Quantitative IR Spectroscopy of H-Bonds: Intensities of ν_s Bands

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In this article we stress the interest of performing precise measurements concerning the IR spectra of H-bonds, as this has been initiated under the impulsion of Professor Hadži. We concentrate on the few measurements which have been made of the intensities of the ν_s bands ($X—\vec{H}\cdots Y$), which are highly characteristic of H-bonds. These intensities have shown some intriguing features: upon deuteration of the H-bond they often decrease far more than expected. This is particularly marked for the H-bonded cyclic dimers of carboxylic acids. It can be explained by electrical anharmonicity but can also be a manifestation of some cooperative effect between the two H-bonds of these dimers.

Despite the fundamental importance of H-bonds, which is the key mechanism implied in all aqueous reactions and particularly in biological reactions, very few quantitive data concerning its properties have been collected until now. A systematic study of this bond, considering it as a phenomenon and not only as an intermolecular bond between two definite molecules, is of quite recent date, and it is one of the merits of Professor Hadži to have presented, in several well-known papers with other coleagues[1,2], the first realistic discussion revealing the mechanisms which are at the origin of most of the spectacular features which H-bonds display in their IR spectra.

These features, which have been for a long time used only to detect H-bonds, are found in the intense ν_s bands ($X—\vec{H}\ldots Y$) of H-bonds, which are broad ($\simeq 300$—500 cm^{-1} or more), shifted to frequencies lower than that of corresponding $X—\vec{H}$ vibrations (when no H-bond is formed) and have a well defined structure. The proposition of Hadži et al. is that these features are due to the simultaneous presence of two important and competing anharmonic couplings of the ν_s vibration, namely couplings with resonant combinations of modes (Fermi resonances) and with low frequency modes. This has been the starting point of several ways of research to determine the relative effects of these two couplings[1-5], which has led to numerous discussions and controversies. As a result, the IR spectroscopy of H-bonds has so gained in precision that it has become quantitative, and it is now possible to measure separately in the ν_s bands the respective magnitudes of these two anharmonic

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* Festschrift of Professor Dušan Hadži.

couplings and to eliminate the parasite effects due to resonance interactions. These interactions are indeed an artefact of IR spectroscopy, because they appear only in the excited states of ν_s, which are thermally inaccessible and have consequently no influence on the properties of H-bonds at room temperature which are the interesting properties to be studied. This development of IR spectroscopy, which Professor Hadži and colleagues have initiated, makes this technique appear nowadays as the most powerful method of studying the dynamical properties of H-bonds and in the next few years it might well be at the origin of new findings in the sphere of H-bonds.

In this note, we shall illustrate this trend of IR spectroscopy as being a highly valuable source of information on the nature of H-bonds by relating some measurements concerning, not the shapes of ν_s bands, but their intensities (or more exactly their transition probabilities $\int \log (I_o/I)_\omega \cdot \dfrac{d\omega}{\omega}$), which are also highly characteristic of H-bonds, because they are typically more than one order of magnitude greater than the corresponding quantities measured for X—H group with no H-bonds. They are nevertheless delicate quantities to measure and may lead to non reproducible results if great care is not fully applied in the control of the physical conditions of the experiments. It explains why only a few measurements only of these interesting quantities have been made[6,7], and why one should perform this kind of measurements only on well defined systems, such as the H-bonded cyclic dimers of carboxylic acids in the vapour phase. These are well defined simple systems of known geometry, which are not polluted by the presence of other H-bonds (which is often the case with H-bonded systems) and can be in a first approximation, regarded as isolated systems. The simultaneous presence of non-bonded monomers can be seen as an advantage, having the possibility of directly comparing the probabilities of O—H...O ν_s bands to those of corresponding O—H groups. An inconvenience of the simultaneous presence of H-bonded dimers and non H-bonded monomers is that their respective concentration n_D and n_M is not known. The value of $n_M + n_D$ is accessible by measuring the pressure of the vapour. We cannot hope to use the constant of equilibrium $K = n_D/n_M^2$ between monomers and dimers in order to deduce the value of n_M and n_D because this nonlinear quantity is measurable with poor precision leading to too great uncertainties. However, by varying the pressure and the temperature of the of O—H stretching bands of monomers and of ν_s bands of dimers, one can deduce with a satisfactory precision the values P_{O-H} and $P\nu_s$ of these transition probabilities for one O—H group or one H-bond[8,9]. The ratio of these quantities has been found to vary between 20 and 30 when the substituant R of the carboxylic acid R—COOH has an increasing mass.

