

Theoretical calculations for spectroscopic constants and anharmonic force field of N₂CO

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Abstract. The anharmonic force fields and spectroscopic constants of electronic ground state (\tilde{X}^1A') of diazirinone (N₂CO) has been investigated employing the DFT (B3LYP, B3PW91, and B3P86) and MP2 methods with the cc-pVnZ (n = D, T, Q) basis sets. The calculated equilibrium geometries, ground state rotational constants, fundamental vibrational frequencies, and equilibrium quartic centrifugal distortion constants of N₂CO are in comparison with experimental or theoretical data. The B3LYP results well reproduce the equilibrium geometries and spectroscopic constants. The anharmonic constants, vibration–rotation interaction constants, equilibrium sextic centrifugal distortion constants, Coriolis coupling constants, cubic and quartic force constants of N₂CO are theoretically predicted. The results show that DFT methods can afford more reliable theoretical values than MP2 method.

Keywords: Spectroscopic constant, anharmonic force field, ab initio calculation, diazirinone

1. Introduction

As a high energy compound, diazirinone (N₂CO) has attracted widespread attention [1]. What's more, together with the similar high-energy metastable compounds [2] such as 7-norbornadienone [3] and tetranitrogen [4], N₂CO can also provide an opportunity to determine the limits of chemical stability. To the best of our knowledge, N₂CO exists with many kinds of isomers instead of a single conformation. During the past decades, the various synthetic [5-9] and quantum chemical calculations [10-12] studies have been conducted on various isomers of the elemental composition N₂CO, however, the more attentions have been paid on cyclic N₂CO, since it is the most stable among the six isomers of the N₂CO species on the singlet potential energy surface (PES) and thermodynamically more stable than NCNO, CNNO, and NCON [5]. As the dimer of the more stable diatomic molecule CO and N₂ [13], cyclic N₂CO is of fundamental interest as well as its isoelectronic analogues tetranitrogen (N₄) [4] and dicarbon dioxide (C₂O₂) [14]. Furthermore, the comparison of the cyclic isomer of N₂CO and cyclopropenone can provide the general insights on the underlying the nature of weakly aromatic systems [7, 15]. In addition, the anticipated polarity of cyclic isomer of N₂CO has become a significant and meaningful target to study the structure and bonding via the rotational spectroscopy.

In 2010, Shaffer et al. [1] attempted to produce and employed the matrix isolation spectroscopy and millimeter-wave rotational spectroscopy to detect diazirinone in the condensed phase and gas phase, respectively. However, their ab initio results of the C=O stretching frequency (2046 cm⁻¹) by CCSD(T)/ANO₂ using the CFOUR software package went against with their experimentally observed IR band 2150cm⁻¹. Interestingly, Zeng et al. [5] observed the C=O stretching mode

of N₂CO by the IR spectrum (in Ar matrix). Their results of observed C=O stretching mode of N₂CO was 2033.6 cm⁻¹, in assistance with theoretical values of Shaffer et al. Perrin and Zeng et al. [16] analyzed the Fermi-coupled ν_1 and $2\nu_5$ bands by using the high-resolution infrared spectra recorded within the scope of 1810–2100 cm⁻¹. Their results pointed that the C=O stretching frequency was 2043.8 cm⁻¹, which was well inoculated with the ab initio result before of 2046 cm⁻¹ [1] and the experimental result of 2033.6 cm⁻¹[5]. In conclusion, the previous studies usually concentrate on the geometry, rotational constants, frequency, and quartic centrifugal distortion constants of N₂CO, however, the anharmonic constants, rotation-vibration interaction constants, sextic centrifugal distortion constants, Coriolis coupling constants, cubic and quartic force constants of N₂CO have not been investigated experimentally and theoretically until now. Therefore, we'll complete the study of the anharmonic force fields and spectroscopic constants of electronic ground state (\tilde{X}^1A') of diazirinone (N₂CO) employing the DFT (B3LYP, B3PW91, and B3P86) and MP2 methods with the cc-pVnZ (n = D, T, Q) basis sets in order to obtain these spectroscopic constants and anharmonic force fields in this paper.

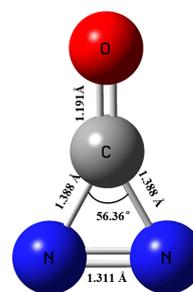


Fig.1 Optimized geometries of N₂CO at the B3LYP/cc-pVDZ theoretical level.

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2. Computational Details

The MP2 and DFT methods including B3LYP, B3P86, and B3PW91 [17-20] are applied to calculate the spectroscopic constants and anharmonic force field of N₂CO. Three basis sets are adopted and designated as cc-pVnZ (n = D, T, Q) [21]. The contracted set is the same for N, C, and O atom on the same basis set. For cc-pVnZ (n = D, T, Q) basis sets, the contracted set are [3s, 2p, 1d]/(9s, 4p, 1d), [4s, 3p, 2d, 1f]/(10s, 5p, 2d, 1f), and [5s, 4p, 3d, 2f, 1g]/(12s, 6p, 3d, 2f, 1g), respectively. All calculations are done with the Gaussian 09 program [22]. In recent years, our group has completed the systematic studies of spectroscopic constants and anharmonic force field of triatomic and tetraatomic molecules using ab initio calculation [23-27]. The calculation detail of the spectroscopic constants and anharmonic force field of N₂CO can be found in Refs. 23-27.

