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Approximate solution of the mode–mode coupling integral: Application to cytosine and its deuterated derivative

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Ab initio Hartree–Fock (HF), density functional theory (DFT) and second-order Møller–Plesset (MP2) methods were used to perform harmonic and anharmonic calculations for the biomolecule cytosine and its deuterated derivative. The anharmonic vibrational spectra were computed using the vibrational self-consistent field (VSCF) and correlation-corrected vibrational self-consistent field (CC-VSCF) methods. Calculated anharmonic frequencies have been compared with the argon matrix spectra reported in literature. The results were analyzed with focus on the properties of anharmonic couplings between pair of modes. A simple and easy to use formula for calculation of mode–mode coupling magnitudes has been derived. The key element in present approach is the approximation that only interactions between pairs of normal modes have been taken into account, while interactions of triples or more are neglected. FTIR and Raman spectra of solid state cytosine have been recorded in the regions 400–4000 cm^{-1} and 60–4000 cm^{-1}, respectively. Vibrational analysis and assignments are based on calculated potential energy distribution (PED) values.

1. Introduction

Hartree–Fock (HF), second-order Møller–Plesset (MP2) and density functional theories are most commonly used for harmonic vibrational normal mode calculations to interpret and understand experimental infrared (IR) and Raman spectra. These calculations neglect the effect of anharmonicity on both the vibrational frequencies and on the IR and Raman intensities. This is one of the reasons why the calculated harmonic frequencies and IR and Raman intensities, are in many cases, not in good agreement with the experimentally observed IR and Raman spectra. To solve this problem, many workers [1–5] have chosen to scale either the HF, MP2 or B3LYP frequencies or force constants. However, these techniques require manual treatment of the theoretical results and, most often, scaling is done by a uniform scaling factor. In light of these facts, development of general theoretical methods beyond the harmonic approximation has acquired greater significance. The vibrational self-consistent field (VSCF) approach [6–8] has emerged as an efficient method for calculating anharmonic vibrational spectra of polyatomic molecules [9,10]. In the VSCF approach, each mode is considered to be vibrating in the average field of the other modes. The correlation-corrected vibrational self-consistent field (CC-VSCF) theory [11,12] provides corrections that significantly improve the accuracy of the standard VSCF approximation. We have used both the VSCF and CC-VSCF approaches to compute the anharmonic spectra.

Ab initio calculations, performed using the harmonic approximation, do not take into account the coupling between various modes. Anharmonic couplings between various modes are of great importance to spectroscopists since they govern the flow of vibrational energy between different normal modes [13] and significantly affect the vibrational frequencies. Hence, in order to properly understand them, it is necessary to ascertain the magnitude of coupling between pair of modes. Brauer et al. [14] have calculated the magnitude of the coupling between pair of modes using the coupling integral (CI). They evaluated the integral numerically over the grid points which were used in VSCF calculations. In this paper, an easy and simple formula based on certain approximations has been derived for the calculation of CI. The quartic force field (QFF) approximation [15] was employed to compute the potential energy surface (PES).

Cytosine is one of the five nucleobases that stores and transports genetic information within a cell in the nucleic acids DNA and RNA. It is a pyrimidine derivative having a heterocyclic aromatic ring structure. Due to its biological importance, cytosine has been an interesting molecule for many spectroscopic investigations [16–21]. The aim of present investigation is to study the anharmonic vibrational spectra of cytosine, using Hartree–Fock, second-order Møller–Plesset and density functional computations. Results of the spectroscopic calculations and their comparison

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with experimental frequencies are discussed in detail. Couplings between various modes have been calculated using the derived formula for CI. Molecular structure parameters of cytosine determined for the energy-minimized structures are compared with the experimentally determined values [22].

2. Methodology

In the present investigation, theoretical calculations have been carried out on a 1.8 GHz IBM computer using the GAMESS-US [23] quantum computation package. Molecular calculations for cytosine and its deuterated derivative were carried out using the Hartree–Fock (HF), second-order Møller–Plesset (MP2) and density functional theory [24–26] methods. In the DFT calculations, Becke3LYP (B3LYP) functional [27,28] 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 [29,30] has been used in calculations.

