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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 ($\tilde{X}^1 A'$) of diazirinone (N_2CO) 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 N_2CO 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 N_2CO 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 (N_2CO) 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], N_2CO can also provide an opportunity to determine the limits of chemical stability. To the best of our knowledge, N_2CO 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 N_2CO, however, the more attentions have been paid on cyclic N_2CO, since it is the most stable among the six isomers of the N_2CO 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 N_2 [13], cyclic N_2CO is of fundamental interest as well as its isoelectronic analogues tetranitrogen (N4) [4] and dicarbon dioxide (C_2O_2) [14]. Furthermore, the comparison of the cyclic isomer of N_2CO 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 N_2CO 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)/ANO$_2$ 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 N_2CO by the IR spectrum (in Ar matrix). Their results of observed C=O stretching mode of N_2CO was 2033.6 cm^{-1}, in assistance with theoretical values of Shaffer et al. Perrin and Zeng et al. [16] analyzed the Fermi–coupled v_1 and $2v_5$ 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 inosculated 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 N_2CO, however, the anharmonic constants, rotation-vibration interaction constants, sextic centrifugal distortion constants, Coriolis coupling constants, cubic and quartic force constants of N_2CO 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 ($\tilde{X}^1 A'$) of diazirinone (N_2CO) 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.
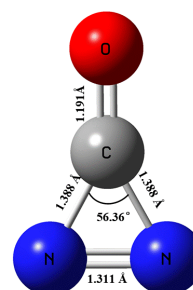

Fig.1 Optimized geometries of N_2CO at the B3LYP/cc-pVDZ theoretical level.

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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 N_2CO. 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 N_2CO can be found in Refs. 23-27.

3. Results and discussion

The calculated equilibrium geometries, anharmonic force fields and spectroscopic constants of $\widetilde{X}^1A'$ for N_2CO 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 N_2CO 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 0.001Å, 0.001 Å, 0.005 Å, and 0.24° for r(C–O), r(C–N), r(N–N) and $\angle$(NCN), respectively. The values of the B3LYP/cc-pVTZ and B3LYP/cc-pVQZ theoretical levels for the molecular structure parameters of N_2CO 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 N_2CO for MP2 method are unsatisfactory. The optimized geometries of N_2CO 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 N_2CO 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).

$$X_\upsilon = X_e - \sum_i \alpha_i^\beta (\upsilon_i + 1/2) + \cdots (X=A,B,C) \tag{1}$$

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 N_2CO 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 v_i are listed in **Table 3**, as well as the experimental [1, 5, 16] data and the previous theoretical [1, 13] results. N_2CO has six vibrational modes: v_1 (CO stretching mode), v_2 (NN stretching mode), v_3 (CN symmetric stretching mode), v_4 (Out of plane bending mode), v_5 (OCN rocking mode), and v_6 (NCN asymmetric stretching mode). Herein, Equation (2) expresses the v_i (i=1-6) fundamental frequency of an asymmetric top molecule.

$$v_i = \omega_i + 2\chi_{ii} + \frac{1}{2}\sum_{i \neq j} \chi_{ij} \tag{2}$$

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 2150cm^{-1} of v_i (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 v_i = 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 $2v_5$ value of 1863.273 cm^{-1}, taking into account the relationship between doubled-frequency and fundamental frequency, the calculated v_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 N_2CO molecule are firstly calculated by us using DTF 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 N_2CO molecule.

Table 5 contains the vibration–rotation interaction constants α_i^X (X = A, B, C; i = 1–6) of N_2CO. The α_i^X (X = A, B, C;

i = 1–6) hinges on the cubic force constants and second–order Coriolis terms. As far as the current researches is concerned, the theoretical and experimental values of α_i^X (X = A, B, C; i = 1–6) have not been reported up to now. Comparing the calculated results of DFT methods with each other, most of the results generally yield vibration–rotation constants with the same sign and magnitude. It is needed to be pointed out that the calculated vibration–rotation interaction constants results by the MP2 method show the obvious gap with the DFT data. Based on the above calculation and analysis of spectroscopic constants for N_2CO such as geometry structure, rotational constant, harmonic and fundamental frequencies, anharmonic constants, and vibration–rotation interaction constants, we believe that the MP2 method is not suitable for the study of N_2CO in the field of spectrum study.

