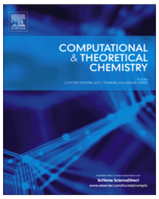
Computational and Theoretical Chemistry 1022 (2013) 70–74

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc



Calculation of infrared absorption intensities of combination bands of cyclic acid dimers by vibrational second order perturbation theory

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ARTICLE INFO

Article history:
Received 31 January 2013
Received in revised form 16 August 2013
Accepted 23 August 2013
Available online 31 August 2013

Keywords:
Anharmonic vibrational calculation
Vibrational second order perturbation theory
Infrared absorption intensity
Combination bands
Hydrogen bonding
Cyclic acid dimer

ABSTRACT

Vibrational second order perturbational theory (VPT2) was applied for anharmonic calculation of vibrational frequencies and infrared absorption intensities of combination bands of OH bending modes in cyclic dimers of carboxylic and sulfonic acids. Simulated IR spectra with calculated frequencies and intensities could reproduce changes in fine structures in the lower wavenumber side of OH stretching region of the measured IR spectra of acetic acid and its deuterated and fluorinated analogues. A weak band in the measured IR spectra of trifluoromethanesulfonic acid was successfully identified as a combination band of its cyclic dimer.

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1. Introduction

In recent years various computational methods have been developed for accurate calculation of anharmonic vibrational frequencies of polyatomic molecules. The energy levels of the highly excited vibrational states of small and medium sized polyatomic molecules can now be calculated by application of variational methods such as vibrational self-consistent field (VSCF) method [1–3]. Configurational and dynamical correlation corrections analogous to the case of electronic structure calculation are also incorporated by the methods such as vibrational configuration interaction (VCI) [4–11]. Methods for efficient calculation of anharmonic force constants also have been developed for these frameworks [12,13]. However, construction and diagonalization of vibrational Hamiltonian matrices required for the variational methods are time consuming. Although an iterative variation-perturbation scheme developed as the VCI-P code [14] leads to truncation of vibrational configuration space, which allows to increase the size of the molecules to be investigated, the variational-based methods still have been mainly limited for small and medium sized molecules.

On the other hand, the vibrational second order perturbation theory (VPT2) method requires no matrix diagonalization and together with effective selection of the normal modes considered for the anharmonicity it is more suitable for application to larger systems [15]. The method has been implemented in the Gaussian09 program package for anharonic vibrational frequency calculation of the fundamental as well as overtones and combination bands and the capability of the Gausian program to calculate analytical Hessians at various levels of electronic structure calculation is also favorable factor for application of anharmonic vibrational frequencies to larger systems.

However, as the molecule becomes larger, the number of the overtones and combination bands increases and assignment of the peaks in the measured vibrational spectra becomes difficult only by referring to the calculated vibrational frequencies. In such cases, simulation of the vibrational spectra with calculated absorption intensities of the vibrational bands would be very helpful for spectral assignment. Unfortunately, anharmonic vibrational calculation of transition intensities is far more complicated than transition frequencies and there are much fewer studies on this subject. Recently Vazquez and Stanton derived a relatively simple expression for transition moments within VPT2 framework [16]. In particular, the equation to calculate transition dipole moment of combination $\nu_j + \nu_k$ or overtone $2\nu_k$ becomes very simple [17] and the method has recently been successfully applied by Barone et al. for several simple molecules [18,19]. As the second derivatives of the dipole moments and the cubic force constants have already been obtained by anharmonic vibrational frequency calculation, infrared absorption intensities of overtones and combination bands can be calculated with very small additional costs. Very recently the method has been extended to circumvent the difficulties with the resonance effects [20,21].

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2210-271X/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.comptc.2013.08.019

In this study the VPT2 method is applied to calculate infrared absorption intensities of the combination bands of doubly hydrogen bonded cyclic Brønsted acid dimers. For example, infrared absorption spectra of acetic acid dimer, which is one of the most extensively species of this type, show very complex profiles in the OH stretching region which are affected by isotopic substitution or fluorination of the methyl group [22–29]. While the complex features of the strong peaks in the OH stretching region have been mainly analyzed by model Hamiltonians in previous studies [30–33], sharp and isolated absorption bands in the lower wavenumber side have been assigned to combination bands of the OH bending modes by referring to the vibrational frequencies of the fundamental bands in the measured spectra [22,23].

Recently Dreyer simulated the infrared absorption spectra of the OH stretching region of $(CH_3COOH)_2$ and $(CD_3COOH)_2$ by using the vibrational Hamiltonian including anharmonic force constants up to sixth order with three-body interactions and large scale basis sets [34]. The simulated spectra successfully reproduced the whole feature of the profiles in the OH stretching region by taking into account Fermi resonance coupling, although the procedure seems not straightforwardly be applied to other cases. As for the simulation of the smaller peaks at the lower wavenumber side of the observed region, i.e., below $\sim$2800 cm^{-1}, vibrational frequencies of the combination bands are fairly separated from the vibrational frequency of the antisymmetric OH stretching mode, which is the sole origin of the infrared absorption intensities of the combination bands. Thus it is expected that this case would be a successful application of the VPT2 method to simulate the combination bands in the infrared absorption spectra.

