Spectroscopic investigations on $NO^+(X^1\Sigma^+, a^3\Sigma^+, A^1\Pi)$ ion using multi-reference configuration interaction method and correlation-consistent sextuple basis set augmented with diffuse functions*

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Three low-lying electronic states ($X^1\Sigma^+$, $a^3\Sigma^+$, and $A^1\Pi$) of NO^+ ion are studied using the complete active space self-consistent-field (CASSCF) method followed by highly accurate valence internally contracted multi-reference configuration interaction (MRCI) approach in combination of the correlation-consistent sextuple basis set augmented with diffuse functions, aug-cc-pV6Z. The potential energy curves (PECs) of the $NO^+(X^1\Sigma^+, a^3\Sigma^+, A^1\Pi)$ are calculated. Based on the PECs, the spectroscopic parameters R_e, D_e, ω_e, $\omega_e\chi_e$, α_e, B_e, and D_0 are reproduced, which are in excellent agreement with the available measurements. By numerically solving the radial Schrödinger equation of nuclear motion using the Numerov method, the first 20 vibrational levels, inertial rotation and centrifugal distortion constants of $NO^+(X^1\Sigma^+, a^3\Sigma^+, A^1\Pi)$ ion are derived when the rotational quantum number J is equal to zero ($J = 0$) for the first time, which accord well with the available measurements. Finally, the analytical potential energy functions of these states are fitted, which are used to accurately derive the first 20 classical turning points when $J = 0$. These results are compared in detail with those of previous investigations reported in the literature.

Keywords: spectroscopic parameter, vibrational level, inertial rotation constant, centrifugal distortion constant

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1. Introduction

The nitric oxide cation (NO^+) is one of the most stable diatomic ions (D_e = 11.0 eV).[1] On the one hand, the exceptional stability of NO^+ makes it one of the most abundant species in the thermosphere and one of the most active ions in atmospheric reaction cycles at lower altitudes;[2−4] on the other hand, it plays an important role as a major source and sink in the thermosphere and also plays a critical role in the energy balance of the thermosphere. NO^+ is the terminal ion in the E-region and as such becomes the dominant positive ion during the day in the lower thermosphere below ∼170 km. For this reason, the detailed spectroscopic investigation of NO^+ is of interest to plasma and atmospheric science. But in contrast to its isoelectronic neutral counterparts N_2 and CO, little spectroscopic information has been obtained about the electronic structure of NO^+, mainly because of the difficulty in studying its band systems in the absorption spectra. The majority of our understanding of the electronic structure of NO^+ comes from high-resolution photoelectron spectroscopy of NO[5−8] and *ab initio* calculations.

In the late 1970s, Albritton *et al.*[1] collected the entire theoretical and experimental knowledge towards understanding its electronic structure. They discussed the potential energy curves (PECs) of the electronic states below 20 eV. A list of constants on the NO^+ ion spectroscopy up to 1979 is given by Huber and Herzberg.[9] In the recent thirty years, the spectroscopic properties of NO^+ have been widely investigated, both experimentally[10−16] and theoretically.[17−29] In experiment, the vibrational structures of valence-ionized $5\sigma^{-1}2\pi(^{1,3}\Pi)$ and $1\pi^{-1}2\pi(^{1,3}\Sigma^{\pm}, \Delta)$ states of NO^+ ion including the $A^1\Pi$, $X^1\Sigma^+$, and $a^3\Sigma^+$ were studied in numerous papers by photoelectron spectroscopy (PES),[11−13] photoabsorption/photoionization spectroscopy (see, e.g.,

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Ref. [14] and references herein) and pulsed field ionization photoelectron (PFI-PE) spectra.[15,16] And the spectroscopic parameters have also been obtained. In theory, a number of *ab initio* computations have been performed to reproduce the PECs of some electronic states[17] of the ion. A number of electric dipole functions and spectroscopic parameters have been obtained for the ground[17−29] and several low-lying electronic states.[17,24,26,27,29] To our knowledge, there are no complete theoretical investigations on its vibrational manifolds to this day. This shortage prevents us from adequately understanding the experimental values. Therefore, it is an urgent task to perform credible *ab initio* calculations for the NO^+ ion.