The constants of equilibrium quartic and sextic centrifugal distortion are given in **Table 6** and **Table 7**, together with previous theoretical results of quartic centrifugal distortion constants calculated by Perrin et al. [16] in **Table 6**. Perrin et al. have given the quartic centrifugal distortion constants calculated by a least squares fit procedure via ground-state combination differences (GSCD). While, they have also pointed out that the terms J_z^2 could not be determined A or ΔK. [16] Furthermore, Perrin et al. only gave the ground-state quartic centrifugal distortion constants. **Table 6** is given equilibrium-state quartic centrifugal distortion constants of N_2CO. What is noteworthy is that if the deviation between the experimental ground state and calculative equilibrium value can't be negligible, comparing the calculated centrifugal distortion constant between the equilibrium and available experimental ground state of N_2CO may be problematic. In general, the equilibrium centrifugal distortion constants are less than the ground state value for four times. In general, the equilibrium centrifugal deformation constant is less than the ground state value for four times. In consequence, the calculated values in **Table 7** are reasonable within the acceptable error.

The Coriolis coupling constants listed in **Table 8** reflect the coupling strengths between normal coordinates Q_i and Q_j rotating around the $\beta_{(y)}$ axis. The reports of Coriolis coupling constants of N_2CO have not been as yet found theoretically and experimentally. The DFT theoretical results are fairly similar each other at current research. We have great expectations of the present calculated DFT results can be used in the future research for the N_2CO molecule.

Tables 9 and **10** list the cubic and quartic force constants of N_2CO. It is clearly from **Tables 9** and **10** that the effect of the different method on the cubic and quartic force constants is dominant in comparing with the effect of different basis sets, and the deviation of the cubic and quartic force constants between DFT and MP2 methods can't be ignored. In **Tables 9** and **10** the cubic and quartic force constants of N_2CO obtained from B3LYP, B3PW91, and B3P86 methods have very close absolute value, therefore, we hope that they can provide the reasonable prediction of the force constants of N_2CO.

4. Conclusions

In this paper, we have investigated the spectroscopic constants and anharmonic force field of N_2CO performing by the B3P86, B3PW91, B3LYP, and MP2 methods with three basis sets cc-pVnZ (n = D, T, Q). Based on the above analysis of N2CO, it is clear DFT methods can give reliable and reasonable theoretical values. In addition, we also firstly predict the anharmonicity constants, vibration–rotation interaction constants, equilibrium sextic centrifugal distortion constants, Coriolis coupling constants, cubic and quartic force constants, which can provide the essential information for future experimental researches of N_2CO. In a word, we anticipate the obtained information of anharmonic effects on the spectroscopic constants and complete quartic force fields may contribute to the future study for N_2CO.

Acknowledgements

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Supporting Information

Theoretical calculations for spectroscopic constants and anharmonic force field of N₂CO

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Table 1 Molecular equilibrium geometries of N_2CO (bond lengths in Å, angle in degree)

Parameters	B3LYP			B3P86			B3PW91			MP2			CCSD[a]	CCSD(T)[a]	CCSD(T)[a]
	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ	ANO0	ANO0	ANO1
r(C–O)	1.191	1.184	1.183	1.188	1.182	1.181	1.189	1.183	1.181	1.195	1.188	1.185	1.190	1.195	1.189
r(C–N)	1.388	1.380	1.378	1.383	1.376	1.375	1.383	1.377	1.376	1.403	1.391	1.387	1.387	1.398	1.387
r(N–N)	1.311	1.304	1.302	1.306	1.299	1.298	1.307	1.300	1.299	1.351	1.339	1.333	1.316	1.335	132.4
∠(NCN)	56.36	56.39	56.36	56.37	56.36	56.34	56.35	56.35	56.33	57.56	56.53	57.45	56.6	57.1	57.0

[a]Calculated bond lengths and angles in from Ref.13.

Table 2 Rotational constants in equilibrium and ground states of N2CO (MHZ)

Parameter	B3LYP			B3P86			B3PW91			MP2			Expt. Ref.16	Theo. Ref.1
	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ		
A_e	42012.51	42477.35	42590.61	42325.81	42763.17	42862.45	42281.24	42697.71	42795.90	39578.72	40273.82	40602.24		
B_e	8359.70	8459.36	8474.91	8409.46	8498.25	8513.71	8398.74	8484.45	8500.19	8288.90	8409.55	8448.16		
C_e	6972.33	7054.47	7068.40	7015.58	7089.39	7102.87	7006.89	7077.98	7091.64	6853.57	6956.89	6993.10		
A_0	41869.96	42333.62	42448.07	42186.74	42624.36	42725.03	42142.56	42559.57	42658.97	39380.81	40080.50	40408.78	41588.34	41360
B_0	8325.58	8424.40	8440.17	8376.57	8464.66	8480.28	8365.81	8450.83	8466.72	8253.75	8373.70	8412.16	8442.29	8400
C_0	6933.20	7014.49	7028.57	6977.54	7050.67	7064.27	6968.88	7039.30	7053.05	6812.09	6914.81	6950.85	7006.19	6970

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Table 3 Calculated harmonic and fundamental vibrational frequencies of N_2CO (cm^{-1}).

