



Rao Prize article

# Vibrational transitions in hydrogen bonded bimolecular complexes – A local mode perturbation theory approach to transition frequencies and intensities



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## ARTICLE INFO

## Article history:

Received 26 October 2016

In revised form 11 January 2017

Accepted 8 February 2017

Available online 14 February 2017

## Keywords:

Vibrational spectroscopy

Explicitly correlated coupled cluster

Frequency redshift

Intensity enhancement

Hydrogen bonds

## ABSTRACT

The local mode perturbation theory (LMPT) model was developed to improve the description of hydrogen bonded XH-stretching transitions, where X is typically O or N. We present a modified version of the LMPT model to extend its application from hydrated bimolecular complexes to hydrogen bonded bimolecular complexes with donors such as alcohols, amines and acids. We have applied the modified model to a series of complexes of different hydrogen bond type and complex energy. We found that the differences between local mode (LM) and LMPT calculated fundamental XH-stretching transition wavenumbers and oscillator strengths were correlated with the strength of the hydrogen bond. Overall, we have found that the LMPT model in most cases predicts transition wavenumbers within  $20\text{ cm}^{-1}$  of the experimental values.

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## 1. Introduction

Hydrogen bonding is widely studied due to its importance in many chemical and biological systems. Hydrogen bonded complexes have in particular received much interest in recent years due to their impact on radiative transfer processes and their role in initial nucleation processes [1–6]. An account and revised definition of the hydrogen bond was formulated by an IUPAC appointed committee in 2011, where the hydrogen bond was redefined as “...an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X-H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation” [7,8]. A list of criteria and characteristics of the hydrogen bond follows this definition. One of these characteristics is that upon hydrogen bond formation, the hydrogen bonded XH-stretching (XH<sub>b</sub>-stretching) transition redshifts and its intensity increases. The size of the redshift and intensity enhancement correlate with the hydrogen bond strength, and for this reason, infrared spectroscopy is commonly used to investigate hydrogen bonded systems. Recently, IR spectroscopy has been utilized in an effort to determine equilibrium constants of complex formation for a series of bimolecular complexes [9–20]. In these studies, the pressure of the two monomers,

A and B, is measured experimentally, but the pressure of the complex, AB, is often too low to be directly determined. Instead, IR spectroscopy is applied to obtain the complex pressure. If the measured integrated absorbance of the XH<sub>b</sub>-stretching transition band,  $\int A(\tilde{\nu}) d\tilde{\nu}$ , is combined with a calculated oscillator strength of that transition,  $f_{\text{calc}}$ , the complex pressure,  $p_{\text{AB}}$ , can be determined from [14,21]:

$$p_{\text{AB}} = 2.6935 \times 10^{-9} \left( \text{K}^{-1} \text{Torr m cm} \right) \frac{T \int A(\tilde{\nu}) d\tilde{\nu}}{l \times f_{\text{calc}}}, \quad (1)$$

where  $T$  is the temperature and  $l$  is the optical path length of the cell used in the experiment. Consequently, the equilibrium constant,  $K$ , is then readily determined from its definition:

$$K = \frac{p_{\text{AB}}/p^{\ominus}}{p_{\text{A}}/p^{\ominus} \cdot p_{\text{B}}/p^{\ominus}}, \quad (2)$$

where  $p_{\text{A}}$  and  $p_{\text{B}}$  denote the pressures of the monomers. As a consequence of the intermolecular modes which appear upon complex formation, accurate transition wavenumbers and oscillator strengths of XH<sub>b</sub>-stretching transitions are a challenge to calculate. Large discrepancies between experimental and calculated results may be introduced, if these are neglected or not treated properly in the calculation [22–26]. In an effort to obtain accurate transition wavenumbers and oscillator strengths of XH<sub>b</sub>-stretching transitions in bimolecular complexes without having to include all  $3N-6$  vibrational modes, a vibrational model, the local mode perturbation the-

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ory (LMPT) model, was recently developed to describe the OH<sub>b</sub>-stretching vibrations in bimolecular complexes with water as the donor unit [25,26]. It is based on a three-dimensional (3D) local mode (LM) model [27–33] of the two OH-stretches and HOH-bend of the donor water unit, and the effect of the six intermolecular modes is included by Rayleigh-Schrödinger perturbation theory.

Here, we present a modified version of the LMPT model such that it is applicable to bimolecular complexes with other types of donor units. These include alcohols, amines and acids. To describe these systems, the 3D LM model of the unperturbed system is reduced to either a two-dimensional (2D) or one-dimensional (1D) LM model depending on the donor unit (see Section 3 for details on these models). In total, 13 complexes are investigated with the modified version of the LMPT model, and these provide a diverse series of complexes with respect to hydrogen bond type and complex binding energy. Ten of these complexes have methanol (MeOH) or dimethylamine (DMA) as donors in combination with DMA, trimethylamine (TMA), dimethylether (DME), dimethylsulfide (DMS), and trimethylphosphine (TMP) as acceptors. The last three complexes are an ethanol (EtOH) complex, EtOH··DMA, and two CH complexes, CH··DMS and CH··acetonitrile (CH··MeCN). Additionally, we include results from a study on a series of FH complexes [34], and we compare our findings to experimental values and previously obtained results with LM models, the LMPT model and the VPT2 [35] (vibrational perturbation theory to the second order) model.

## 2. Computational details

All electronic structure calculations were performed with the MOLPRO 2012 software [36], and all geometries were optimized at the CCSD(T)-F12a/VDZ-F12 level of theory. The 13 complexes were chosen to get a series of complexes with different types of hydrogen bonding for which experimental gas phase transition frequencies had been measured. Some of the complexes have been found to have two conformers with significant abundance according to calculated Gibbs free energies [12,17,19]. We have applied the LMPT model only to the most abundant conformer. Visualization of the structures of these conformers is shown in Fig. 1. For additional details, see the Supplementary material, SM.