In the present work, we investigate three electronic states of the ions: $X^1\Sigma^+$, $a^3\Sigma^+$, and $A^1\Pi$. The spectroscopic parameter and vibrational manifold calculations are performed for each electronic state. The PECs of three electronic states ($X^1\Sigma^+$, $a^3\Sigma^+$, and $A^1\Pi$) of NO^+ are evaluated using the highly accurate valence internally contracted multireference configuration interaction (MRCI) approach[30,31] together with the largest correlation-consistent sextuple basis set augmented with diffuse functions, aug-cc-pV6Z of Dunning and co-workers[32−34] in the valence range. Based on PECs, by solving the radial Schrödinger equation of nuclear motion in the adiabatic approximation with the Numerov method,[35] the molecular properties of three electronic states of the NO^+ are calculated and compared with the results obtained in previous studies. As a whole, the present investigations provide more complete and accurate theoretical predictions on the NO^+($X^1\Sigma^+$, $a^3\Sigma^+$, $A^1\Pi$) molecular constants to this day.

2. Computational details

All the calculations are made with the full valence complete active space self-consistent field (CASSCF) method[36] followed by the highly accurate valence internally contracted MRCI approach.[30,31] A full configuration interaction (CI) exactly solves the Schrödinger equation within some basis sets, but is usually too complex a calculation to compute molecules containing more electrons. The single reference methods can almost always be done and usually are not very challenging (to the computer or the user), however, their accuracies are limited. MRCI is a way to systematically include the configuration state functions (CSFs) that contribute most significantly to the correlation energy study.[37] It is accurate enough in treating small systems, especially dimmers.

The present calculations are performed with the MOLPRO 2008.1 package.[38] The one electron correlation-consistent basis set of Dunning and coworkers[32−34] is used throughout the present work. In particular, for the N and O atoms, the spdfghi aug-cc-pV6Z basis set is employed, which means (16s, 10p, 5d, 4f, 3g, 2h, 1i) → [7s, 6p, 5d, 4f, 3g, 2h, 1i] for N and O. Generally speaking, on the one hand, the larger the basis set used, the closer to the experimental results are the spectroscopic parameters determined at this basis set; on the other hand, the diffuse functions can improve the description of long-range interactions. More accurate interaction potential can be obtained at larger internuclear separations at such a basis set. Therefore, we choose the PECs obtained at the basis set, aug-cc-pV6Z, for the further calculation of spectroscopic parameters and molecular constants in the present work. We also believe that the very large basis sets, coupled with the effectiveness of the high-quality *ab initio* quantum chemical method MRCI procedure in treating the electron correlation, can give reliable PECs.

With the aid of module VIBROT in MOLCAS 7.4 program package,[39] the spectroscopic parameters R_e, D_e, ω_e, $\omega_e\chi_e$, α_e, B_e, and D_0, and the first 20 vibrational levels $G(\upsilon)$, inertial rotation constants B_υ and centrifugal distortion constants D_υ of the $X^1\Sigma^+$, $a^3\Sigma^+$, and $A^1\Pi$ electronic states are calculated using the PECs obtained here. And finally, the classical turning points (R_{min} and R_{max}) are determined with self-programming. All the calculations are carried out on our supercomputer Dawning TC4000A.

3. Results and discussion

3.1. Spectroscopic parameters

The PECs for the NO^+($X^1\Sigma^+$, $a^3\Sigma^+$, $A^1\Pi$) ion are obtained at MRCI theoretical level with basis set aug-cc-pV6Z for N and O. The cation interaction energies are generated in 0.005-nm interval. In order to display the equilibrium positions and the dissociation energies of the three states accurately, their values are determined from the PECs by interpolation, which is carried out with VIBROT module of MOLCAS program package. The results are collected in Table 1. Based on the reliable PECs, we determine their intact spectroscopic constants also with VIBROT module. The spectroscopic constants as well as the available experimental results[1,9,13,15,16] and other theoretical results[17,20−29] are also listed in Table 1.

Table 1. Spectroscopic parameter comparisons between available measurements and other calculations for $NO^+(X^1\Sigma^+, a^3\Sigma^+, A^1\Pi)$ at the MRCI/aug-cc-pV6Z level of theory.

