have been carried out for hydrogen-bonded systems in solution where non-definite structure of the hydrogen bonded molecular aggregates prevents any quantitative interpretation. The carboxylic acids which form stable dimers, in gas, liquid or solid state, or imidazol, which forms linear structures in solid state [8], may serve as a convenient example of systems with a definite structure.

Recently, a new theoretical approach to the interpretation of the infrared spectra of the O–H stretching modes in the hydrogen bonded carboxylic acid dimers has been proposed by one of us (WITKOWSKI) [9]. This author points out that in the excited O–H vibrational state, the O–H stretching modes are no longer separable from the hydrogen bond vibrations (in the spirit of the Born-Oppenheimer approximation), suggests the physical nature of the coupling, and derives the fundamental hamiltonian describing the coupling of these modes.

In this note, we present a similar approach, for the coupling of X–H vibrations with other modes (specially X...Y) in linear crystals (Fig. 1). We first establish the general hamiltonian describing the coupling of X–H motions with X...Y vibrations. Then we give general expressions for the intensity, center of gravity and bandwidth of an infrared line in the 3000 cm^{-1} region. As we are mostly interested in the infrared spectra of the crystal, we limit ourselves to the case where, in the whole crystal we have no more than one X–H mode excited. Thus, all problems of interactions between excitons will be discarded.

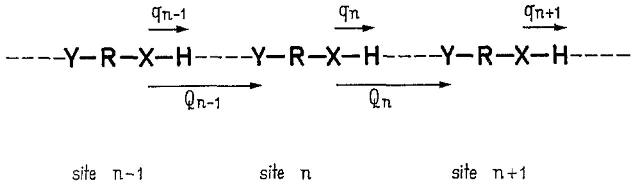

Fig. 1

A Simplified Model for a Linear Crystal

Let us consider a linear crystal composed of N units which are H-bonded together (Fig. 1). In the site n lies one molecule. The X–H component of this molecule is H-bonded to the Y atom of the molecule in the $(n + 1)^{\text{th}}$ site. The X–H stretching mode in the n^{th} site will be defined by the coordinate q_n, and reduced mass m. The intermolecular stretching mode X...Y [X in the n^{th} site, Y in the $(n + 1)^{\text{th}}$ site] will be labeled by the coordinate Q_n and effective mass M. P_n and p_n will be the conjugate momenta of Q_n and q_n. Here, we will only consider these two kinds of modes.

The corresponding hamiltonian will be

$$\mathscr{H} = \sum_{n=0}^{N-1} \left\{ \frac{P_n^2}{2M} + \frac{p_n^2}{2m} + V'(q_n, Q_n) + \tilde{V}(q_n, q_{n+1}; Q_n) \right\} . \qquad (1)$$

$V'(q_n, Q_n)$ is the oscillation potential for the X–H motion (in the n^{th} site) and X...Y motion [X in the n^{th} site, Y in the $(n + 1)^{\text{th}}$ site]. $\tilde{V}$ stands for the interaction potential between adjacent sites. This term is responsible for the bandwidth of the energy levels of the X–H stretching modes. We will treat it as a perturbation term, and thus assume an exciton-like behavior for the X–H modes [4].

Let us now suppose that the vibrational eigenfunctions of the X–H stretching mode in the n^{th} sire are known. They are $\theta^{\alpha}(q_n, Q_n)$, where α labels the α^{th} eigenfunction of h_n, ($\alpha = 0, 1, 2 \ldots$) with

$$h_n = \frac{p_n^2}{2m} + V'(q_n, Q_n)\,.$$

We have thus

$$h_n\, \theta^{\alpha}(q_n, Q_n) = E^{\alpha}(Q_n)\, \theta^{\alpha}(q_n, Q_n)\,.$$

The wave function of the crystal, with all X–H vibrations in the ground state will be Ψ_i^V (V for vacuum, see later. i labels the different states of the X...Y modes), which may be approximated by

$$\Psi_i^V = \varphi_g(q)\, \alpha_i^V(Q)\,,$$

where q (and Q) stand for the whole set of coordinates q_n (and Q_n). In the zeroth-order approximation, φ_g is equal to

$$\varphi_g = \prod_l \theta^0(q_l, Q_l)\,.$$

The function $\alpha_i^V(Q)$ will thus obey the equation

$$\sum_n \left\{\frac{P_n^2}{2M} + E^0(Q_n)\right\} \alpha_i^V(Q) = W_i^V\, \alpha_i^V(Q)\,.$$

