



Anharmonic vibrational spectroscopy and investigation of intramolecular mode couplings in adenine

Tabish Rasheed*, Shabbir Ahmad

Department of Physics, Aligarh Muslim University, Aligarh 202002, India

ARTICLE INFO

Article history:

Received 1 April 2010

Received in revised form 17 August 2010

Accepted 18 August 2010

Available online 25 September 2010

Keywords:

Adenine

VSCF

HF

DFT

MP2

Mode coupling

ABSTRACT

Vibrational frequencies for the nucleobase adenine are calculated by the vibrational self-consistent field (VSCF) and correlation corrected vibrational self-consistent field (CC-VSCF) methods using Hartree–Fock (HF), density functional theory (DFT) and second order Møller–Plesset (MP2) theories. A large number of potential energy surface (PES) points were computed in the anharmonic calculations corresponding to each method. The quartic force field (QFF) approximation was used to generate the full grid of points for the VSCF solver. We have implemented our new procedure for computing the mode–mode coupling integrals in the 2-mode coupling representations of the quartic force field (2MR-QFF) for prediction of coupling magnitudes. Calculations were performed using the 6-31G(d,p) basis set. Comparison of the calculated ab initio anharmonic spectra with Ar matrix experimental data of adenine reported in the literature reveals that, the CC-VSCF (DFT) wavenumbers show the best agreement. The experimental geometric parameters of adenine are compared with the theoretically optimized molecular structural parameters. These are found to be in good agreement. Vibrational assignments are based on the calculated potential energy distribution (PED) values.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The molecular wave equation may be separated by the Born–Oppenheimer procedure into two equations, one of which governs the electronic motion and gives the forces between the atoms. The other equation concerns with the rotational and vibrational motion of atoms [1]. Nearly all of the ab initio methods utilize the Born–Oppenheimer approximation which involves the setting up of a potential energy surface (PES) on which the nuclear motion takes place. The nuclear Schrödinger equation for this potential is solved and the vibrational energies and wavefunctions are determined. When this evaluation is based on the harmonic approximation of the PES, it ignores the strong anharmonicity or mode–mode couplings among normal modes. In the case of vibrational spectra of large molecules, this leads to large deviations from experimental data. Vibrational self-consistent field (VSCF) method is one of the most sophisticated approaches to perform anharmonic vibrational calculations which provide excellent results without manual scaling of theoretical frequencies. In the VSCF approach, each mode is assumed to be vibrating in the average field of other modes. The vibrational wavefunction is represented by a product of single normal-coordinate functions that are determined variation-

ally using the mean-field approximation. The correlation corrected vibrational self-consistent field (CC-VSCF) [2] method is an extension of the VSCF method which provides much better results. In this method, the VSCF wavefunction is corrected for correlation effects between different vibrational modes by using second-order perturbation theory (PT2) [3].

In the direct VSCF approach, the PES is generated directly on all grid points involving a large number of energy evaluations. In the n -mode coupling representation (n MR-PES), the number of quadrature points required to be evaluated is $\sim (f!/n!(f-n)!) \times M^n$, where M is the number of grid points along each normal coordinate and $f(=3N-6)$ denotes the normal coordinates [4]. N is the number of atoms in the molecule and it is evident that the computational burden increases very rapidly as the number of atoms increase. Yagi et al. [4] have described the quartic force field (QFF) approximation method which employs the least-mean-square method to fit the potential energies at selected reference points. This method is usually only slightly less accurate, but it greatly reduces the computational time.

Adenine is an important component of biological systems and workers have performed a large number of spectroscopic investigations on it [5–11]. Lappi et al. [12] have reported density functional analysis of anharmonic contributions to adenine matrix isolation spectra. In the present study, we have applied the VSCF/QFF and CC-VSCF/QFF schemes to perform anharmonic vibrational spectroscopy study of the adenine molecule. In the anharmonic

* Corresponding author. Tel.: +91 9410060416.

E-mail address: tabish.rasheed.physics@yahoo.co.in (T. Rasheed).

approximation, coupling between different vibrational modes significantly affect the vibrational frequencies. In order to understand intramolecular couplings in adenine, an approximate method for calculation of couplings between pair of normal modes has been presented and couplings for certain modes are discussed.

2. Methodology

Theoretical calculations were performed with the GAMESS-US [13] quantum computation package on an Intel® Core™ 2 Quad (2.4 GHz) personal computer. Molecular calculations for adenine were carried out using the Hartree–Fock (HF), second order Møller–Plesset (MP2) and density functional theory [14,15] methods. In the DFT calculations, Becke's three-parameter exchange functional [16,17] and the gradient-corrected functional of Lee et al. [18] termed as B3LYP was used. Valence double- ζ basis set augmented by d-polarization functions for heavy atoms and p-polarization functions for hydrogen atoms named as 6-31G(d,p) basis set has been used in calculations.

The global energy minimum structures of adenine were calculated utilizing the Monte Carlo procedure incorporated in GAMESS [13] to generate a random set of starting structures to look for those with the lowest energy at a single temperature [19,20]. The optimized molecular structures so obtained for adenine were used to calculate the harmonic vibrational frequencies. Anharmonic calculations were carried out using the VSCF and CC-VSCF methods. These steps of calculations were carried out using HF, DFT and MP2 theories separately to obtain three sets of data. The potential energy distribution (PED) values were calculated by using the GAMESS [13] program.