## 3. The local mode perturbation theory model

The LMPT model was developed to describe the donor vibrations, especially the OH<sub>b</sub>-stretch, in hydrated bimolecular complexes such as the water dimer. For a detailed discussion on the LMPT model, see Refs. [25,26]. Briefly, the LMPT model is based on a 3D LM model of the two OH-stretches and the HOH-bend of the donor water unit, with each of the six intermolecular modes included as a 1D oscillator. The effect of the intermolecular modes on the donor vibrational modes is included by Rayleigh-Schrödinger perturbation theory, where each intermolecular mode couples to each of the donor vibrational modes through the potential energy surface. The kinetic energy couplings are expected to be negligible as discussed previously [25,26]. Perturbative corrections are obtained up to the fourth order in the energy, but only first order corrections to the wavefunctions are needed for the transition dipole moments to converge [25,26].

Here, we develop a modified version of the LMPT model, such that it applies to complexes with donor units such as alcohols, amines and acids. For systems with a donor water unit, the unperturbed system is defined by a 3D LM model of the donor water unit as previously described [25,26]. For these type of systems, the 3 active modes are the 3 donor vibrations; the two OH-stretches and the HOH-bend. For systems with alcohol or amine

donor units, a 2D LM model of the XH<sub>b</sub>-stretching oscillator and the ZXH-bending mode is employed to describe the unperturbed system. Here, Z denotes the C atom of the COH group in the alcohol complexes, and for the DMA (amine) complexes, Z denotes a dummy atom midway between the two C atoms of the donor unit. The choice of a 2D LM model was made to have a model similar to that employed for the hydrated complexes, but since there is no free XH-oscillator in the alcohol and amine complexes, a 2D LM model was employed instead of a 3D LM model. In previous studies, a 1D LM model has often been employed to describe XH<sub>b</sub>-stretching transitions in these complexes. As a test, we compared the results obtained with the 1D and 2D LM models described in this study, when the models were applied to the complexes with an alcohol or amine donor unit (see Fig. 2). We found a noticeable effect for the complexes with an alcohol donor unit and an amine acceptor unit, but for the other complexes no significant difference was found. For the alcohol-amine complexes, differences of up to ~30 cm<sup>-1</sup> were found for the fundamental XH<sub>b</sub>-stretching transition wavenumbers and for the oscillator strengths, a reduction of ~15% was found for the results with the 2D LM model relative to those obtained with the 1D LM model. The Hamiltonian operator for the 2D LM system is:

$$\hat{H}_{2D} = -\frac{\hbar^2}{2} \sum_{ij} \frac{\partial}{\partial q_i} g_{ij} \frac{\partial}{\partial q_j} + V(q_b) + V(\theta) + V(q_b, \theta). \quad (3)$$

where the summation is over all pair combinations (coupling and non-coupling) of  $\theta$  and  $q_b$ . The  $g$ -matrix elements,  $g_{ij}$ , are given by [39]:

$$g_{q_b q_b} = \frac{1}{m_X} + \frac{1}{m_H}, \quad (4)$$

$$g_{\theta\theta} = \left( \frac{1}{m_X} + \frac{1}{m_Z} \right) \frac{1}{r_{XZ}^2} + \left( \frac{1}{m_X} + \frac{1}{m_H} \right) \frac{1}{r_{XH}^2} - 2 \frac{\cos \phi_{ZXH}}{m_X r_{XZ} r_{XH}}, \quad (5)$$

$$g_{q_b \theta} = g_{\theta q_b} = -\frac{\sin \phi_{ZXH}}{m_X r_{XZ}}, \quad (6)$$

where  $m_X$  and  $m_H$  are the masses of the X and H atom, respectively. For  $m_Z$ , we have used the total mass of the donor unit minus the mass of the XH group,  $r_{XZ}$  and  $r_{XH}$  are the XZ and XH distances, respectively, and  $\phi_{ZXH}$  is the ZXH angle (see Fig. 3).

The 1D potentials,  $V(q_b)$  and  $V(\theta)$ , are represented by spline fits. The points needed to generate the spline fit for the XH<sub>b</sub>-stretch were obtained by displacing the XH<sub>b</sub>-bond from -0.40 Å to +0.70 Å in steps of 0.05 Å around the equilibrium structure. For the ZXH-bending oscillator, the points needed for the spline fit were generated by displacing the ZXH angle from -50 degrees to +80 degrees in steps of 5 degrees around the equilibrium structure. All coordinates associated with the other vibrational modes of the system are kept at their equilibrium value. Due to the relatively large intermolecular distance between the donor and acceptor unit (~3 Å), we avoid the problem of atoms getting too close to each other. The 2D PES,  $V(q_b, \theta)$ , consist of quadratic, cubic, and quartic coupling terms. The coefficients of the coupling terms have been calculated using numerical differences from a 9 × 9 potential energy grid obtained by simultaneously displacing along the two donor modes [40]. The displacements in this case were from -0.20 Å to +0.20 Å in steps of 0.05 Å for the XH-stretch, and from -20 degrees to +20 degrees in steps of 5 degrees for the ZXH-bend. Again all other coordinates are kept at their equilibrium value. A 1D Schrödinger equation was set up for each of the two donor vibrations and solved [41]. For this purpose, the  $g$ -matrix elements were evaluated at the equilibrium structure. The products of the eigenfunctions obtained by solving these Schrödinger equations were used as a basis to set up a vibrational Hamiltonian

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