So far we have made implicitly the approximations that

$$\langle \varphi_g(q, Q) \left| \sum_n \frac{P_n^2}{2M} \right| \varphi_g(q, Q) \rangle_q = 0\,,$$

$$\langle \varphi_g(q, Q) \mid \tilde{V}(q_n, q_{n+1}; Q_n) \mid \varphi_g(q, Q) \rangle_q = 0;$$

$\langle \mid \rangle_q$ means integrations over the set of coordinates q_n.

Now let φ_n^+ represent the wavefunction for the X–H vibrations in the crystal when in all the sites except n, the X–H vibrations are in the ground state; in the n^{th} site, the X–H vibration is in the first excited state. We take then, as a basis,

$$\varphi_n^+(q, Q) = \prod_{l \neq n} \theta^0(q_l, Q_l) \cdot \theta^1(q_n, Q_n)\,.$$

Definying $\delta E(Q_l) = E^1(Q_l) - E^0(Q_l)$ we thus write

$$h_l\, \varphi_n^+ = \{E^0(Q_l) + \delta\, E(Q_l) \cdot \delta_{nl}\}\, \varphi_n^+\,.$$

We furthermore make the hypothesis that

$$\langle \varphi_i^+ \mid P_n^2 \mid \varphi_j^+ \rangle_q = 0\,.$$

Though intuitively justified, this approximation will be studied in more details later.

Having defined this basis of eigenfunctions for the X–H vibrations, we find it convenient to use the second quantization formalism. If a_n^+ and a_n stand for the creation and destruction operators of an excitation of the X–H vibration at the site n, we may then write $\mathscr{H}$ in the form:

$$\mathscr{H} = \sum_n \left\{\frac{P_n^2}{2M} + E^0(Q_n) + \delta E(Q_n)\, a_n^+ a_n\right\} + \\ + \sum_n V(Q_n)\,[a_n^+ a_{n+1} + a_{n+1}^+ a_n]\,, \qquad (2)$$

$$V(Q_n) = \langle \varphi_n^+ \mid \tilde{V}(q_n, q_{n+1}; Q_n) \mid \varphi_{n+1}^+ \rangle_q ;$$

(the vacuum state is defined by Ψ_0^V).

The term $V(Q_n)$ is the equivalent of the Davydov splitting, in the electronic spectra. In the carboxylic acid dimers, it leads to a 50 cm^{-1} difference between the C=O modes which are active in the infrared and Raman spectra respectively. It is expected that for the O–H modes in carboxylic acid dimers, and for X–H modes in crystals, it is even more important [9].

At this stage, we make the hypothesis that the vibrations are harmonic: the X–H vibrations with frequency ω and the X...Y vibrations with frequency Ω. Furthermore, we make the simplifying assumption that when, at the site n, the X–H vibrationnal state is in the first excited state ($\alpha = 1$), then the X...Y vibration is still harmonic, with frequency $\Omega' = \Omega$, but with a shift in the equilibrium position equal to $-\gamma \sqrt{\frac{2\hbar}{M\Omega}}$ (γ is dimensionless). As a more sophisticated assumption, we could take $\Omega' \neq \Omega$. This could be treated in the same way. But for simplicity, we shall take $\Omega' = \Omega$ here.

We have thus:

$$E^0(Q_n) = \tfrac{1}{2} M\Omega^2 Q_n^2$$

$$\delta E(Q_n) = \hbar\omega - \gamma\hbar\Omega \sqrt{\frac{2M\Omega}{\hbar}}\, Q_n\,.$$

