A study of the low-lying states at multi-reference configuration interaction level of N_2 molecule

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Abstract: The effect of different basis sets of the spectroscopic data of the ground state $X^1\Sigma_g^+$ of nitrogen molecule (N_2) is analyzed using complete active space self-consistent field/multi-reference configuration interaction theory. Then the augmented correlation consistent polarized valence quintuple ζ basis sets (Aug-cc-pV5Z) are selected to compute nine low-lying excited states of N_2 molecule. Potential energy curves of these states are also plotted. The spectroscopic constants R_e, ω_e and D_e for the ten states have been evaluated and critically compared with the available experimental values and the other theoretical data. And the spectroscopic constants of the $A'^5\Sigma_g^+$ state are obtained which are not yet observed through experiment.

Keywords: Nitrogen molecular; CASSCF/MRCI method; Excited electronic states; Potential energy curves; Spectroscopic constants

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1. Introduction

The determination of the electronic structure of N_2 molecule is one of the most difficult challenges for ab initio calculations. In recent years, with the development of quantum chemistry and computer science, it is possible to study the detailed electronic state structure of small molecules with high accuracy through ab initio calculation [1–9]. There has been a great deal of theoretical and experimental studies of N_2 molecule [10–23]. Ermler et al. [15] reported 17 low-lying states of N_2. They just gave a little spectroscopic constant, such as equilibrium bond distances R_e and harmonic frequencies ω_e. For the ground state, dissociation energies D_e had reported. The best result they reported was 10.27 eV, which was about 0.36 eV larger than experimental value of 9.9051 eV reported by Lofthus [22]. Larsen et al. [16] studied five singlet states ($X^1\Sigma_g^+$, $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$, $b^1\Pi_u$) using full configuration interaction (FCI), the coupled-cluster singles and doubles model

(CCSD) method. The dissociation energies were 8.74, 5.71, 5.75 and 5.26 eV for the $X^1\Sigma_g^+$, $a^1\Pi_g$, $a'^1\Sigma_u^-$ and $w^1\Delta_u$ states, respectively. The corresponding experimental values are 9.9051, 6.16, 6.22, 5.73 eV [22]. San-Fabian et al. [18] calculated several singlet and triplet states using a complete-active-space self-consistent-field and density functional theory and the augmented correlation-consistent polarized-valence quintuple-ζ Dunning basis sets. They had given several spectroscopic constants under different methods. The results of Vasko-Will-Nussair function with self-interaction correction (VWN-2) method were the most similar to experimental data. The values of D_e were also largely different from experimental data for the ground state, which was about 0.89 eV larger than experimental data. Recently, Hochlaf et al. [19] computed the spectroscopic data and spin–orbit couplings of the $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$, $G^3\Delta_g$, $a''^1\Sigma_g^+$, $E^3\Sigma_g^+$, $1^3\Sigma_g^-$ and $1^1\Gamma_g$ high excited states at MRCI/Aug-cc-pVQZ level, without discussing the dissociation energies for the studied states.

As seen from the above survey of theoretical studies on N_2 molecule, most of these studies focused on singlet and triplet states. And the dissociation energies had a large

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difference from experimental values. The $A'^5\Sigma_g^+$ state had a few experimental data and theoretical studies. Equilibrium bond distances and harmonic frequencies were about 1.55 Å and 650 cm^{-1}, respectively. There were no experimental data for the dissociation energies of $A'^5\Sigma_g^+$.

In this paper, we have studied the electronic state structures of the ground state and the low-lying excited states. We have used the complete active space self-consistent field/multi-reference configuration interaction theory (CASSCF/MRCI) and augmented correlation consistent polarized valence quintuple ζ basis sets (Aug-cc-pV5Z) for single point energy calculations. The dissociation energies D_e, the equilibrium bond distances r_e, the harmonic frequencies ω_e and the analytic potential energy curves (PECs) are fitted to Murrell-Sobie function.

2. Computational details

The electronic structure calculations are performed with the MOLPRO program package [24]. Because of the limitation of the program, all computations of N_2 molecule are performed in the D_{2h} point group.