	Source	D_e/eV	R_e/nm	ω_e/cm^{-1}	$\omega_e\chi_e$/cm^{-1}	B_e/cm^{-1}	α_e/cm^{-1}	D_0/eV
$X^1\Sigma^+$								
	This work	11.0754	0.10650	2375.17	16.1000	1.99059	0.01856	10.9286
	Exp[13]		0.10632	2376.72	16.255	1.9972	0.01879	10.693±0.231
	Exp[16]			2382.997	17.4378	1.9966	0.02010	
	Exp[1,9]	10.997	0.10632	2376.72	16.262	1.99727	0.01889	10.8506
	Theory[20]		0.1061	2415	16	2.005	0.018	10.17
	Theory[21]		0.10568	2466.5	16.82		0.01834	
	Theory[22]		0.1096	2262				
	Theory[23]	10.97	0.1069	2359				
	Theory[17]		0.10748	2322				
	Theory[24]		0.1066	2354				
	Theory[25]		0.1068	2368				10.70
	Theory[26]		0.10658	2369	20.2082	1.98748	0.01836	
	Theory[27]		0.10636	2362	16.2	1.99		
	Theory[28]	10.889	0.10637	2374	16.30	2.000	0.0188	
	Theory[29]		0.1070	2367	16.7			10.64
$a^3\Sigma^+$								
	This work	4.5301	0.12903	1295.51	14.9431	1.35609	0.01993	4.4502
	Exp[13]		0.12810	1303.07	15.158	1.3750	0.02020	
	Exp[15]			1295.2	15.198	1.3562	0.0221	
	Exp[1,9]	—	0.1284	1293	15.1	1.369	0.0192	4.452
	Theory[17]		0.13002	1209				
	Theory[24]		0.1289	1318				
	Theory[26]		0.12946	1275	18.0128	1.34710	0.02106	
	Theory[27]		0.12707	1283	19.2	1.37		
	Theory[29]		0.1298	1273	15.3			4.27
$A^1\Pi$								
	This work	2.7659	0.11951	1602.23	20.1708	1.58122	0.02301	2.6672
	Exp[13]		0.11938	1601.92	20.207	1.5840	0.02219	
	Exp[1,9]	—	0.11931	1601.93	20.207	1.5860	0.0245	2.705
	Theory[17]		0.12060	1654				
	Theory[24]		0.1201	1469				
	Theory[26]		0.11984	1580	22.4723	1.57202	0.02335	
	Theory[27]		0.12012	1548	24.4	1.57		
	Theory[29]		0.1203	1567	16.5			2.58

From Table 1, we can find that a number of theoretical spectroscopic investigations[17,20–29] have been made for the ground state of the ion. Of these investigations, Werner and Rosmus[20] performed the $NO^+(X^1\Sigma^+)$ spectroscopic calculations using the multi-configuration-self-consistent field (MCSCF) potential energy function. As can be seen in Table 1, some spectroscopic constants, especially D_0 and ω_e, were not obtained in a comparable accuracy. Peterson and Wood[21] calculated some spectroscopic parameters by five approaches. In Table 1, we list their best results obtained by the MΦller–Plesset many-body perturbation theory through MP4DQ (fourth order with double and quadruple substitutions). Basis sets of 66 contracted Gaussian-type orbitals (CGTO's) consisted of (11s, 7p, 2d) contracted to [8, 5, 2] on each atom were used. Unfortunately, the ω_e of the $NO^+(X^1\Sigma^+)$ was too large when compared with measurements,[1,9,13,16] and the important constants, B_e and D_e, were not evaluated. Several theoretical spectroscopic investigations[17,22,24] obtained only R_e and ω_e values. Obviously, other spectroscopic parameters, such as D_e, $\omega_e\chi_e$, B_e, α_e, and D_0, were not derived in their work. Partridge *et al.*[23] performed the D_e, R_e, and ω_e calculations by the averaged coupled-pair functional (ACPF) method with

the [5s4p3d2f1g] basis set. Fehér and Martin[25] carried out the R_e, ω_e and D_0 calculations at Hartree–Fock, CASSCF, MR–CI and MP2 levels using an [8s6p3d] basis set. By comparison, one can find that the favourable results were obtained by the CASSCF approach. Palmieri *et al.*[26] performed the CASSCF/MRICCI calculations for the spectroscopic constants. Hutter *et al.*[27] calculated the spectroscopic constants using the SCF/MRD-CI method with a (13, 8, 5, 4)/[8, 4, 2, 1] basis set for N and a (13, 8, 6, 4)/[7, 5, 2, 1] basis set for O. As shown in Table 1, their results[23,25−27] are inferior to ours when compared with the measurements[1,9,13,16] as a whole.