	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
B3LYP/DZ	2073.05	1424.38	940.88	574.15	964.29	528.06	2066.584	1400.983	921.17	571.23	933.61	522.280
B3LYP/TZ	2060.15	1414.84	942.37	582.91	966.41	538.30	2056.029	1391.904	922.57	579.43	935.10	531.556
B3LYP/QZ	2053.78	1419.23	943.60	581.71	967.61	536.87	2051.145	1396.612	923.99	578.38	936.77	530.919
B3P86/DZ	2104.90	1453.57	959.48	578.78	995.72	534.32	2102.981	1430.938	939.70	575.96	965.84	528.626
B3P86/TZ	2090.01	1443.42	959.48	586.72	995.66	542.87	2090.671	1421.482	939.89	583.71	965.67	536.591
B3P86/QZ	2084.20	1447.16	960.48	585.61	996.68	541.70	2086.376	1425.273	940.976	583.15	967.07	536.155
B3PW91/DZ	2101.45	1452.17	958.58	578.52	995.81	534.42	2100.269	1429.627	938.84	575.90	966.03	528.851
B3PW91/TZ	2085.95	1441.10	958.02	586.28	994.80	542.73	2087.088	1419.343	938.52	583.38	965.03	536.559
B3PW91/QZ	2080.15	1444.68	959.07	585.22	995.80	541.67	2082.826	1422.975	939.65	582.87	966.44	536.222
MP2/DZ	2078.25	1233.96	907.39	574.08	1034.08	530.11	2104.548	1210.237	887.28	570.49	1019.43	523.136
MP2/TZ	2066.86	1240.77	911.84	577.92	1030.19	535.00	2095.157	1218.673	891.92	574.02	1013.97	527.874
MP2/QZ	2060.04	1253.64	916.93	577.88	1030.83	534.27	2092.033	1230.959	897.017	574.02	1013.84	527.556
IR[a]							2150					
CCSD(T)/ANO2[b]							2046	1325	903	565	961	529
IR(Ar matrix)[c]							2033.6		902	564.4	959.6	528.7
FTIR][d]							2043.8					
CCSD/ANO0[e]							2085.5	1398.0	934.8	590.0	1029.6	547.9
CCSD(T)/ANO0[e]							2038.0	1298.4	898.2	570.1	974.2	530.6
CCSD(T)/ANO1[e]							2043.5	1335.6	917.7	567.7	983.5	535.01

[a]The experimental values from Ref. 1.
[b]From CCSD(T)/ANO2 in Ref. 1.
[c]The experimental values from Ref. 5.
[d] The experimental values from Ref. 16.
[e]Using various methods from Ref. 13.

Table 4 Anharmonic constants χ_{ij} of N_2CO (cm^{-1}).