For the ground state of N_2 molecule, we have used augmented correlation consistent polarized valence n-ζ basis sets, denoted by Aug-cc-pVnZ (n = 3, 4, 5). These augmented basis sets add an extra set of diffuse functions for each angular momentum in the basis set. For each basis set, we have performed CASSCF [25, 26] followed by MRCI [27, 28] calculations of the ground state and nine low-lying excited states for N_2 molecule over a wide range of geometries. In MRCI calculation, all CASSCF configuration state functions (CSFs) are taken as the reference. Then, we choose the best basis set to calculate potential energy function of the nine low-lying excited states.

There are several functions to fit accurate analytical potential energy function (APEF) of diatomic molecule. Murrell-Sorbie (M-S) potential energy function could accurately reproduce interaction potential of diatomic molecule. This function has been applied to many diatomic molecules [29–32]. The M-S function [33] is $V(\rho) = -D_e(1 + a_1\rho + a_2\rho^2 + a_3\rho^3)\exp(-a_1\rho)$, where $\rho = R - R_e$; R_e is the equilibrium bond distances and D_e is the dissociation energy.

The force constants are derived from the parameters of M-S function as.

$$f_2 = D_e(a_1^2 - 2a_2) \tag{1}$$

$$f_3 = 6D_e(a_1 a_2 - a_3 - \frac{a_1^3}{3}) \tag{2}$$

$$f_4 = D_e(3a_1^4 - 12a_1^2 a_2 + 24a_1 a_3) \tag{3}$$

Then, the spectroscopic parameters were,

$$B_e = \frac{h}{8\pi c\mu R_e^2} \tag{4}$$

$$\omega_e = \sqrt{\frac{f_2}{4\pi^2 mc^2}} \tag{5}$$

$$\alpha_e = -\frac{6B_e^2}{\omega_e}\left(\frac{f_3 R_e}{3f_2} + 1\right) \tag{6}$$

$$\omega_e\chi_e = \frac{B_e}{8}\left[-\frac{f_4 R_e^2}{f_2} + 15\left(\frac{\omega_e\chi_e}{6B_e^2} + 1\right)^2\right] \tag{7}$$

From Eqs. (1)–(7), we have derived the spectroscopic constants of diatomic molecule.

3. Results and discussion

3.1. The effect of different basis and methods

Using CASSCF and MRCI methods described above, we investigate the performance of various basis sets (Aug-cc-pVnZ, n = 3, 4, 5) on the spectroscopic parameters of the ground state ($X^1\Sigma_g^+$). Then, we choose the best basis set to calculate the other excited states.

PECs of the ground state using different basis sets and methods of N_2 are shown in Fig. 1. It can be seen that the larger basis sets have lower energies under the same method, and MRCI method has lower energy using the same basis set.

In Table 1, we have compared the equilibrium bond length R_e, the harmonic frequency ω_e and the dissociation energy D_e obtained using CASSCF and MRCI methods for different basis sets. The results of larger basis set are better using the same method, especially D_e, for instance, the result of Aug-cc-pv5z/MRCI 9.908 eV is better than 9.577 and 9.819 eV of Aug-cc-pVnZ (n = 3, 4)/MRCI compared with experimental values 9.9051 eV [22].
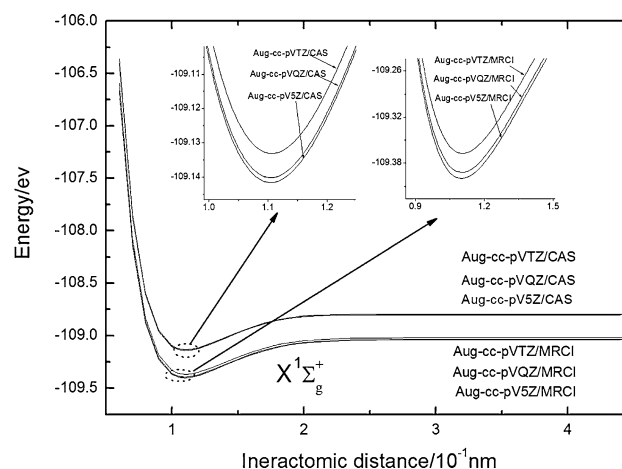

Fig. 1 PECs of the ground state ($X^1\Sigma_g^+$) of N_2 molecule: comparison of different basis sets and methods

3.2. Potential energy curves

PECs and the spectroscopic constants of N_2 ($X^1\Sigma_g^+$, $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $a'^1\Sigma_u^-$, $a^1\Pi_g$, $w^1\Delta_u$, $A'^5\Sigma_g^+$, $G^3\Delta_g$) are computed at MRCI/Aug-cc-pv5z level.