Recently, to investigate molecular properties, Polák and Fišer[28] used the internally contracted multi-reference configuration interaction (icMRCI) level with augmented correlation-consistent basis sets. The best results were determined by icMRCI+Q method combined with the aug-cc-pCV5Z basis set. To our knowledge, these spectroscopic results are the most complete to this day. However, on the one hand, some spectroscopic parameters, such as D_e, ω_e, and B_e, are inferior to the present ones when compared with the available measurements;[1,9,13,16] on the other hand, some molecular constants, such as vibrational levels, inertial rotation and centrifugal distortion constants, were not yet computed in their investigations. Ehresmann *et al.*[29] used the MCSCF method with a triple-zeta valence basis set to investigate the spectroscopic properties. However, limited parameters were still calculated. Therefore, the present investigation for the ground state of the NO^+ is the most complete and accurate up to now when compared with these previous theories.

For the $a^3\Sigma^+$ and $A^1\Pi$ electronic states, fewer theoretical spectroscopic investigations[17,24,26,27,29] have been carried out. Partridge *et al.*[17] used the MRCI approach with the (13s8p6d4f)/[4s3p2d1f] atomic natural orbital (ANO) basis set to obtain the R_e and ω_e values. Manaa and Yarkony[24] also performed only the R_e and ω_e calculations by the second order CI (SOCI) expansions combined with the (14s8p2d|8s5p2d) contracted Gaussian basis set. Among the spectroscopic parameters, however, only R_e and ω_e values were calculated in their investigations.[17,24] Afterwards, Palmieri *et al.*[26] performed the CASSCF/MRICCI calculations for the spectroscopic parameters. However, this method did not yield sufficiently accurate values. Taking the ω_e as an example, the deviations from the measurements[13] are 2.15% for the $a^3\Sigma^+$ and 1.37% for $A^1\Pi$ electronic states. Very recently, Hutter *et al.*[27] and Ehresmann *et al.*[29] also performed the spectroscopic calculations of $a^3\Sigma^+$ and $A^1\Pi$ electronic states of the NO^+ ion. However, on the one hand, their results[28,29] are inferior to the present ones when compared with the measurements;[13] on the other hand, their investigations are not complete.

From the above discussion, it is easy to find that the present spectroscopic investigations are more accurate and complete than those obtained by previous theories.[17,20−29] From Table 1, on the one hand, we see that these spectroscopic parameters, such as R_e, D_e, ω_e, $\omega_e\chi_e$, α_e, B_e, and D_0, are in excellent agreement with the available measurements.[1,9,13,15,16] For the ground state of the NO^+ ion, the percent errors from the measurements[13] are only 0.17% for the R_e, 0.07% for the ω_e, 0.95% for the $\omega_e\chi_e$ and 0.66% for the B_e.

As to the ω_e, B_e, and α_e of the $a^3\Sigma^+$ electronic state, different experiments[1,9,13,15] gave different results and the differences among these measurements[1,9,13,15] are very large as can be seen in Table 1. This makes it difficult for us to accurately compare the present values with them. However, on the one hand, the present basis set, aug-cc-pV6Z, is a very large one; on the other hand, the MRCI is a way to systematically include the CSFs that contribute most significantly to the correlation energy study. It has been proved that this method is especially accurate in treating small diatomic systems. As a result, we have reason to believe that the spectroscopic parameters obtained here are reliable and accurate. For example, for the $A^1\Pi$ electronic state, the percent errors from the measurements[13] are only 0.11% for the R_e, 0.02% for the ω_e, 0.18% for the $\omega_e\chi_e$ and 0.18% for the B_e. The percent errors from the measurements[1,9] are also only 0.17% for the R_e, 0.02% for the ω_e, 0.18% for the $\omega_e\chi_e$ and 0.30% for the B_e. The α_e value determined by the present calculation is between measurements given in Refs. [1], [9], and [13]. The deviation of the calculated D_0 from the experimental data[1,9] is only 0.0378 eV, which is much smaller than the result, 0.125 eV, obtained by Ehresmann *et al.*[29]