Formation of cyclic dimers has also been identified in the infrared absorption spectra of sulfuric acids from the broad OH stretching bands at $\sim$3000 cm^{-1} [35,36]. A small peak is associated at $\sim$2400 cm^{-1} in the infrared absorption spectrum of triflic acid (CF_3SO_3H) assigned as an overtone of the OH bending mode enhanced by Fermi resonance [36]. The VPT2 calculation of triflic acid dimer is performed to confirm this assignment, as the peak is similar to the one observed in the case of CF_3COOH [22] and seems to be explained by the anharmonic coupling within the framework of the perturbation theory.

2. Computational method

All the calculations were performed with the Gaussian09 program (Rev.C01) [37]. The hybrid density functional based on the gradient corrected exchange correlation functional of Perdew–Burke–Erzenhoff (PBE) [38] and the Pople's triple zeta 6-311G basis sets with polarization functions on heavy atoms [39–42] were employed throughout this study. This selection of PBE0/6-311G* is based on our previous study in which this combination gave the most accurate values of the optimized geometries and the vibrational frequencies of trifluoromethanesulfonic acid monomer (CF_3SO_3H) and its anion ($CF_3SO_3^-$) among several hybrid functionals and basis sets [43]. For example, mean absolute errors in harmonic vibrational frequencies of CF_3SO_3H and $CF_3SO_3^-$ were 2.34% and 4.50% with the B3LYP functional, respectively, which were reduced to 1.73% and 0.97% with the PBE0 functional. As for the basis sets, although the more extensive basis set like aub-cc-PV(T+d)Z gave smaller mean absolute error of 0.50% for CF_3SO_3H after scaling, the value increased to 1.87% without scaling, which was almost the same as the case of the 6-311G* basis set. Actually, application of such an extended basis set to the dimers containing up to eighteen atoms were impractical with our limited resources for computation. Molecular geometries were optimized with very tight convergence criteria and ultrafine grids for integral calculation. Hessians were analytically calculated at the optimized geometries and vibrational frequencies and infrared absorption intensities of the normal modes were calculated under the harmonic approximation. Molecular geometries and normal mode vectors were visualized with Avogadro [44].

An equation to calculate a transition dipole moment of a combination band of normal modes i and j is expressed as [18–20]

$$\langle\mu^{\alpha}\rangle_{0,ij} = \frac{1}{2}\mu^{\alpha}_{ij} + \frac{1}{4}\sum_{k}\Phi_{ijk}\mu^{\alpha}_{k}\left(\frac{1}{\omega_i+\omega_j-\omega_k} - \frac{1}{\omega_i+\omega_j+\omega_k}\right) \quad (1)$$

where $\alpha = x, y, z$, μ_k and μ_{ij} are the first and the second derivatives of the dipole moment along the mode k and the modes i and j, respectively, Φ_{ijk} is the cubic force constant of the modes i, j, k, and ω_i, ω_j, ω_k are the harmonic vibrational frequencies of the modes i, j and k, respectively. The second derivatives of the dipole moments and the cubic force constants were calculated numerically from the first derivatives of the dipole moments and the Hessians at the geometries displaced from the equilibrium geometries. Infrared absorption intensities were then calculated from the transition dipole moments by [16]

$$I_{ij}(\mathrm{km\ mol^{-1}}) = 2.5066\nu_{ij}\sum_{\alpha=x,y,z}\langle\mu^{\alpha}\rangle^{2}_{0,ij} \quad (2)$$

where ν_{ij} is the anharmonic vibrational frequency of the combination band of the normal modes i and j.

3. Results and discussion

3.1. Cyclic dimers of acetic and trifluoroacetic acids

Fig. 1 shows schematic illustration of an optimized geometry of acetic acid dimer. This geometry belongs to the C_{2h} point group and their normal modes are characterized as either symmetric or antisymmetric combinations of the normal modes of a monomer. For example, symmetric and antisymmetric OH stretching modes of the dimer belong to a_g and b_u symmetries, respectively, and the latter has exceedingly large calculated transition dipole moment under harmonic approximation.

Optimized geometries in Cartesian coordinates of doubly hydrogen bonded cyclic homodimers of acetic acid CH_3COOH and trifluoroacetic acid CF_3COOH are listed in Supporting Information. Table 1 shows calculated vibrational frequencies and infrared absorption intensities of fundamental bands of the cyclic dimers of CH_3COOH, CD_3COOH and CF_3COOH which are relevant to the combination bands at around 2400–3000 cm^{-1}. While calculated vibrational frequencies listed in this table are obtained by anharmonic vibrational analyses, infrared absorption intensities are within harmonic approximation. The calculated values of the antisymmetric OH stretching mode of b_u symmetry are also included in the table: They are very large compared to the calculated intensities of the fundamental bands of the other normal modes contributing to the combination bands. Thus it can be assumed that this antisymmetric OH stretching mode is the only source of the infrared absorption intensities of the combination bands as the mode k in Eq. (1). Then the normal modes i and j must belong to a_g and b_u symmetries so that cubic force constant Φ_{ijk} becomes nonzero and the sum of their vibrational frequencies has to be close to that of

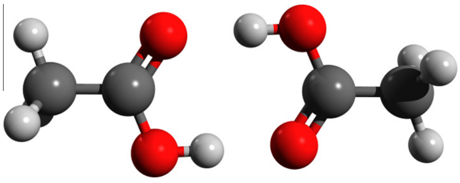

Fig. 1. Optimized geometry of $(CH_3COOH)_2$.

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