An initial structure of the molecule was taken as input and it was optimized to obtain an energy-minimized structure, which was used to calculate the harmonic and anharmonic vibrational frequencies. The potential energy distribution (PED) values [31] were calculated by GAMESS program. Raman scattering activity S_i is calculated in the static limit for the polarizability derivatives [32–34]. The expression for S_i [35] is written as

$$S_i = g_i[45(\alpha_i')^2 + 7(\gamma_i')^2]. \tag{1}$$

where α_i' and γ_i' are the derivatives of isotropic and anisotropic polarizability tensor, respectively. They are defined as

$$(\alpha_i')^2 = \frac{1}{9}\sum_u \left(\frac{\partial \alpha_{uu}}{\partial Q_i}\right)^2, \quad u = x, y, z \tag{2}$$

$$(\gamma_i')^2 = \frac{1}{2}\sum_{uw}\left[3\left(\frac{\partial \alpha_{uw}}{\partial Q_i}\right)^2 - \left(\frac{\partial \alpha_{uu}}{\partial Q_i}\frac{\partial \alpha_{ww}}{\partial Q_i}\right)\right], \quad u, w = x, y, z; \quad u \neq w. \tag{3}$$

The relative Raman intensities are calculated from the values of S_i using the expression:

$$I_i = \frac{f(\nu_o - \nu_i)^4 S_i}{\nu_i[1 - \exp(-hc\nu_i/kT)]}, \tag{4}$$

where I_i is the relative Raman intensity obtained by the above relationship derived from the basic theory of Raman scattering [36–38]; ν_o is the exciting frequency (in cm^{-1}); ν_i is the vibrational wave number of the *i*th normal mode; *h*, *c* and *k* are Planck's constant, speed of light and Boltzmann constant, respectively, and *f* is a suitably chosen common normalization factor for all peak intensities.

Anharmonic calculations were carried out using the VSCF and CC-VSCF methods, which predict the vibrational frequencies including anharmonic effects. The anharmonic correction by VSCF method provides a good improvement over harmonic level. The second-order perturbation theory (PT2) has been used in the CC-VSCF calculations. In the following sections, VSCF, CC-VSCF, anharmonic intensities, QFF and anharmonic couplings are discussed.

2.1. VSCF and CC-VSCF methods

The vibrational Schrödinger equation [39] in mass-weighted normal coordinates $Q_1, \cdots, Q_N$ can be written as

$$\left[-\frac{\hbar^2}{2}\sum_{j=1}^{N}\frac{\partial^2}{\partial {Q_j}^2} + V(Q_1, \cdots, Q_N)\right]\psi_n(Q_1, \cdots, Q_N) = E_n\psi_n(Q_1, \cdots, Q_N), \tag{5}$$

where *N* is the number of the vibrational modes and $V(Q_1, \cdots, Q_N)$ represents the potential energy function for the system. The wavefunction, $\psi_n(Q_1, \cdots, Q_N)$, is written as

$$\psi_n(Q_1, \cdots, Q_N) = \prod_{j=1}^{N}\psi_j^{(n)}(Q_j). \tag{6}$$

The basic principle of the VSCF method is based on the separability approximation, which reduces the problem of solving the *N*-dimensional vibrational Schrödinger equation for the *N*-mode system to solving *N* single-mode VSCF equations [6–8,40] of the form:

$$\left[-\frac{\hbar^2}{2}\frac{\partial^2}{\partial Q_j^2} + \bar{V}_j^{(n)}(Q_j)\right]\psi_j^{(n)} = \varepsilon_n\psi_j^{(n)}, \tag{7}$$

where $\bar{V}_j^{(n)}(Q_j)$ represents the effective VSCF potential for the mode Q_j:

$$\bar{V}_j^{(n)}(Q_j) = \left\langle \prod_{l \neq j}^{N}\psi_l^{(n)}(Q_l)\left|V(Q_1, \cdots, Q_N)\right|\prod_{l \neq j}^{N}\psi_l^{(n)}(Q_l)\right\rangle. \tag{8}$$

Eqs. (7) and (8) for the single-mode wavefunctions are solved self-consistently. The VSCF approximation for the total energy is then given by

$$E_n^{\text{VSCF}} = \sum_{j=1}^{N}\varepsilon_j^{(n)} - (N-1)\left\langle \prod_{j=1}^{N}\psi_j^{(n)}(Q_j)\left|V(Q_1, \cdots, Q_N)\right|\prod_{j=1}^{N}\psi_j^{(n)}(Q_j)\right\rangle. \tag{9}$$

The above expression for the total VSCF energy of vibrational state *n* 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.

In the CC-VSCF calculations [11], 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

$$E_n^{\text{CC-VSCF}} = E_n^{\text{VSCF}} + \sum_{m \neq n}\frac{\left|\left\langle \prod_{j=1}^{N}\psi_j^{(n)}(Q_j)\left|\Delta V\right|\prod_{j=1}^{N}\psi_j^{(m)}(Q_j)\right\rangle\right|^2}{E_n^{(0)} - E_m^{(0)}}, \tag{10}$$

where ΔV represents the difference between the true potential $V(Q_1, \cdots, Q_N)$ and the separable VSCF potential:

$$\Delta V = V(Q_1, \cdots, Q_N) - \sum_{j=1}^{N}\bar{V}_j^{(n)}(Q_j) \tag{11}$$

2.2. Anharmonic intensities

In the present investigation, the anharmonic IR intensities are calculated using the dipole moment estimated along the normal coordinate and the VSCF wavefunctions for the ground and excited