

# Anharmonic analysis of the vibrational spectra of some cyanides and related molecules of astrophysical importance

V.P. Gupta\*, Archana Sharma

*Department of Physics, University of Jammu, Jammu-Tawi 180006, India*

Received 23 December 2005; received in revised form 7 January 2006; accepted 8 January 2006

## Abstract

A detailed analysis of the vibrational spectra of carbonyl cyanide, diethynyl ketone and acetyl cyanide has been conducted in harmonic and anharmonic approximations. RHF, MP2 and density functional theory (DFT) methods with 6-311++G(2df,2p) basis sets and B3LYP functionals have been employed. Spectroscopic constants such as anharmonicity constants, rotational and centrifugal distortion constants, rotation–vibration coupling constants and Coriolis coupling coefficients have been calculated for each molecule and compared with the experimental data, where available. A close agreement between the calculated and experimental values of the spectroscopic constants has been obtained. Complete assignments have been provided to the fundamental bands, overtones and combination tones of the molecules. Density functional theory based anharmonic frequencies compare well with the experimental frequencies within  $\pm 18 \text{ cm}^{-1}$  on an average. RHF and MP2 methods, however, give much higher values for the frequencies that need scaling even in the anharmonic approximation.

© 2006 Elsevier B.V. All rights reserved.

*Keywords:* Anharmonic frequencies; Carbonyl cyanide; Diethynyl ketone; Acetyl cyanide; DFT; Coupling constants; Anharmonic constants; Fundamental bands; Overtones; Combination tones

## 1. Introduction

Detection of photofragments of medium sized carbonyl and cyanide compounds in the interstellar medium [1–6] has generated significant interest in understanding the structural and spectral characteristics and dissociation dynamics of such molecules. While understanding of dissociation dynamics reveals the making and breaking of molecular bonds, the spectral analysis helps in the detection of these molecules in space. Botschwina and co-workers [7,8] reported experimental studies and the results of their coupled-cluster ab initio calculations on some astrophysically important molecules cyanopolyenes and their isotopomers. Several experimental studies on photodissociation of carbonyl cyanide [1–3], acetyl cyanide [4] and formyl cyanide [4] supported by quantum chemical studies using G2 theory have also been reported. Botschwina and co-workers [7,8], Martin and Taylor [9] and Dateo and Lee [10] have used ab initio calculations in the Hartree–Fock formalism to obtain the anharmonic frequencies, cubic and quartic force fields and spectroscopic

constants of several small molecules. More recently, Boese et al. [11–13] and Barone and co-workers [14,15] have extensively used density functional theory (DFT) in the computation of vibrational spectra, anharmonicities and spectroscopic constants and the anharmonic vibrational properties. Boese and Martin [11] have also assessed the performance of density functional theory for the anharmonic vibrational spectra of a series of medium sized molecules. Based upon their studies, Boese and Martin [11] and Barone [14] have concluded that DFT methods using hybrid functional such as B3LYP can give fairly accurate values for the fundamental frequencies and may be useful in computing vibrational corrections to rotational constants. Sinnokrot and Sherrill [16] have concluded that density functional theory predictions of the spectroscopic constants for B3LYP functionals are reliable. From the study of anharmonic vibrational properties by second-order perturbative approach Barone [14] has concluded that accurate band origins can be effectively computed at the DFT level without any ad hoc scaling. In the light of the above studies, detailed anharmonic analysis of the vibrational spectra and a second-order perturbative evaluation of the vibro-rotational parameters from density functional theory was undertaken for a number of astrophysically significant molecules like carbonyl cyanide, acetyl cyanide and diethynyl

\* Corresponding author. Tel.: +91 191 2453079; fax: +91 191 2453079.  
E-mail address: [vguptal@indiatimes.com](mailto:vguptal@indiatimes.com) (V.P. Gupta).

ketone, the results of which are being reported presently. In an earlier communication [17], we have reported quantum chemical studies on photodecomposition mechanism in these molecules and a complete analysis of their electronic spectra.