Parameter	B3LYP			B3P86			B3PW91			MP2		
	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ
χ_{11}	-10.26	-10.61	-10.60	-10.05	-10.24	-10.25	-9.98	-10.14	-10.14	-8.18	-8.34	-8.47
χ_{12}	-0.28	-0.53	-0.14	-0.79	-0.88	-0.53	-0.84	-0.91	-0.55	-1.46	-1.41	-1.38
χ_{13}	-2.68	-2.15	-1.97	-2.55	-1.99	-1.86	-2.58	-1.98	-1.86	1.32	1.30	1.30
χ_{14}	-7.43	-7.49	-7.26	-6.70	-6.73	-6.63	-6.69	-6.71	-6.61	10.17	8.39	7.72
χ_{15}	-9.51	-9.73	-9.64	-9.11	-9.25	-9.18	-9.11	-9.21	-9.15	-5.32	-6.03	-6.51
χ_{16}	-0.43	-0.29	-0.25	-0.42	-0.15	-0.0026	-0.43	-0.16	-0.014	-1.31	-1.32	-1.24
χ_{22}	-0.67	-0.90	-0.70	-0.65	-0.84	-0.64	-0.63	-0.82	-0.63	-0.79	-0.85	-0.78
χ_{23}	-8.07	-8.21	-8.19	-8.07	-8.18	-8.22	-8.00	-8.11	-8.14	-7.23	-7.57	-7.53
χ_{24}	0.74	0.83	0.98	1.13	1.22	1.17	1.17	1.26	1.22	0.18	0.48	0.62
χ_{25}	-2.70	-3.10	-2.98	-2.50	-2.76	-2.68	-2.48	-2.74	-2.66	-3.10	-3.11	-2.97
χ_{26}	1.41	1.14	1.23	1.44	1.39	1.72	1.51	1.43	1.74	0.85	0.75	0.96
χ_{33}	-9.80	-9.79	-9.78	-9.53	-9.52	-9.50	-9.41	-9.45	-9.43	-8.03	-8.26	-8.34
χ_{34}	-5.45	-5.42	-5.36	-5.33	-5.25	-5.24	-5.32	-5.21	-5.21	-9.07	-7.67	-7.07
χ_{35}	-6.71	-6.48	-6.30	-7.52	-6.50	-6.39	-6.76	-6.51	-6.41	-9.33	-8.33	-7.84
χ_{36}	-8.88	-9.02	-9.02	-8.84	-8.90	-8.88	-8.68	-8.80	-8.79	-8.32	-8.30	-8.26
χ_{44}	-7.36	-7.18	-7.16	-7.34	-7.09	-7.09	-7.31	-7.04	-7.03	-11.12	-10.23	-10.31
χ_{45}	-7.22	-7.21	-7.02	-6.89	-6.77	-6.69	-6.82	-6.69	-6.61	-10.89	-10649	-10.72
χ_{46}	2.01	2.15	2.06	1.86	2.00	1.96	1.84	1.98	1.93	6.63	6.18	5.30
χ_{55}	-1.26	-1.37	-1.36	-1.29	-1.38	-1.39	-1.30	-1.39	-1.39	-1.51	-1.49	-1.45
χ_{56}	-8.22	-7.61	-7.83	-9.14	-8.38	-8.51	-9.08	-8.31	-8.44	-5.56	-5.77	-5.99
χ_{66}	2.07	1.67	1.79	2.36	2.01	2.20	2.40	2.02	2.22	0.13	0.17	0.38

Table 5 Vibration–rotation interaction constants of N_2CO (MHz).

Parameter	B3LYP			B3P86			B3PW91			MP2		
	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ
α_1^A	-388.24	-404.82	-404.08	-365.29	-378.79	-378.07	-363.14	-377.11	-376.53	-453.08	-449.66	-445.32
α_2^A	2023.22	2081.34	2082.87	2202.90	2242.59	2251.16	2224.37	2257.63	2267.43	1552.85	1683.83	1706.32
α_3^A	40.97	42.03	42.56	40.88	41.53	41.89	40.87	41.41	41.80	46.93	47.85	48.55
α_4^A	424.18	425.70	424.02	415.22	415.42	413.07	413.86	413.78	411.60	538.90	526.02	526.66
α_5^A	57.63	58.28	57.20	54.45	53.99	52.94	53.86	53.29	52.35	141.60	132.02	125.81
α_6^A	-1872.66	-1915.07	-1917.48	-2070.03	-2097.11	-2106.15	-2092.46	-2112.73	-2122.80	-1431.38	-1553.38	-1575.11
α_7^A	35.84	36.22	36.23	35.03	35.37	35.39	34.91	35.22	35.24	38.80	39.14	39.41
α_8^A	-13.53	-12.96	-13.30	-14.20	-13.86	-14.16	-14.15	-13.80	-14.08	-11.06	-11.37	-11.94
α_9^A	55.86	55.80	55.80	55.21	55.18	55.18	55.17	55.13	55.14	53.25	54.01	54.48
α_{10}^A	-9.46	-9.31	-9.35	-9.33	-9.20	-9.20	-9.27	-9.14	-9.13	-4.98	-5.24	-5.69
α_{11}^A	10.99	11.09	11.18	11.02	11.15	11.24	11.06	11.19	11.28	4.64	5.58	6.27
α_{12}^A	-11.44	-10.88	-11.05	-11.91	-11.42	-11.57	-11.85	-11.34	-11.48	-10.33	-10.40	-10.52
α_{13}^A	-48.52	-48.40	-48.26	-19.05	-20.21	-19.98	-17.43	-19.08	-18.91	17.66	17.18	17.04
α_{14}^A	5.14	6.00	5.83	4.48	5.08	4.93	4.46	5.07	4.94	9.24	9.26	8.83
α_{15}^A	39.55	39.50	39.51	39.09	39.06	39.06	39.07	39.02	39.04	37.10	37.66	38.04
α_{16}^A	2.36	2.43	2.33	1.99	1.98	1.91	1.97	1.97	1.90	8.05	7.32	6.98
α_{17}^A	96.15	96.71	96.70	66.27	68.12	68.03	64.60	66.91	66.88	26.30	28.41	29.45
α_{18}^A	-16.45	-16.31	-16.47	-16.73	-16.61	-16.76	-16.67	-16.54	-16.69	-15.41	-15.70	-15.86

Table 6 Equilibrium quartic centrifugal distortion constants of N_2CO (MHz).