3.2. Vibrational manifolds

Based on the PECs obtained here, by solving the Schrödinger equation of the nuclear motion with VIBROT module, we determine the first 20 vibrational levels $G(\upsilon)$, inertial rotation constants B_υ and centrifugal distortion constants D_υ of the $NO^+(X^1\Sigma^+, a^3\Sigma^+, A^1\Pi)$ ion when $J = 0$. Here, we collect the $G(\upsilon)$ from experiments[13] and other theories[20,21,24]

of the $X^1\Sigma^+$ and $a^3\Sigma^+$ electronic states in Tables 2 and 3, respectively. We tabulate the $G(\upsilon)$, B_υ and D_υ from the available measurements[13,10] for $NO^+(A^1\Pi)$ in Table 4. The B_υ and D_υ of the $NO^+(X^1\Sigma^+, a^3\Sigma^+)$ as well as the available measurements[1,15,16] are listed in Table 5.

To our knowledge, in experiment, only Reddy *et al.*[13] determined the G_υ values when $\upsilon = 0, 1, 2, \ldots, 7$ for the $NO^+(X^1\Sigma^+, a^3\Sigma^+, A^1\Pi)$ ion. These results are listed in Tables 2, 3, and 4, respectively. Jarvis *et al.*[15,16] obtained the B_υ values for the $X^1\Sigma^+$ and $a^3\Sigma^+$ electronic states of the NO^+ ion. For the convenience of comparison, we collect these values in Table 5. Cosby and Helm[10] evaluated the B_υ and D_υ values of the $A^1\Pi$ electronic state when $\nu = 3$. In theory, Werner and Rosmus[20] and Peterson and Woods[21] performed the G_υ calculations when $\nu \leq 5$ for the $X^1\Sigma^+$ state. Manaa and Yakony[24] carried out the G_υ calculations when $\nu \leq 4$ for the $a^3\Sigma^+$ states. Their results[10,20,21,24] are also collected in the corresponding tables.

The present $G(\upsilon)$ results in Tables 2, 3 and 4 conform almost perfectly to the measurements.[13] Taking the ground state $X^1\Sigma^+$ for example, the percent errors from the corresponding experiments are only 0.067%, 0.058%, 0.049%, 0.042%, 0.036%, 0.029%, 0.024%, and 0.020% for the $G(\upsilon)$ when $\upsilon = 0, 1, 2, \ldots, 7$, respectively. It is to be noted that percentage error decreases as the vibrational level increases. From Table 2, we also find that all of these values are better than other calculations.[20,21] It is similar to the findings of the $a^3\Sigma^+$ and $A^1\Pi$ excited states. According to these, we believe that the remaining $G(\upsilon)$ results in Tables 2, 3 and 4 are also reliable and accurate.

For the B_υ, the experimental results of the $NO^+(X^1\Sigma^+, a^3\Sigma^+)$ ion can be found in Refs. [15] and [16] to our knowledge. The values in Ref. [1], listed in Table 5, are also found in Refs. [15] and [16]. By comparison, we can conclude that the present theories agree well with these experiments.[1,15,16] For example, the deviations of the $X^1\Sigma^+$ state from the experimental ones[16] are only 0.327%, 0.323%, 0.324%, 0.329%, 0.340%, 0.176%, 0.635%, 0.626%, 0.661%, 0.588%, 0.633%, 0.616%, 0.535%, 0.504%, 0.464%, 0.415%, 0.176%, 0.286%, 0.144%, and 0.737% for the B_υ when υ from 0 to 19, respectively. The largest deviation of the $a^3\Sigma^+$ state from the experimental one[15] is 0.01995 cm^{-1} at most. Only one group of experimental results for the B_υ and D_υ of the $NO^+(A^1\Pi)$ ion can be found. The percentage errors in B_υ and D_υ are only 0.198% and 0.431% when $\upsilon = 3$, respectively.