We can then define the creation and destruction operators, b_n^+, b_n for the X...Y vibrations:

$$i\,P_n = -\sqrt{\frac{M\hbar\Omega}{2}}\,(b_n^+ - b_n),$$

$$Q_n = \sqrt{\frac{\hbar}{2M\Omega}}\,(b_n^+ + b_n)\,. \qquad (3)$$

$\mathscr{H}$ is then written, in this local representation:

$$\mathscr{H} = \hbar\Omega \sum_n (b_n^+ b_n + \tfrac{1}{2}) + \hbar\omega \sum_n a_n^+ a_n - \gamma\hbar\Omega \sum_n (b_n^+ + b_n)\, a_n^+ a_n + \\ + \sum_n V(Q_n)\,(a_n^+ a_{n+1} + a_{n+1}^+ a_n)\,. \qquad (4)$$

In view of the translationnal invariance of the whole crystal, it will prove useful to define the creation and destruction operators in the reciprocal space of the crystal. These are:

$$a_n = \frac{1}{\sqrt{N}} \sum_k e^{-ikn}\, a_k\,, \qquad a_n^+ = \frac{1}{\sqrt{N}} \sum_k e^{ikn}\, a_k^+$$

$$b_n = \frac{1}{\sqrt{N}} \sum_w e^{-iwn}\, b_w \qquad b_n^+ = \frac{1}{\sqrt{N}} \sum_w e^{iwn}\, b_w^+ \qquad (5)$$

which is equivalent with the B.V.K. boundary conditions to

$$a_k = \frac{1}{\sqrt{N}} \sum_n e^{ikn}\, a_n\,, \qquad a_k^+ = \frac{1}{\sqrt{N}} \sum_n e^{-ikn}\, a_n^+\,,$$

$$b_w = \frac{1}{\sqrt{N}} \sum_n e^{iwn}\, b_n\,, \qquad b_w^+ = \frac{1}{\sqrt{N}} \sum_n e^{-iwn}\, b_n^+\,. \qquad (6)$$

The unit translation operator T is

$$T = \exp\,[i\,(\sum_k k\, a_k^+ a_k + \sum_w w\, b_w^+ b_w)]\,.$$

Since $\mathscr{H}$ commutes with T, the eigenfunctions of $\mathscr{H}$ will be also eigenfunctions of T. We thus define the projection operator P^K as

$$P^K = \frac{1}{\sqrt{N}} \sum_{l=0}^{N-1} T^l\, e^{-ilK}\,.$$

From the relation $T P^K = e^{iK} P^K$, we see that P^K projects any function on its component which is an eigenfunction of T, with eigenvalue e^{iK}. We will then take the one exciton eigenfunctions of $\mathscr{H}$ in the form $P^K \sum\limits_k \frac{a_k^+}{\sqrt{N}} \mid \Psi_0\rangle$, where Ψ_0 is a function such that $a_k \mid \Psi_0\rangle = 0$ for all k.

Due to the equivalence of all sites, we could have chosen, as a basis, the function $P^K \sum\limits_k a_k^+/\sqrt{\mathrm{N}}\cdot e^{ink} \mid \Psi_0\rangle$. The final result would have been exactly the same: We have

$$\mathscr{H}\, P^K \sum_k \frac{a_k^+}{\sqrt{N}} \mid \Psi_0\rangle = P^K \sum_k \frac{a_k^+}{\sqrt{N}}\, \mathscr{H}_K \mid \Psi_0\rangle\,, \tag{7}$$

where

$$\begin{aligned}\mathscr{H}_K = \hbar\Omega \sum_w (b_w^+ b_w + \tfrac{1}{2}) + \hbar\,\omega - \frac{\gamma\,\hbar\,\Omega}{\sqrt{N}} \sum_w b_{-w}^+ + b_w + {}\\ + \{V(Q_0) \exp\,[i \sum_w w\, b_w^+ b_w]\, e^{-iK} + \exp\,[-i \sum_w w\, b_w^+ b_w]\, e^{iK}\, V(Q_0)\}\,.\end{aligned} \tag{8}$$

The problem of finding the eigenvalues and eigenfunctions of $\mathscr{H}$ is then reduced to finding the eigenvalues and eigenfunctions of $\mathscr{H}_K$, which are $\Psi_{0,K}^i$ (we specify now Ψ_0 by adding the indices i and K; the index i labels the i^{th} eigenfunction of $\mathscr{H}_K$). The hamiltonian $\mathscr{H}_K$ is similar to Merrifield's [5]. The problem which arises in solving the problem $\mathscr{H}_K \mid \Psi_{0,K}^i\rangle = E_K^i \mid \Psi_{0,K}^i\rangle$ originates from the non-commut ability of the terms in $V(Q_0)$ and the term in γ. It can be solved exactly in the weak-coupling case $[V(Q_0) = 0]$ and in the strong coupling case $(\gamma = 0)$.

