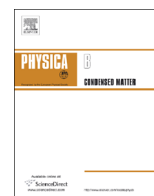




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# Toward accurate prediction of potential energy surfaces and the spectral density of hydrogen bonded systems



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## ABSTRACT

Despite the considerable progress made in quantum theory and computational methods, detailed descriptions of the potential energy surfaces of hydrogen-bonded systems have not yet been achieved. In addition, the hydrogen bond (H-bond) itself is still so poorly understood at the fundamental level that it remains unclear exactly what geometry constitutes a “real” H-bond. Therefore, in order to investigate features essential for hydrogen bonded complexes, a simple, efficient, and general method for calculating matrix elements of vibrational operators capable of describing the stretching modes and the H-bond bridges of hydrogen-bonded systems is proposed. The derived matrix elements are simple and computationally easy to evaluate, which makes the method suitable for vibrational studies of multiple-well potentials. The method is illustrated by obtaining potential energy surfaces for a number of two-dimensional systems with repulsive potentials chosen to be in Gaussian form for the stretching mode and of the Morse-type for the H-bond bridge dynamics. The forms of potential energy surfaces of weak and strong hydrogen bonds are analyzed by varying the asymmetry of the Gaussian potential. Moreover, the choice and applicability of the selected potential for the stretching mode and comparison with other potentials used in the area of hydrogen bond research are discussed.

The approach for the determination of spectral density has been constructed in the framework of the linear response theory for which spectral density is obtained by Fourier transform of the autocorrelation function of the dipole moment operator of the fast mode. The approach involves anharmonic coupling between the high frequency stretching vibration (double well potential) and low-frequency donor-acceptor stretching mode (Morse potential) as well as the electrical anharmonicity of the dipole moment operator of the fast mode. A direct relaxation mechanism is incorporated through a time decaying exponential according to Rösch and Ratner theory.

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## 1. Introduction

Hydrogen bonding is undoubtedly one of the chemical world's most interesting phenomena due to the crucial role it plays in the structure and interactions of biomolecules. Systems with hydrogen bonds (H-bonds) are prevalent in chemistry and biology. The structure of DNA is dictated by H-bonding between the nucleic acid base pairs and, more generally, protein structures may be stabilized by H-bonding interactions. H-bonds have also been found in the active sites of several enzymes and, therefore, may play an important role in catalysis [1–9]. Nowadays scientists are convinced that the growing interest in H-bonds, especially in biological systems, should be usefully accompanied by the development of theoretical tools in the field of vibrational spectroscopy.

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With such tools, experimentalists should be able to compare experimental and theoretical data in an easy-to-use way. However, the problem with the quantitative theoretical treatment of the spectral properties of hydrogen-bonded systems still constitutes a real challenge in the area of hydrogen bond research. There are still many problems to solve in this area because even the most advanced theories, when applied to the description of the IR spectra of hydrogen bonded systems, are unable to reliably explain a number of effects such as those observed in the case of strong hydrogen bonding [10–14].

Generally, the influence of mechanical anharmonicity on a mode's intensity cannot be neglected [15] and the strong intensity of overtones and combinations are connected with the dipole moment anharmonicity. The relationship between second-order hyperpolarizabilities and anharmonic vibrations was the subject of theoretical studies in which the vibrational contribution connected with mechanical and electrical anharmonicities turned out to be even more significant than the electronic contribution [16–22]. In an important paper, Melikova et al. [23] showed that

the simple anharmonic dipole moment model predicts characteristic features in the spectra of H-bonded complexes with different strengths. Using their model, they obtained a correlation between the angular force constants and the first derivative of the induced dipole moment of the complex. In a further study, Melikova et al. [24] applied a model of an anharmonic dipole moment function to the analysis of the hydrogen bridge  $\overline{X}-H\cdots\overline{Y}$  vibrations. This model allows the prediction of the features of the hydrogen bond formation characterized by the intensities of  $\nu(X-\overline{H}\cdots Y)$  and  $\nu(\overline{X}-H\cdots\overline{Y})$  transitions. Recently, Stare et al. [25,26] have proposed an approach which makes possible the solution of vibrational problems in two or more dimensions in terms of internal coordinates. The method tested on different molecular systems, containing strong hydrogen bonds, gives good agreement between calculated and observed vibrational frequencies. More recently, Frost et al. [27] predicted that intensity in combination bands can arise from electrical anharmonicity, mechanical anharmonicity, or large amplitude motions. In a moderate-strength hydrogen-bonded complex, mechanical anharmonicity should not be particularly great, and electrical anharmonicity seems a more likely source of combination band intensity. Later, Fillaux [28] has shown that the complexity of the infrared spectrum is due to mainly electrical anharmonicity. Sandorfy and co-workers [29] have shown that neither mechanical nor electrical anharmonicity can explain the most important intensity changes that occur upon hydrogen bond formation. As we can see, the different approaches proposed in the literature lead to opposite conclusions, with some claiming that the electrical anharmonicity has a very substantial effect on the intensity of the hydrogen-bonded stretching vibration, while others predict that this effect is minimal. In the present paper we take into account the electrical vibrational anharmonicity on the IR intensities of hydrogen-bonded complexes since we believe that the electrical anharmonicity is quite a strong effect that cannot be discarded in the treatment of the infrared lineshape of the stretching mode of a H-bonded species, especially for strongly H-bonded systems in polar solvents [30].