Table 2. Comparisons of vibrational levels and classical turning points between this work and other experiments and theories for $NO^+(X^1\Sigma^+)$ when $J = 0$ at the MRCI/aug-cc-pV6Z level of theory.

υ	$G(\upsilon)/cm^{-1}$				R_{min}/nm		R_{max}/nm	
	This work	Exp.[13]	Theory[21]	Theory[20]	This work	Exp.[13]	This work	Exp.[13]
0	1183.51	1184.3	1229	1204	0.10240	0.1022	0.11110	0.1109
1	3526.47	3528.5	3662	3587	0.09969	0.0995	0.11484	0.1147
2	5837.32	5840.2	6061	5938	0.09795	0.0977	0.11761	0.1175
3	8115.99	8119.4	8427	8257	0.09660	0.0963	0.12001	0.1199
4	10362.42	10366.1	10759	10544	0.09549	0.0953	0.12219	0.1221
5	12576.55	12580.2	13057	12799	0.09453	0.0943	0.12423	0.1241
6	14758.32	14761.9			0.09369	0.0934	0.12617	0.1261
7	16907.67	16911			0.09293	0.0926	0.12805	0.1280
8	19024.54				0.09225		0.12987	
9	21108.86				0.09162		0.13166	
10	23160.59				0.09104		0.13341	
11	25179.65				0.09051		0.13515	
12	27165.99				0.09001		0.13687	
13	29119.54				0.08954		0.13859	
14	31040.25				0.08910		0.14030	
15	32928.05				0.08869		0.14201	
16	34782.89				0.08830		0.14372	
17	36604.70				0.08793		0.14545	
18	38393.43				0.08758		0.14718	
19	40149.00				0.08724		0.14893	

Table 3. Comparisons of vibrational levels and classical turning points between this work and other experiments and theories for $NO^+(a^3\Sigma^+)$ when $J = 0$ at the MRCI/aug-cc-pV6Z level of theory.

υ	$G(\upsilon)/cm^{-1}$			R_{min}/nm			R_{max}/nm		
	This work	Exp.[13]	Theory[24]	This work	Exp.[13]	Theory[26]	This work	Exp.[13]	Theory[26]
0	648.42	647.7	647.7	0.12361	0.1231	0.12395	0.13535	0.1349	0.13592
1	1920.51	1920.5	1920.4	0.12013	0.1206	0.12041	0.14068	0.1412	0.14139
2	3160.11	3162.9	3162.8	0.11794	0.1194	0.11820	0.14477	0.1464	0.14553
3	4367.81	4375	4374.9	0.11628	0.1188	0.11651	0.14837	0.1510	0.14916
4	5544.20	5556.9	5556.7	0.11492	0.1186	0.11513	0.15173	0.1555	0.15249
5	6689.88	6708.3		0.11377	0.1186	0.11396	0.15493	0.1599	0.15564
6	7805.44	7829.5		0.11276	0.1189		0.15804	0.1643	
7	8891.47	8920.4		0.11187	0.1193		0.16108	0.1686	
8	9948.57			0.11107			0.16409		
9	10977.32			0.11034			0.16707		
10	11978.33			0.10967			0.17004		
11	12952.19			0.10906			0.17300		
12	13899.48			0.10849			0.17596		
13	14820.81			0.10797			0.17893		
14	15716.77			0.10748			0.18190		
15	16587.95			0.10702			0.18488		
16	17434.94			0.10659			0.18787		
17	18258.33			0.10618			0.19087		
18	19058.73			0.10580			0.19388		
19	19836.72			0.10544			0.19689		

Table 4. Comparisons of vibrational levels, classical turning points, inertial rotation constants B_υ and centrifugal distortion constants D_υ between this work and other experiments for NO^+ $(A^1\Pi)$ when $J = 0$ at the MRCI/aug-cc-pV6Z level of theory.