Infrared Spectra

In this section, we shall briefly study the kind of I.R. spectra (in the 3000 cm^{-1} region) to be expected for such a model. The detailed spectra will be published later. We shall be interested here, in selection rules and the integral quantities of the spectra, which are: intensity and the different moments of the spectrum. The effect of the coupling of the X–H vibrations with the X…Y vibrations will be most marked on the linewidth.

Selection Rule

The operator for a transition in the X–H vibrations is an electric dipole-type operator $\vec{\mu}\cdot\vec{\mu}$ is symmetric for the whole crystal, so that $T\vec{\mu} = \vec{\mu}T$ (it is assumed that the wevelength λ of the incident light is very long, compared to the unit translation vector. (This assumption is made for convenience, but does not at all alter the final result.) Since the ground state for the X–H vibrations (or vacuum) is the totally symmetrical state Ψ_0^V (we shall not consider here "hot bands", but the adaptation of the theory to them is straightforward), the only possible transition will be to a totally symmetrical one exciton state $(K = 0)$. If we had taken into account the fact that the wavelength of the incident light is finite, then we would have had to consider the transitions to the state $K = K_0$, where K_0 is the wavenumber vector of the light, and is very small.

From now on we shall be interested only in the totally symmetrical states with $K = 0$. For convenience we shall write $\Psi_{0,0}^i$ as Ψ^i, and E_0^i as E^i:

$$\mathscr{H}_0 \,|\, \Psi^i\rangle = E^i \,|\, \Psi^i\rangle \,. \tag{9}$$

Transition Probability

Within a multiplicative constant, the transition probability from the ground state Ψ_0^V to the state Ψ^i is D^i:

$$D^i = |\langle\, \Psi_0^V \,|\, \vec{\mu}\, P^0 \sum_k \frac{a_k^+}{\sqrt{N}} \,|\, \Psi^i\rangle_{q,Q}\,|^2 \,. \tag{10}$$

From the closed-form (8) of $\mathscr{H}_0$, we can write:

$$\Psi^i = \varphi_g(q)\,\alpha^i\,(Q)\,,$$

We have seen that $\Psi_0^V = \varphi_g(q)\,\alpha_0^V(Q)$.
Thus

$$D^i = |\,\langle\alpha_0^V \,|\, \langle\varphi_g \,|\, \vec{\mu} P^0 \sum_k \frac{a_k^+}{\sqrt{N}} \,|\, \varphi_g\rangle_q \,|\, \alpha^i\rangle_Q\,|^2\,.$$

Using the relation $P^0\,\vec{\mu} = \vec{\mu}\,P^0$, we can write:

$$D^i = |\,\langle\alpha_0^V \,|\, \vec{\mu}_0 \,|\, \alpha^i\rangle_Q\,|^2$$

where

$$\vec{\mu}_0(Q) = \langle\varphi_g \,|\, \vec{\mu} \sum_k \frac{a_k^+}{\sqrt{N}} \,|\, \varphi_g\rangle_q \,.$$

Due to the translational invariance of the whole crystal, we could also have written:

$$D^i = |\,\langle\alpha_0^V \,|\, \vec{\mu}_1 \exp\,[i \sum_w w b_w^+ b_w] \,|\, \alpha^i\rangle_Q\,|^2$$

where

$$\vec{\mu}_1(Q) = \langle\varphi_g \,|\, \vec{\mu} \sum_k e^{ik} \frac{a_k^+}{\sqrt{N}} \,|\, \varphi_g\rangle_q \,.$$

We can thus write D^i, in the symmetric form:

$$D^i = \sum_{n=0}^{N-1} \langle\alpha_0^V \,|\, \vec{\mu}_n \exp\,[in \sum_w w\, b_w^+ b_w] \,|\, \alpha^i\rangle_Q\,|^2$$

where

$$\vec{\mu}_n(Q) = \langle\varphi_g \,|\, \vec{\mu} \sum_k e^{ink} \frac{a_k^+}{\sqrt{N}} \,|\, \varphi_g\rangle_q \,. \tag{11}$$

The total intensity of the spectrum is $I = \sum\limits_i D^i$.