## 2. Methodology

The potential energy function for an anharmonic oscillator may be written as

$$V = \frac{1}{2} \sum_{ij} f_{ij} S_i S_j + \frac{1}{6} \sum_{ijk} f_{ijk} S_i S_j S_k + \frac{1}{24} \sum_{ijkl} f_{ijkl} S_i S_j S_k S_l + \dots \quad (1)$$

$\{S_i\}$  represent a displacement internal coordinate and  $f_{ij}, f_{ijk}$  and  $f_{ijkl}$ , etc. are the quadratic, cubic and quartic, etc. force constants. Using the Dunham potential functions, the energy of an anharmonic oscillator is given by

$$E_{n_1, n_2, \dots} = \sum_i v_{0i} \left( n_i + \frac{1}{2} \right) + \sum_{\substack{i, k \\ k \geq i}} X_{ik} \left( n_i + \frac{1}{2} \right) \left( n_k + \frac{1}{2} \right) + \dots \quad (2)$$

where  $X_{ii}$  and  $X_{ik}$  are the diagonal and non-diagonal anharmonicity constants. While  $X_{ii}$  characterizes anharmonicity of the given vibration, the coefficients  $X_{ik}$  characterizes coupling between different normal modes resulting from anharmonicity and are determined from cubic and quartic force constants. The fundamental frequencies of the anharmonic oscillator are given by

$$v_i = v_{0i} + 2X_{ii} + \frac{1}{2} \sum_{j \neq i} X_{ij} \quad (3)$$

The rotational vibrational couplings are determined in terms of the rotational, centrifugal distortion and rotation–vibration interaction constants and Coriolis coupling coefficients.

It has been shown by Barone [14] that the combination of harmonic frequencies computed at a very high level (both quantum mechanical methods and basis sets) and anharmonic corrections computed by even a relatively cheap model (typically hybrid functional such as B97-1 or B3LYP and 6-31G basis set augmented by diffuse functions and polarization functions) could provide a very effective procedure for medium-sized molecules. As such, in the present computations we attempted to use RHF, MP2 and density functional theories with the 6-311++G(2df,2p) basis set involving diffuse functions and polarization functions and B3LYP functionals both for the harmonic and anharmonic frequencies so that a comparison could be made between their results. All the calculations have been performed using G03W [18] software and the forms of vibrations were analysed using the software Gauss View [19]. The vibrational frequencies have been obtained after optimizing the molecular geometry by the same theory and basis sets. Harmonic frequencies in DFT have

been suitably scaled using the direct scaling method of Yoshida et al. [20,21] by the expression:

$$\nu_{\text{obs}} = (1.0087 - 0.0000163\nu_{\text{calc}})\nu_{\text{calc}}$$

## 3. Results and discussion

The results of harmonic and anharmonic vibrational analysis for carbonyl cyanide, diethynyl ketone and acetyl cyanide are being presented and discussed separately. While the anharmonic frequencies obtained from RHF and MP2 methods are much higher than the experimental frequencies, a reasonable agreement, in general, has been obtained from the DFT theory with B3LYP functionals. Larger deviations are, however, found for the higher frequency modes such as C≡C and C≡N stretch modes. Boese et al. [12] trace the origin of large errors in high frequency and low frequency modes in their DFT based calculations to finite difference step-sizes. In the present calculations a step-size of 0.025 Å has been used for anharmonic calculations. Owing to large difference between RHF and MP2 based frequencies and experimental frequencies, only the results of our DFT calculations have been used for spectral assignments. These are given in Tables 1–3.

### 3.1. Carbonyl cyanide

Carbonyl cyanide is a planar molecule belonging to the  $C_{2v}$  symmetry point group. Its 12 fundamental vibrations are distributed among the various symmetry species as  $5A_1 + 1A_2 + 2B_1 + 4B_2$ . Starting with the geometry reported by Sutor et al. [22] from MP2/6-311+G(2d) calculations, the molecular geometry of carbonyl cyanide was reoptimized by B3LYP/6-311++G(2df,2p). This geometry was then used to calculate the harmonic and anharmonic vibrational frequencies and the various anharmonicity and vibro-rotational constants by B3LYP/6-311++G(2df,2p) calculations. The optimized geometry of carbonyl cyanide is given in Fig. 1(a).

#### 3.1.1. Vibrational analysis

Table 1 contains the calculated vibrational frequencies and intensities of the fundamental modes, the first overtones and combination tones in the harmonic and anharmonic approximations. These have been compared with the experimental frequencies and intensities, where available, and a complete vibrational assignment has been provided. It is noted that not only in the harmonic but also in the anharmonic approximation, the calculated frequencies from extended basis RHF and MP2 methods are much higher than the experimental frequencies and as such need scaling in both the cases. In contrast, the DFT frequencies are much closer to the experimental ones and the scaling of the calculated frequencies to match with the experimental frequencies is needed only in the harmonic approximation. The anharmonic frequencies using density functional theory agree with the experimental values on an average within  $\pm 20 \text{ cm}^{-1}$  even without further scaling. Results of DFT calculations alone are, therefore, included in Table 1.

Download English Version:

<https://daneshyari.com/en/article/1236315>

Download Persian Version:

<https://daneshyari.com/article/1236315>

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