Parameter	B3LYP			B3P86			B3PW91			MP2			Expt. Ref.16
	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ	
$10^3\Delta_J$	2.0190	2.0810	2.0900	1.9860	2.0470	0.2057	1.9840	2.0450	0.2057	2.0520	2.1330	2.1470	2.7612
Δ_K	0.1270	0.1350	0.1342	0.1240	0.1310	0.1307	0.1240	0.1310	0.1307	0.1540	0.1590	0.1584	0.0000
Δ_{JK}	0.0470	0.0480	0.0485	0.0460	0.0470	0.0474	0.0460	0.0470	0.0474	0.0460	0.0470	0.0478	0.0440
$10^3\delta_J$	0.3650	0.3750	0.3764	0.3570	0.3670	0.3685	0.3570	0.3670	0.3685	0.3780	0.3900	0.3916	0.6792
δ_K	0.0290	0.0300	0.0302	0.0290	0.0290	0.0295	0.0290	0.0290	0.0295	0.0280	0.0290	0.0293	0.0906

Table 7 Equilibrium sextic centrifugal distortion constants of N$_2$CO (MHz).

Parameter	B3LYP			B3P86			B3PW91			MP2		
	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ
$10^3\Phi_J$	-0.600	-0.627	-0.626	-0.529	-0.555	-0.554	-0.525	-0.552	-0.551	-0.270	-0.313	-0.337
Φ_K	11.157	11.026	11.268	11.224	11.178	11.400	11.187	11.133	11.346	7.705	8.363	8.780
Φ_{JK}	0.094	0.089	0.092	0.097	0.094	0.097	0.096	0.093	0.096	0.084	0.087	0.092
Φ_{KJ}	-11.138	-10.958	-11.193	-11.190	-11.094	-11.308	-11.150	-11.044	-11.249	-8.197	-8.734	-9.127
$10^3\varphi_J$	0.673	0.705	0.710	0.630	0.664	0.668	0.627	0.661	0.666	0.568	0.614	0.625
φ_K	-2.740	-2.634	-2.691	-2.855	-2.784	-2.839	-2.855	-2.779	-2.831	-1.494	-1.659	-1.774
$10^1\varphi_{JK}$	0.676	0.066	0.678	0.677	0.670	0.069	0.673	0.666	0.682	0.582	0.610	-0.337

Table 8 Coriolis coupling constants ζ_{ij} of N$_2$CO.

Parameter	B3LYP			B3P86			B3PW91			MP2		
	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ	DZ	TZ	QZ
ζ_{63}^{α}	-0.981	-0.980	-0.980	-0.981	-0.981	-0.980	-0.981	-0.981	-0.980	-0.982	-0.982	-0.982
ζ_{64}^{α}	0.068	0.063	0.064	0.074	0.069	0.069	0.074	0.068	0.069	-0.012	-0.010	-0.006
ζ_{65}^{α}	-0.183	-0.188	-0.189	-0.179	-0.184	-0.185	-0.179	-0.183	-0.184	-0.187	-0.189	-0.189
ζ_{31}^{β}	0.625	0.634	0.633	0.616	0.622	0.622	0.616	0.622	0.622	0.707	0.702	0.697
ζ_{32}^{β}	0.774	0.766	0.767	0.782	0.777	0.777	0.783	0.777	0.777	0.693	0.699	0.703
ζ_{41}^{β}	-0.552	-0.540	-0.543	-0.565	-0.556	-0.559	-0.566	-0.557	-0.559	-0.408	-0.418	-0.429
ζ_{42}^{β}	0.526	0.534	0.535	0.520	0.527	0.528	0.520	0.527	0.528	0.559	0.562	0.564
ζ_{51}^{β}	-0.552	-0.554	-0.552	-0.548	-0.551	-0.549	-0.548	-0.550	-0.548	-0.578	-0.577	-0.574
ζ_{52}^{β}	-0.352	-0.357	-0.354	-0.343	-0.346	-0.343	-0.343	-0.345	-0.342	-0.454	-0.443	-0.433
ζ_{61}^{γ}	0.752	0.760	0.760	0.745	0.750	0.750	0.744	0.749	0.749	0.798	0.794	0.791
ζ_{62}^{γ}	-0.659	-0.650	-0.650	-0.667	-0.662	-0.662	-0.668	-0.663	-0.662	-0.603	-0.608	-0.612