We have thus:

$$I = \sum_{n=0}^{N-1} \langle\alpha_0^V \,|\, \vec{\mu}_n \cdot \vec{\mu}_n^+ \,|\, \alpha_0^V\rangle \tag{12}$$

with $\vec{\mu}_n^+$ being the adjoint operator of $\vec{\mu}_n$.

Successive Moments

The j^{th} moment of the transition is defined by

$$M_j = \frac{1}{I} \sum_i D^i \left(E^i - \frac{\hbar\,\Omega}{2}\right)^j .$$

The first moment ($j = 1$) is directly connected to the center of gravity of the line $\overline{E}$, and the square root of the second moment represents a measure of the absolute value of the linewidth $\varDelta E$. It is thus interesting to find general expressions for them.

From the definition of M_j, we write:

$$M_j = \frac{1}{I} \sum_i \sum_{n=0}^{N-1} |\langle \alpha_0^V \,|\, \vec{\mu}_n \exp\left[i\, n \sum_w w\, b_w^+\, b_w\right] (\mathscr{H}_0)^j \,|\, \alpha^i \rangle_Q \cdot$$
$$\cdot \langle \alpha^i \,|\, \exp\left(-i\, n \sum_w w\, b_w^+\, b_w\right) \vec{\mu}_n^+ \,|\, \alpha_0^V \rangle_Q \qquad (13)$$
$$M_j = \frac{1}{I} \sum_{n=0}^{N-1} \langle \alpha_0^V \,|\, \vec{\mu}_n \exp\left(i\, n \sum_w w\, b_w^+\, b_w\right) (\mathscr{H}_0)^j \exp\left(-i\, n \sum_w w\, b_w^+\, b_w\right) \vec{\mu}_n^+ \,|\, \alpha_0^V \rangle_Q \,.$$

This formula is quite general. We can as a particular example, suppose that the dipolar moment $\vec{\mu}_p$ is equal to $\vec{\mu}$ for all p (independant of the X...Y coordinates). We have thus:

$$I = N\mu^2$$
$$M_j = \langle \alpha_0^V \,|\, (\mathscr{H}_0)^j \,|\, \alpha_0^V \rangle_Q \,.$$

If we suppose, for instance, that $V(Q^0) = V_0$, we obtain then:

$$\overline{E} = M_1 = \hbar\,\omega + V_0$$

and

$$|\varDelta E| = |\gamma|\,\hbar\,\Omega\,.$$

Conclusion

We have established the general Eqs. (7) and (8) leading to the energy levels as well as the eigenfunctions describing the states of H-bonded crystals, where the X–H stretching vibrations are coupled to the X...Y stretching vibrations, of lower energy. General equations have been given (11), (12), (13) for measurable quantities found in the 3000 cm^{-1} region of the infrared spectra of these crystals. It is believed that these equations may serve as a support for explaining the details of the experimentally known I.R. spectra of H-bonded solids, such as imidazol. This work is being completed and will be published later.

References

1. Bellock, A. M., C. Perchard, A. Novak, and M. L. Josien: J. Chim. physique **62**, 1334 (1965).
2. Bratoz, S., and D. Hadzi: J. chem. Physics **27**, 991 (1957).
3. Hadzi, D. (Editor): Hydrogen bonding. Proceedings of the Ljubljana Symposium. London: Pergamon Press 1960.
4. Hexter, R. M.: J. chem. Physics **33**, 1833 (1960).
5. Merrifield, R. E.: J. chem. Physics **40**, 445 (1964).
6. Pimentel, G. C., and A. L. McClellan: The hydrogen bond. San Francisco: W. H. Freeman & Co. 1960.
7. Stepanov, B. I.: Nature **157**, 808 (1946).
8. Will, G.: Nature **198**, 575 (1963).
9. Witkowski, A.: J. chem. Physics **47**, in press (1967).

Dr. Y. Maréchal
Centre d'études nucléaires
Laboratoire de chimie organique physique
Chemin des Martyrs
Grenoble, B. P. 269, France