A more interesting comparison comes from the value of the ratios $P\nu_s^H/P\nu_s^D$ concerning the ν_s bands of one O—H...O bond and one O—D...O bond, which has been found equal to 2 for all studied carboxylic acids. The normally expected value for this ratio is $\sqrt{2}$, which is that of an harmonic oscillator and is effectively found for the ratio P_{O-H}/P_{O-D} of monomers. Attempts to explain the value of this ratio by supposing that the ν_s mode is a strongly anharmonic vibration (or is strongly anharmonically coupled to other modes) has proved unsuccessfull. Even such a strong anharmonic character as that of a double well potential leads to values much closer to $\sqrt{2}$ than to 2.

One can explain this value with the supposition that the dipole moment of the H-bond is not a pure linear function of the stretch of the O—H group in the O—H ... O bond. This is usually referred to as electrical anharmonicity. More precisely, if q is the O—H distance in the O—H...O bond (it is the coordinate representing, the ν_s vibration) and Q the O...O distance of the same bond, a development of the dipole moment μ of the form $\mu = \mu_o + q \mu_1 (Q) + \ldots$ can lead to a value close to 2 for the ratio $P\nu_s^H/P\nu_s^D$. With this form, electrical anharmonicity originates with the Q dependence of μ_1. Such a Q dependence does not seem arbitrary when one realizes that H-bonds having shorter O...O equilibrium distances have more intense ν_s bands (at least for weak and intermediate strength H-bonds). It is then reasonable to suppose that this is also true for any value of the O...O distance departing from its equilibrium value. With this form we may calculate the transition probability of the ν_s band which is equal to:

$$\left\langle \frac{\hbar}{2m\omega (Q)} \mu_1^2 (Q) \right\rangle_Q \simeq \frac{\hbar \langle \mu_1^2 (Q) \rangle_Q}{2m \langle \omega (Q) \rangle_Q}$$

where $\langle \ \rangle_Q$ means thermal average over the various levels of the Q mode. This quantity $\langle \mu_1^2 (Q) \rangle_Q$ can be written as

$$\mu_1^2 (\langle Q \rangle) + \langle (Q - \langle Q \rangle)^2 \rangle \left[\left(\frac{d \mu_1^2}{d Q^2} \right) + \frac{1}{2} \frac{d^2 \mu_1^2}{d Q^2} + \ldots \right]$$

The latter term is the same for a D-bond and for a H-bond, because the dipolar moment term μ_1 is mass independent and the mean square amplitude of vibration of the low-frequency ($\simeq 150$ cm^{-1}) vibration in Q, $\langle (Q - \langle Q \rangle)^2 \rangle$, is hardly affected by deuteration. The first term $\mu_1^2 (\langle Q \rangle)$ may however vary with deuteration because the equilibrium distances $\langle Q \rangle$ are known to be longer in D-bonds than in H-bonds. This is known as the Ubbelohde effect and is a consequence of the Q dependence of the frequency ω of the ν_s mode.