2.1. VSCF and CC-VSCF methods

The total wavefunction in VSCF is separable into product of single mode wavefunctions and is given as

$$\psi_n(Q_1, \dots, Q_N) = \prod_{j=1}^N \psi_j^{(n)}(Q_j), \quad (1)$$

where N is the number of the vibrational modes and Q_1, \dots, Q_N are the mass-weighted normal coordinates. The Schrödinger equation [1] for the molecular vibration is written as

$$\left[-\frac{\hbar^2}{2} \sum_{j=1}^N \frac{\partial^2}{\partial Q_j^2} + V(Q_1, \dots, Q_N) \right] \psi_n(Q_1, \dots, Q_N) = E_n \psi_n(Q_1, \dots, Q_N), \quad (2)$$

where $V(Q_1, \dots, Q_N)$ represents the potential energy function for the system. The VSCF method is based on the separability approximation. In this approximation each vibrational mode is assumed to be affected by a mean field of other vibrational modes. The mean field and wavefunctions of the modes are obtained self-consistently. It reduces the problem of solving the N dimensional vibrational Schrödinger equation for the N -mode system to solving N single-mode VSCF equations [21] of the form

$$\left[-\frac{\hbar^2}{2} \frac{\partial^2}{\partial Q_j^2} + \bar{V}_j^{(n)}(Q_j) \right] \psi_j^{(n)} = \varepsilon_n \psi_j^{(n)}, \quad (3)$$

where $\bar{V}_j^{(n)}(Q_j)$ is the effective VSCF potential for the mode Q_j and is represented by

$$\bar{V}_j^{(n)}(Q_j) = \left\langle \prod_{l \neq j} \psi_l^{(n)}(Q_l) \middle| V(Q_1, \dots, Q_N) \middle| \prod_{l \neq j} \psi_l^{(n)}(Q_l) \right\rangle. \quad (4)$$

Eqs. (3) and (4) for the single-mode wavefunctions are solved self-consistently. The VSCF approximation for the total energy is then given by

$$E_n^{\text{VSCF}} = \sum_{j=1}^N \varepsilon_j^{(n)} - (N-1) \left\langle \prod_{j=1}^N \psi_j^{(n)}(Q_j) \middle| V(Q_1, \dots, Q_N) \middle| \prod_{j=1}^N \psi_j^{(n)}(Q_j) \right\rangle. \quad (5)$$

The total VSCF energy of vibrational state n , E_n^{VSCF} , is a sum of all the individual mode energies minus a term which accounts for the double counting of the interactions in the energy calculation.

For the CC-VSCF computations [2], the VSCF wavefunction is corrected for correlation effects between different vibrational modes using second-order perturbation theory. The CC-VSCF approximation for the total energy is then given as

$$E_n^{\text{CC-VSCF}} = E_n^{\text{VSCF}} + \sum_{m \neq n} \frac{\left| \left\langle \prod_{j=1}^N \psi_j^{(n)}(Q_j) \middle| \Delta V \middle| \prod_{j=1}^N \psi_j^{(m)}(Q_j) \right\rangle \right|^2}{E_n^{(0)} - E_m^{(0)}}, \quad (6)$$

where ΔV represents the difference between the true potential $V(Q_1, \dots, Q_N)$ and the separable VSCF potential and is represented by

$$\Delta V = V(Q_1, \dots, Q_N) - \sum_{j=1}^N \bar{V}_j^{(n)}(Q_j). \quad (7)$$

Calculation of IR intensities involves the use of dipole moment [22]. The expression for intensity is given as

$$I_i = \frac{8\pi^3 N_A}{3hc} \omega_i |\langle \psi_0^{(i)}(Q_i) | \bar{\mu}(Q_i) | \psi_1^{(i)}(Q_i) \rangle|^2, \quad (8)$$

where ω_i is the VSCF vibrational frequency for mode i and $\psi_0^{(i)}(Q_i)$ and $\psi_1^{(i)}(Q_i)$ are the ground and first excited-state VSCF wavefunctions, respectively.

2.2. Quartic force field (QFF)

The PES for an N -atom molecule can be expressed as a Taylor expansion about the equilibrium structure. When terms higher than fourth order in the Taylor expansion are neglected, QFF [4] is written as

$$V^{\text{QFF}}(Q) = V_0 + \frac{1}{2} \sum_{i=1}^f h_i Q_i^2 + \frac{1}{6} \sum_{i,j,k} t_{ijk} Q_i Q_j Q_k + \frac{1}{24} \sum_{i,j,k,l} u_{ijkl} Q_i Q_j Q_k Q_l, \quad (9)$$

where V_0 , h_i , t_{ijk} , and u_{ijkl} represent the potential energy, its second-, third-, and fourth-order derivatives with respect to the normal coordinates, respectively, at the equilibrium geometry. $V^{\text{QFF}}(Q)$ is partitioned in the n MR-PES scheme [4] as,

$$V_{\text{QFF}}^{(1)} = V_0 + \sum_{i=1}^f \left[\frac{1}{2} h_i Q_i^2 + \frac{1}{6} t_{iii} Q_i^3 + \frac{1}{24} u_{iiii} Q_i^4 \right], \quad (10)$$

$$V_{\text{QFF}}^{(2)} = V_{\text{QFF}}^{(1)} + \sum_{i \neq j}^f \left[\frac{1}{2} t_{ijj} Q_i Q_j^2 + \frac{1}{6} u_{ijjj} Q_i Q_j^3 \right] + \frac{1}{4} \sum_{i < j}^f u_{ijij} Q_i^2 Q_j^2, \quad (11)$$

$$V_{\text{QFF}}^{(3)} = V_{\text{QFF}}^{(2)} + \sum_{i < j < k}^f t_{ijk} Q_i Q_j Q_k + \frac{1}{2} \sum_{i \neq j < k}^f u_{ijjk} Q_i^2 Q_j Q_k, \quad (12)$$

Download English Version:

<https://daneshyari.com/en/article/1250646>

Download Persian Version:

<https://daneshyari.com/article/1250646>

[Daneshyari.com](https://daneshyari.com)