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Mario Ageno

Resonance Stabilization and the Collective Model of the Hydrogen Bond

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Fisica degli stati condensati. — *Resonance Stabilization and the Collective Model of the Hydrogen Bond.* Nota (*) del Corrisp. MARIO AGENO.

RIASSUNTO. — Si fa vedere, in risposta ad un recente lavoro di E. G. Bass, che il modello collettivo del legame a idrogeno non è basato sulla idea che ogni protone di un anello di ponti a idrogeno si muova in un potenziale a due buche e che la conseguente risonanza porti ad una stabilizzazione del legame. Questo effetto, quando esiste, è assai piccolo. Il modello collettivo si basa invece sul fatto che lungo ogni ponte a idrogeno dell'anello cariche positive e negative provenienti da due molecole diverse possono accostarsi senza provocare accumulo di carica del segno opposto sugli atomi elettro–negativi che costituiscono le «spalle» dei ponti. Così, non vi è limitazione elettrostatica all'energia di legame.

In a recent paper [1] by G. E. Bass one reads that according to me [2] " resonance stabilization of cyclic groups of hydrogen-bonded water molecules might play an important role in dictating the structure of liquid water ". Accordingly Bass demonstrates that the effect is quite small and that with reasonable values for the double potential well in which each proton moves can be neglected. Bass's calculations are obviously correct, the same result having already been obtained by Coulson about twelve years ago [3].

However, Bass's reference to my paper is erroneous because I never spoke of resonance stabilization of the cyclic groups when proposing the collective model of the hydrogen bond. Perhaps, it is worth while to spend a few words in order to avoid some kind of misunderstanding of my previous paper. This is the aim of the present Note.

My calculation is almost a copy of a classical one and closely follows Heitler and London demonstration of the existence of a bond between two hydrogen atoms. I take four water molecules whose centers of mass have definite positions in space (the arrangements of fig. 1 for instance) and I write down the *exact* Hamiltonian of the system. Then I drop all the terms of the Hamiltonian which correspond to interactions of any kind between two or more molecules. The unperturbed Hamiltonian thus obtained corresponds to a known value of the energy (four times the total energy of a single molecule). Such Hamiltonian represents four *free* molecules but does not correspond to any physical situation. This procedure is only a mathematical device I use to demonstrate that a physical state exists, in which the four molecules are bound together. In fact, the unperturbed Hamiltonian does not eliminate any ambiguity with regard to the location of the various particles to the different molecules and the elimination of the terms which represent interactions between molecules can be performed in more than one way. This degeneracy

(*) Presentata nella seduta del 15 novembre 1969.

is the starting point of a process of subsequent approximations to the exact solution of the problem , arrested in my paper at the first stage, owing to the fact that this is sufficient to demonstrate the existence of a bound state of the system.

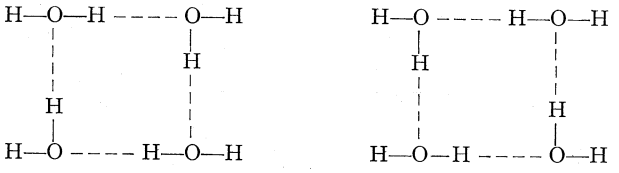

Fig. 1.

Thus, in spite of the formal similarity between Bass's expressions and mine, their meaning is completely different. A further proof is offered by the fact that if in the ground state the proton of a bridge moves in a single potential well (and it is actually possible) the meaning of Bass's calculation becomes undefined whereas mine is not affected at all.

Obviously, no hint is given in my first paper on how to evaluate the order of magnitude of the binding energy and this is not an easy task. However it is easy to show [4] that a closed ring of hydrogen-bridges possesses a much higher binding-energy per bridge than a single isolated hydrogen bridge. Let us consider for instance two water molecules as in fig. 2, at a distance at which they do not practically interact. If the distance is gradually reduced at a given moment the proton of the molecule on the left being adjacent to the lone pair electrons of the molecule on the right, increases its distance from the remaining parts of the molecule itself. The same occurs to the lone pair electrons and both molecules are thus polarized. These deformations however develop electric charges of opposite signs on the respective oxygen atoms, and this fact prevents any further relative displacement of the charges. The electrostatic interaction thus limits the binding energy.

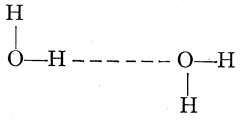

Fig. 2.

If, however, we have at the beginning four non interacting molecules at the corners of a square, as in fig. 3, and the side of the square is gradually reduced, the relative displacements of the protons and the lone pair electrons along each side do not generate any charge of opposite sign on the oxygen atoms, because each molecule removes a positive charge along one side and the corresponding negative charge along the other side of the square.

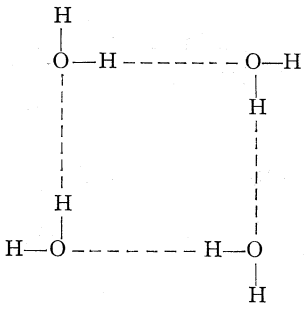

Fig. 3.

Thus there is now no electrostatic limitation to the binding energy. This is the physical reason why a ring of hydrogen-bridges is much more stable than a single one.

BIBLIOGRAFIA.

[1] G. E. BASS, « Proc. Nat. Acad. Sci. U.S. », *62*, 345 (1969).
[2] M. AGENO, « Proc. Nat. Acad. Sci. U.S. », *57*, 567 (1967).
[3] C. A. COULSON, « Research », *10*, 149 (1957).
[4] M. AGENO, *Problemi attuali di scienza e di cultura*, n. 102, « Acc. Naz. Lincei », 1967, p. 27.