It has been recognized, both theoretically and experimentally, that the shape of the  $\nu(X-\overline{H}\cdots Y)$  stretching vibration band is mainly generated by the anharmonic coupling between the high  $X-\overline{H}\cdots Y$  and the low  $\overline{X}-H\cdots\overline{Y}$  vibrational modes of the hydrogen bond  $X-H\cdots Y$ . However, at least for medium-strong [31] and strong [32] hydrogen bonds, a few additional mechanisms should be taken into account: the mechanical anharmonicity of the fast and slow modes, the Davydov effect and Fermi resonances. Whereas the Davydov effect [33–35], Fermi resonances [36–41] and relaxation theory [42–46] have been extensively studied, it is not so for the intrinsic anharmonicity of the fast mode potential [47], concerning which there are only a few papers working in different directions. One instance that should be cited is the 1–D approach of Robertson and Lawrence [48] using a symmetrical double Morse function. In an older important paper, Singh and Wood [49] presented a quantum 2–D treatment of strong symmetric H-bonds, which incorporated a double minimum in the potential energy function and an anharmonic coupling between the symmetric and anti-symmetric stretching motions, as well as an electrical anharmonicity for the dipole moment. However, their approach did not take into account the possibility of dissociation in the symmetric coordinate. More recently, Romanowski and Sobczyk [50] have proposed for strong symmetric H-bonds a stochastic model taking into consideration the double minimum potential function of the proton motion in the form  $V(r) = -Ar^2 + Br^4$ . However, the cost to be paid for that was the abandonment of a quantum treatment for the symmetric stretching motion. The stochastic model considered by these authors is very similar to that of Hadzi and Bratos [31]. They considered the quantum mechanical motion of the proton within a

symmetric double minimum potential and supposed this potential to be modulated by the Gaussian-like statistical distribution of the symmetric stretching amplitude, i.e. of the H-bond bridge. In this model, the slow mode is treated as a classical stochastic oscillator, which leads to broadening of the lineshapes, contrary to the predictions of pure quantum theory [44]. Later, Abramczyk [51,52] incorporated tunnelling involving a symmetric double well potential into the model of Boulil et al. [44]. In the Abramczyk model, the strong anharmonic coupling between the slow and fast modes and the symmetric double well potential are assumed to be completely decoupled, an assumption which is questionable. Despite spectacular achievements in the quantitative description of the intensity distributions of the  $\nu(X-\overline{H}\cdots Y)$  bands, which the above theories attribute to the proton stretching vibrations in the  $X-H\cdots Y$  bridges, the understanding of anharmonicity effects of the fast mode of the hydrogen bond is far from complete [53–61].

From the above account, it is apparent that the theoretical works available to date on hydrogen-bonded complexes make it possible to propose a unified model by describing the anharmonic dynamics of all of the different modes. It can be hoped that such a consideration will enable the main spectral manifestations of hydrogen-bonded complexes to be described. In this paper, we revisit the least understood mechanism relating to H-bonding, i.e. that involving the anharmonicity of the stretching mode. For this aim, we propose a H-bonding model for which the anharmonic coupling between the high frequency and the low frequency modes is treated by the strong anharmonic coupling theory. Intrinsic anharmonicity of the fast mode  $X-\overline{H}\cdots Y$  is described by a double well potential constructed from a harmonic oscillator perturbed by a repulsive potential of Gaussian form, whereas the slow mode  $\overline{X}-H\cdots\overline{Y}$  is considered to be of Morse-type. The model is treated within the adiabatic approximation [34] and direct relaxation mechanism is incorporated through a time decaying exponential according to Rösch and Ratner theory [42]. Attention is focused on the calculation of the matrix elements and potential energy surface of this vibrational operator, applicable to the description of the stretching modes of a hydrogen bond. Two questions will be addressed: (1) How well can a double well potential constructed from an harmonic oscillator perturbed by a repulsive potential of Gaussian form describe the stretching modes of H-bonds? (2) Can this type of potential be useful to give a general model that can describe the evolution of H-bond from weak to strong ones? These two questions are addressed in the following sections where, as examples, we consider systems with strong symmetrical, and weak asymmetrical to symmetrical hydrogen bonds. In the next section we briefly review the H-bond Hamiltonian, and gather all the necessary tools, e.g., the determination of the eigenvalues and eigenvectors of the Hamiltonian, which allow us to introduce the calculation of the matrix elements of the Gaussian and Morse potentials. We introduce the concept of the potential energy surface of the hydrogen bond treated within the present approach and we discuss details of their implementation using different asymmetries of the double well potential. In Section 3 we discuss the choice and the utility of the asymmetric double well potential used in the present approach. In Section 4, we present a detailed discussion of the theoretical results. Finally, Section 5 closes the paper with some concluding remarks.

## 2. Model

### 2.1. Spectral density of H-bond within linear response theory

We use the standard treatment within linear response theory [62,63], which allows one to link the infrared spectral density (SD)

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