Presently, these singlet, triplet and quintuplet electronic states correlating to the four lowest dissociation limits of N_2 molecule, i.e., $^4S + ^4S$, $^4S + ^2D$, $^4S + ^2P$, $^2D + ^2D$ atomic states, are investigated. The dissociation relationships and electronic configurations of ten valence states of N_2 are listed in Table 2. It is noted that the configuration of ground state is dominated by a closed configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4$; five states ($A^3\Sigma_u^+$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $a'^1\Sigma_u^-$ and $w^1\Delta_u$) have the same configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^3 1\pi_g^1$, as $1\pi_u \rightarrow 1\pi_g$, i.e., a electron excites from $1\pi_u$ to $1\pi_g$ molecular orbit. The configuration of $B^3\Pi_g$ and $a^1\Pi_g$ is $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^1 1\pi_u^4 1\pi_g^1$, as $3\sigma_g \rightarrow 1\pi_g$ excitation. These seven excited states are single orbital excitations from the ground state. The $A'^5\Sigma_g^+$ and $G^3\Delta_g$ states are double excitations from ground state with the configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^2 1\pi_g^2$, as $1\pi_u^2 \rightarrow 1\pi_g^2$, i.e., two electrons excite from $1\pi_u$ to $1\pi_g$ orbit.

The PECs of singlet, triplet and quintuplet electronic states of N_2 molecule correlating with a few lowest dissociation limits are plotted in Fig. 2, while the fitted spectroscopic constants (R_e, ω_e and D_e) of the states are listed in Tables 3 and 4.

3.2.1. Equilibrium bond distances

From Table 3, considering MRCI method, we can see that the equilibrium bond distances R_e of the ground state $X^1\Sigma_g^+$

is in agreement with the experimental values. The obtained value of R_e is 1.09895 Å, which is very close to the experimental value 1.09769 Å by Lofthus et al. [22] and

Table 2 Dissociation relationships and electronic configurations of the calculated states of N_2 molecule

| States	Electronic configurations	Atomic state (N + N)
$X^1\Sigma_g^+$	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4$	$^4S + ^4S$
$A^3\Sigma_u^+$	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^3 1\pi_g^1$	$^4S + ^4S$
$B^3\Pi_g$	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^1 1\pi_u^4 1\pi_g^1$	$^4S + ^2D$
$W^3\Delta_u$	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^3 1\pi_g^1$	$^4S + ^2D$
$B'^3\Sigma_u^-$	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^3 1\pi_g^1$	$^4S + ^2P$
$a'^1\Sigma_u^-$	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^3 1\pi_g^1$	$^2D + ^2D$
$a^1\Pi_g$	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^1 1\pi_u^4 1\pi_g^1$	$^2D + ^2D$
$w^1\Delta_u$	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^3 1\pi_g^1$	$^2D + ^2D$
$A'^5\Sigma_g^+$	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^2 1\pi_g^2$	$^4S + ^4S$
$G^3\Delta_g$	$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^2 1\pi_g^2$	$^4S + ^2D$
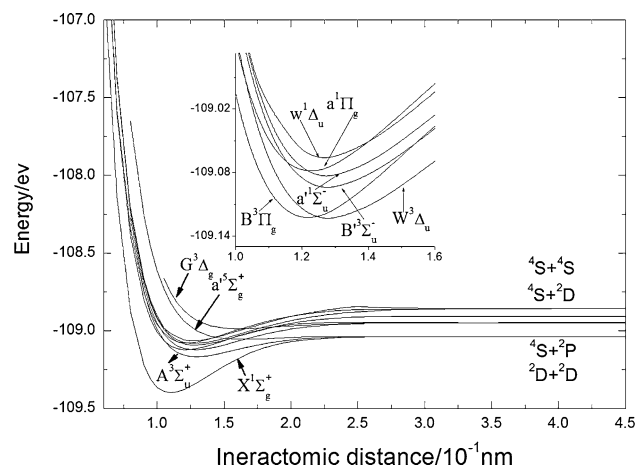
Fig. 2 PECs of the all calculated states of N_2 molecule: at MRCI/Aug-cc-pV5Z level