Electrical anharmonicity may, therefore, explain the anomalous value of the ratio $P^{\nu_s H}/P^{\nu_s D}$, which has also been found for the H-bonded cyclic dimers of dicarboxylic acids in crystals, at all temperatures ranging from 4 K to room temperature. An intriguing point is that in the other few H-bonded systems having no such cyclic dimers, where this kind of measurement has been performed, no such anomalous value for this ratio has been found: in acetic acid crystals or imidazole crystals where H-bonds form zig-zag chains, this ratio falls in the vicinity of $\sqrt{2}$. One can therefore naturally ask whether this anomalous value ($\simeq 2$) measured in the case of dimers is not a consequence of the peculiar geometry of dimers or whether it is not due to some cooperative effect between the two interacting H-bonds of a dimer. Until such a time as a greater number of experimental data will be collected, no definite answer can be given to this question. Furthermore, as transition probabilities are closely related to the dipole moments and have consequently much to do with the electronic structure of H-bonds, we may ask how can we integrate these results into a more synthetic description of the electronic structure of H-bonds. Such a description has been treated mostly by quantum chemistry methods, which are not particularly suited for the treatment of the electronic structure of H-bonds, because they imply using excited electronic states, which is badly adaptable to the treatment of a low energy bond. Although these methods

have definitely established that the energy of weak and intermediate strength
H-bonds is mainly electrostatic in nature, it is not astonishing that they often
fail in describing other properties of H-bonds, and particularly their dynamical
properties which have not yet received any satisfactory description. This may
nevertheless be due to the lack of precise experimental data concerning
H-bonds. We have emphasized in this paper that IR spectroscopy is a most
interesting technique for obtaining such data. We also feel that it can give a
far greater number of results and that it has not yet been fully exploited, and
that it has been infrequently used as a valuable source of information on the
intimate structure of H-bonds. It stresses the importance of Professor Hadži's
work which opened up research in this direction.

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IZVLEČEK

Kvantitativna infrardeča spektroskopija H-vezi: intenzitete ν_s trakov

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Članek opisuje, kako s pomočjo infrardeče spektroskopije dobimo z merjenjem
intenzitete ν_s traku nov podatek o naravi H-vezi. Količina, ki ima fizikalni pomen

je verjetnost za prehod $P_{X-H\ldots Y}$ ($\int \log I_0/I \dfrac{d\omega}{\omega}$) vodika v vezi in P_{X-H} v primeru,

ko vezi ni. Tako se je pokazalo, da se razmjerje obeh verjetnosti za prehod pri različno substituiranih karboksilnih kislinah (R—COOH) v plinasti fazi poveča od 20
do 30, pri tem ko se zvečuje masa substituente R.

Več zanimivih primerjav izhaja iz razmjerja $P\,\nu_s{}^H/P\,\nu_s{}^D$, ki ima vrednost 2 in ne

$\sqrt{2}$, kot je pričakovana vrednost za harmonski oscilator. Tudi močna anharmoničnost potenciala, celo v primeru dvojnega minimuma in s tem sklopitev ν_s z drugimi
nihanji, ne more razložiti nesorazmerno velikega razmjerja.

Električna anharmoničnost, ki izvira iz odvisnosti dipolnega momenta ν_s nihanja od razdalje O...O (koordinata simetričnega valenčnega nihanja Q vezi O...O)
razloži, vsaj v primeru cikličnih dikarboksilnih kislin, nesorazmerno visoko vrednost tega razmjerja.

Presenetljivo je, da merjenja intenzitete trakov ν_s pri kristalih ocetne kisline

in kristalu imidazola, pokažejo običajne vrednosti razmjerja, torej vrednost blizu $\sqrt{2}$.

Tako pridemo do vprašanja, če specifična ciklična struktura dimera ali kakšen
drug vpliv, ki se lahko pojavlja zaradi dveh medseboj delujočih H-vezi v dimeru,
odloča o velikosti razmjerja $P\,\nu_s{}^H/P\,\nu_s{}^D$. Na dokončen odgovor bo treba počakati,
dokler ne bo na razpolago več izmerjenih zgledov.

Ker so verjetnosti za prehod povezane z dipolnimi momenti, ti pa so v tesni
zvezi z elektronsko strukturo H-vezi, si lahko iz tovrstnih meritev obetamo bolj
strnjen popis elektronske strukture H-vezi.