3. Results and discussion

The calculated equilibrium geometries, anharmonic force fields and spectroscopic constants of \tilde{X}^1A' for N₂CO are generalized in **Tables 1–10** (Supporting information). The MP2, B3LYP, B3P86, and B3PW91 methods with the cc-pVnZ (n = D, T, Q) basis sets in order that we can appreciate to be brief fully the change of the calculated results. The corresponding experimental and theoretical values that exist also be listed in Tables 1–10. In following tables, the basis sets cc-pVnZ (n = D, T, Q) are respectively named DZ, TZ, and QZ briefly.

Calculated equilibrium geometries of N₂CO are listed in **Table 1**, along with the previous theoretical results [13]. One can clearly find that the calculated bond length of C–O, C–N, and N–N gradually diminish with the basis sets increasing. In current research, B3LYP/cc-pVDZ results are reasonable and practicable with the theoretical value by CCSD/ANO0. The gap between B3LYP/cc-pVDZ and the theoretical value by CCSD/ANO0 is 0.001 Å, 0.001 Å, 0.005 Å, and 0.24° for r(C–O), r(C–N), r(N–N) and ∠(NCN), respectively. The values of the B3LYP/cc-pVTZ and B3LYP/cc-pVQZ theoretical levels for the molecular structure parameters of N₂CO are very close to the B3LYP/cc-pVDZ results. Besides, the B3PW91 and B3P86 methods can also give the desirable results as the B3LYP method at the same basis set. However, the calculated equilibrium geometries of N₂CO for MP2 method are unsatisfactory. The optimized geometries of N₂CO at the B3LYP/cc-pVDZ theoretical level are shown in **Fig. 1**.

Table 2 contains the calculated rotational constants for N₂CO in equilibrium and ground states at B3LYP, B3PW91, B3P86, and MP2 methods with basis sets DZ, TZ, and QZ, respectively, along with the available experimental data of rotational constants in ground states of N₂CO reported by Perrin et al. in ref.16 and the theoretical values predicted at the ab initio CCSD(T)/ANO2 level in ref.1. Considering the effects of vibration–rotation coupling by the perturbation theory, the relationship between the theoretical ground–state rotational constants (A_0 , B_0 , C_0) and the related equilibrium rotational constants (A_e , B_e , C_e) can be expressed in Equation (1).

$$X_0 = X_e - \sum_i \alpha_i^\beta (v_i + 1/2) + \dots (X=A,B,C) \quad (1)$$

The contribution of α_i^β in Equation (1), which has been summarized in **Table 6**, represents vibration–rotation interaction constant.

Comparing with the experimental value, the results of the A_0 , B_0 , and C_0 in this work are much better than the previous theoretical value. The relative error between the A_0 , B_0 , and C_0 of N₂CO at the B3LYP/QZ level and the experimental results are 2.03%, 0.025%, and 0.32%. Hence, the value of $A_e = 42012.51$, $B_e = 8359.70$, and $C_e = 6972.33$ in the B3LYP/QZ level are reasonable.

The computational harmonic vibrational frequency ω_i and fundamental vibrational frequency ν_i are listed in **Table 3**, as well as the experimental [1, 5, 16] data and the previous theoretical [1, 13] results. N₂CO has six vibrational modes: ν_1 (CO stretching mode), ν_2 (NN stretching mode), ν_3 (CN symmetric stretching mode), ν_4 (Out of plane bending mode), ν_5 (OCN rocking mode), and ν_6 (NCN asymmetric stretching mode). Herein, Equation (2) expresses the ν_i (i=1-6) fundamental frequency of an asymmetric top molecule.

$$\nu_i = \omega_i + 2\chi_{ii} + \frac{1}{2} \sum_{i \neq j} \chi_{ij} \quad (2)$$

In Equation (2), ω_i is the harmonic frequency and χ_{ii} is the anharmonic constant, which has shown in **Table 4**

The experimentally observed IR band 2150 cm⁻¹ of ν_1 (the C=O stretching frequency) by Shaffer et al. [1] went against with their theoretical results (2046 cm⁻¹) and the experimental results (2033.6 cm⁻¹) observed by Zeng et al. [5] While, the experimental data 2043.8 cm⁻¹ pointed by Perrin and Zeng et al. [16] is in good agreement with the previous the *ab initio* prediction of 2046 cm⁻¹ [1] and the experimental value of 2033.6 cm⁻¹ [5]. In comparing with the experimental value in ref.16, the results of $\nu_1 = 2051.145$ cm⁻¹ employing the B3LYP/cc-pVQZ in this work are better than the previous theoretical value [5] with the relative error 0.36%. Perrin and Zeng et al. [16] also experimentally obtained the $2\nu_5$ value of 1863.273 cm⁻¹, taking into account the relationship between doubled-frequency and fundamental frequency, the calculated ν_5 value of 936.77 cm⁻¹ at B3LYP/cc-pVQZ theoretical level is very excellent with the deviation of 5.13 cm⁻¹. The other fundamental vibrational frequencies of the B3LYP/cc-pVQZ theoretical levels also well reproduce the previous theoretical and experimental value. Hence, the harmonic vibrational frequencies by the B3LYP method with three basis sets could serve as references.

The anharmonicity of a molecule can modify its vibrational term values and wave functions; therefore, it may contribute to overtone intensities. The anharmonic constants of the N₂CO molecule are firstly calculated by us using DFT and MP2 methods with three basis sets in this article (showed in **Table 4**). The calculated DFT results are usually fairly similar; however, the MP2 results are drastically different from the DFT values. We expect that the current calculated DFT results can be regarded as a reliable prediction for the anharmonicity constants of the N₂CO molecule.

Table 5 contains the vibration–rotation interaction constants α_i^X (X = A, B, C; i = 1–6) of N₂CO. The α_i^X (X = A, B, C;