Table 1 Spectroscopic constants of the ground state ($X^1\Sigma_g^+$) of N_2 molecule: comparison of different basis sets and methods

State	Basis set	R_e (Å)	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})	D_e (eV)
$X^1\Sigma_g^+$	Aug-cc-pvtz(CAS)	1.1014	2477.2	15.69	1.9848	0.016	9.343
	Aug-cc-pvqz(CAS)	1.09999	2469.3	15.67	1.9899	0.0159	9.384
	Aug-cc-pv5z(CAS)	1.09961	2462.1	15.69	1.9906	0.01586	9.42
	Aug-cc-pvtz(MRCI)	1.103	2432.1	15.1	1.979	0.0164	9.577
	Aug-cc-pvqz(MRCI)	1.0999	2423.94	14.87	1.989	0.0162	9.819
	Aug-cc-pv5z(MRCI)	1.09895	2409.87	14.83	1.9936	0.01612	9.908
	Expt[a]	1.0977	2359	14.456	1.99823	0.017292	9.9051
	Expt[b]	1.0977	2358.6	14.324	1.99824	0.017318	

[a] [22]

[b] [23]

Table 3 Equilibrium bond distances R_e for the ten states of the N_2 molecule (in Å)

	$X^1\Sigma_g^+$	$A^3\Sigma_u^+$	$B^3\Pi_g$	$W^3\Delta_u$	$B'^3\Sigma_u^-$	$a'^1\Sigma_u^-$	$a^1\Pi_g$	$w^1\Delta_u$	$A'^5\Sigma_g^+$	$G^3\Delta_g$
Present[a]	1.09961	1.2906	1.2122	1.2819	1.2833	1.2904	1.2345	1.2783	1.6143	1.635
Present[b]	1.09895	1.2922	1.2123	1.2781	1.2773	1.2819	1.2265	1.2694	1.6106	1.6054
Present[c]	1.099	1.2855	1.213	1.2786	1.2779	1.276	1.224	1.2688	1.6068	1.609
Cal[d]	1.106	1.299	1.227	1.291	1.292	1.291	1.238	1.282	1.673	1.636
Cal[e]	1.096	1.278	1.213	1.274	1.275	1.271	1.224	1.264	1.595	1.585
Cal[f]	1.1128	–	–	–	–	1.2639	1.2214	1.2587	–	–
Cal[g]	1.1019	1.2927	1.218	1.2854	1.2838	1.2807	1.2266	1.2737	–	1.6201
Cal[h]	1.1016	1.2916	1.2174	1.284	1.2825	1.2804	1.2261	1.2734	–	1.6187
Cal[i]	1.1091	1.3013	1.2289	1.2908	1.2929	1.2855	1.2326	1.2791	–	1.615
Cal[j]	1.0919	1.2818	1.2167	1.2775	1.2802	1.2754	1.2204	1.2696	–	1.5769
Cal[k]	–	–	–	–	–	1.278	1.225	1.271	–	1.615
Expt	1.0977[l]	1.2866[l]	1.2126[l]	1.2797[m]	1.2784[l]	1.2754[l]	1.2203[l]	1.2688[l]	–	1.6107[l]
Expt	1.0977[n]	1.2866[n]	1.2126[n]	–	1.2784[n]	1.2755[n]	1.2203[n]	1.268[n]	(1.55)[m]	1.6107[n]

[a] Present work, CASSCF calculations using Aug-cc-pv5z basis set

[b] Present work, MRCI calculations using Aug-cc-pv5z basis set

[c] Present work, MRCI calculations using CBS basis set

[d] [15] using first-order wave functions

[e] [15] single- and double-replacement method

[f] [16] at CCSD/cc-pVDZ level

[g] [17] at MR-AQCC/cc-pVQZ level

[h] [17] at MR-CISD/cc-pVQZ level

[i] [18] at MC/aug-cc-pVDZ level

[j] [18] at VWN-2/aug-cc-pVDZ level

[k] [19] at MRCI/aug-cc-pVQZ level

[l] [22]

[m] [34]

[n] [23]

1.09768 Å by Herzberg et al. [23]. The five states ($A^3\Sigma_u^+$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $a'^1\Sigma_u^-$, $w^1\Delta_u$) come from the excited electronic configurations $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^3 1\pi_g^1$. In principle, the five $1\pi_u^3 1\pi_g^1$ states A, W, B', A', and w should have the similar equilibrium bond distances, because they result from the same electronic configuration, for instance, 1.29217 Å of $A^3\Sigma_u^+$, 1.27807 Å for $W^3\Delta_u$, 1.27728 Å for $B'^3\Sigma_u^-$, 1.28193 Å for $a'^1\Sigma_u^-$ and 1.28224 Å for $w^1\Delta_u$. The errors were only 0.001 Å −0.015 Å. In the same agreement, equilibrium bond distances of (B, a) and (A', G) are similar, respectively. The difference of R_e obtained from CASSCF/MRCI method is not too large. The result of $G^3\Delta_g$ seems a big large (about 0.03 Å). The error is 1.86 %, close to experimental values of 1.6107 Å by Lofthus [22] and Herzberg [23]. Overall, at MRCI level, the equilibrium distances of the various singlet, triplet and quintuplet states of N_2 are in very good agreement with the experimental data. On the other hand, the value of R_e are also very similar that obtained by other authors [15–19].

The experimental value of $A'^5\Sigma_g^+$ quintuplet electronic states was not surely, about 1.55 Å in this paper. The value was 1.6143 and 1.6106 Å at CASSCF and MRCI level, and the errors were only 4.15 and 3.9 %, respectively.

3.2.2. Harmonic frequencies and dissociation energies

Though, the equilibrium bond distances R_e of N_2 molecule are very similar using two methods (CASSCF and MRCI). From Table 4, we can easily find that the big errors of harmonic frequencies ω_e and dissociation energies D_e are obtained between CASSCF and MRCI calculations. Considering with D_e, The D_e of CASSCF is smaller than that of MRCI, the absolute error are 0.998, 0.792, 0.682, 0.845, 0.57, 0.791, 0.464 eV for $A^3\Sigma_u^+$, $B^3\Pi_g$, $W^3\Delta_u$, $B'^3\Sigma_u^-$, $a'^1\Sigma_u^-$ and $w^1\Delta_u$ states, the relative errors to MRCI being 27.8, 16.8, 14.1, 16.2, 9.25, 12.8 %, respectively. Similar to R_e, we can find that the results of ω_e obtained from the two methods are similar; the errors are smaller than 3 %.

Table 4 Harmonic frequencies ω_e (cm^{-1}) and dissociation energies D_e (eV) for the calculated states of the N_2 molecule

States	Spectroscopic constants	This work	Other work	Expt
$X^1\Sigma_g^+$	ω_e	2332.1[a], 2377.2[b], 2356.4[c]	2323[d]; 2337[e]; 2342[f]; 2292[g]; 2381[h]	2359[j]; 2358.6[k]
	D_e	9.908[a], 9.42[b], 9.903[c]	8.74[d]; 9.22[g]; 10.79[h]	9.9051[k]
$A^3\Sigma_u^+$	ω_e	1461.8[a], 1499.3[b], 1461.2[c]	1436[f]; 1445[f]; 1431[g]; 1515[h]	1461[j]; 1460.37[k]
	D_e	3.588[a], 2.59[b], 3.637[c]	2.8[g]; 4.01[h]	3.6806[k]
$B^3\Pi_g$	ω_e	1737.1[a], 1781.6[b], 1735.4[c]	1716[e]; 1720[f]; 1665[g]; 1709[h]	1733[j]; 1734.11[k]
	D_e	4.691[a], 3.899[b], 4.827[c]	4.1[g]; 4.89[h]	4.8967[k]
$W^3\Delta_u$	ω_e	1539.2[a], 1540.2[b], 1530.8[c]	1489[e]; 1496[f]; 1484[g]; 1534[h]	1507[j]; 1501[k]
	D_e	4.832[a], 4.15[b], 4.85[c]	4.05[g]; 4.94[h]	4.87[k]
$B'^3\Sigma_u^-$	ω_e	1539.7[a], 1547[b], 1529.3[c]	1502[e]; 1509[f]; 1469[g]; 1520[h]	1517[j]; 1516.88[k]
	D_e	5.231[a], 4.386[b], 5.23[c]	4.29[g]; 5.07[h]	5.264[k]
$a'^1\Sigma_u^-$	ω_e	1527.2[a], 1506.1[b], 1530.7[c]	1512[d]; 1514[e]; 1517[f]; 1505[g]; 1538[h]; 1523.6[i]	1530[j]; 1530.25[k]
	D_e	6.16[a], 5.59[b], 6.18[c]	5.71[d]; 5.48[g]; 6.08[h]	6.22[k]
$a^1\Pi_g$	ω_e	1693.6[a], 1795.9[b], 1694.2[c]	1686[d]; 1676[e]; 1691[f]; 1666[g]; 1719[h]; 1687.5[i]	1694[j]; 1694.2[k]
	D_e	6.059[a], 5.686[b], 6.12[c]	5.75[d]; 5.72[g]; 6.06[h]	6.16[k]
$w^1\Delta_u$	ω_e	1525.7[a], 1607.7[b], 1531.1[c]	1546[d]; 1544[e]; 1545[f]; 1583[g]; 1597[h]; 1559.1[i]	1559[j]; 1559.26[k]
	D_e	5.88[a], 5.31[b], 5.86[c]	5.26[d]; 5.45[g]; 6.03[h]	5.73[k]
$A'^5\Sigma_g^+$	ω_e	656.71[a], 658.05[b], 655.4[c]	–	(650)[j]
	D_e	0.4025[a], 0.3539[b], 0.4039[c]	–	
$G^3\Delta_g$	ω_e	734.57[a], 631.25[b], 740.3[c]	750[e]; 731[f]; 732[g]; 854[h]; 749.6[i]	766[j]; 742.29[k]
	D_e	1.101[a], 0.537[b], 1.109[c]	0.55[g]; 1.08[h]	1.39[k]

[a] Present work, MRCI calculations using Aug-cc-pv5z basis set

[b] Present work, CASSCF calculations using Aug-cc-pv5z basis set

[c] Present work, MRCI calculations using CBS basis set

[d] [16]: at FCI/cc-pVDZ level

[e] [17]: at MR-AQCC/cc-pVQZ level

[f] [17]: at MR-CISD/cc-pVQZ level

[g] [18]: at MC/aug-cc-pVDZ level

[h] [18]: at VWN-2/aug-cc-pVDZ level

[i] [19]: at MRCI/aug-cc-pVQZ level

[j] [22]

[k] [23]

ω_e and D_e of MRCI calculations in good agreement with experimental values [22, 23]. For example, the calculated dissociation energies D_e of ground state $X^1\Sigma_g^+$ is 9.908 eV using MRCI method, but 9.42 eV using CASSCF method, compared with experimental data of 9.9051 by Lofthus [22], the relative errors being 0.03 and 4.89 %, respectively.

Our results with MRCI method are better than other works [15–19] compared with the available experimental data. For instance, the D_e values are in good agreement with those of Larsen et al. [16] whose D_e values are too short for these states ($X^1\Sigma_g^+$, $a'^1\Sigma_u^-$, $a^1\Pi_g$ and $w^1\Delta_u$), the ground state is 1.15 eV which is smaller than experimental value reported of Lofthus [22], the other states being 0.4–0.5 eV smaller. There is no available experimental data of the $A'^5\Sigma_g^+$ state. Based on the reliable data, we have calculated the D_e and ω_e are 656.71 cm^{-1} and 0.4025 eV. The value of ω_e is only 6.7 cm^{-1} bigger than dubious experimental data of 650 cm^{-1}.

4. Conclusions

In this paper, The potential energy curves (PECs) and the spectroscopic constants of the ground state $N_2 X^1\Sigma_g^+$ molecule were computed using the CASSCF/MRCI method and Aug-cc-pVnZ (n = 3, 4, 5) basis sets. Compared with experimental data, we find that the MRCI method in combination with Aug-cc-pV5Z basis set can be utilized to produce the reliable dissociation energy calculation of the

ground state. The same level (MRCI/Aug-cc-pV5Z) is applied in the other excited states. Compared with experimental data for each state, the results of MRCI calculations are much better than those of CASSCF, especially the dissociation energy De. Based on the reliable data, at MRCI level, we calculated the $A'^5\Sigma_g^+$ state, the harmonic frequencies ω_e is 656.71 cm^{-1}, which is only 6.7 cm^{-1} bigger than dubious experimental data 650 cm^{-1}. We have predicted the dissociation energy D$_e$ is 0.4025 eV.

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