υ	$G(\upsilon)/cm^{-1}$		R_{min}/nm		R_{max}/nm		B_υ/cm^{-1}		$D_\upsilon(\times10^{-5})/cm^{-1}$	
	This work	Exp.[13]	This work	Exp.[13]	This work	Exp.[13]	This work	Exp.[10]	This work	Exp.[10]
0	795.63	795.9	0.11467	0.1144	0.12517	0.1251	1.56971		0.62323	
1	2358.78	2357.4	0.11154	0.1112	0.12998	0.1299	1.54660		0.63688	
2	3881.76	3878.5	0.10957	0.1092	0.13373	0.1336	1.52273		0.65478	
3	5361.35	5395.2	0.10808	0.1076	0.13710	0.1368	1.49798	1.50095	0.67638	0.67931
4	6794.29	6799.5	0.10686	0.1064	0.14030	0.1398	1.47215		0.70275	
5	8177.37	8199.3	0.10582	0.1053	0.14342	0.1427	1.44504		0.73702	
6	9507.35	9558.7	0.10493	0.1043	0.14653	0.1455	1.41637		0.77651	
7	10780.98	10877.8	0.10415	0.1034	0.14967	0.1482	1.38578		0.83022	
8	11995.04		0.10346		0.15289		1.35290		0.89119	
9	13146.28		0.10285		0.15621		1.31726		0.97510	
10	14231.49		0.10230		0.15969		1.27837		0.10817	
11	15247.41		0.10182		0.16335		1.23573		0.12044	
12	16190.82		0.10138		0.16726		1.18897		0.13551	
13	17058.48		0.10100		0.17149		1.13789		0.15369	
14	17847.15		0.10066		0.17613		1.08272		0.17294	
15	18553.60		0.10036		0.18129		1.02407		0.19473	
16	19174.60		0.10011		0.18714		0.96305		0.21577	
17	19706.91		0.09990		0.19386		0.90103		0.23571	
18	20147.30		0.09973		0.20157		0.83929		0.25399	
19	20492.52		0.09959		0.20996		0.77878		0.27122	

Table 5. Comparisons of inertial rotation constants B_υ and centrifugal distortion constants D_υ between this work and other experiments for the $NO^+(X^1\Sigma^+, a^3\Sigma^+)$ when $J = 0$ at the MRCI/aug-cc-pV6Z level of theory.

υ	$NO^+(X^1\Sigma^+)$				$NO^+(a^3\Sigma^+)$			
	B_υ/cm^{-1}			$10^5 D_\upsilon/cm^{-1}$	B_υ/cm^{-1}			$10^5 D_\upsilon/cm^{-1}$
	This work	Exp.[16]	Exp.[a]	This work	This work	Exp.[15]	Exp.[a]	This work
0	1.98130	1.9878	1.9878	0.559106	1.34610	1.3470	1.3645	0.600993
1	1.96264	1.9690	1.9690	0.562096	1.32606	1.3240	1.3447	0.603276
2	1.94389	1.9502	1.9502	0.563745	1.30592	1.3010	1.3245	0.610397
3	1.92504	1.9314	1.9314	0.565432	1.28567	1.2750	1.3043	0.615873
4	1.90609	1.9126	1.9126	0.567345	1.26536	1.2550	1.2841	0.623009
5	1.88712	1.8838	1.8939	0.570242	1.24499	1.2350	1.2639	0.629262
6	1.86808	1.8563	1.8751	0.572512	1.22456		1.2437	0.637523
7	1.84900	1.8375	1.8563	0.575424	1.20406	1.1930	1.2235	0.643948
8	1.82982	1.8178	1.8375	0.578468	1.18348	1.1680	1.2033	0.650499
9	1.81058	1.8000	1.8187	0.581419	1.16286	1.1460	1.1831	0.656812
10	1.79127	1.7800	1.7999	0.584674	1.14221	1.1240	1.1629	0.662146
11	1.77185	1.7610	1.7811	0.587855	1.12155		1.1427	0.667026
12	1.75233	1.7430	1.7623	0.590895	1.10093	1.1020	1.1225	0.672560
13	1.73269	1.7240	1.7435	0.594134	1.08038	1.0810	1.1023	0.676246
14	1.71291	1.7050	1.7247	0.597537	1.05995	1.0400	1.0821	0.682873
15	1.69300	1.6860	1.7059	0.600978	1.03968		1.0619	0.685616
16	1.67294	1.6700	1.6872	0.604844	1.01964	1.0200	1.0417	0.686226
17	1.65272	1.6480	1.6684	0.609063	0.99988			0.691147
18	1.63234	1.6300	1.6496	0.613914	0.98044			0.687142
19	1.61179	1.6000	1.6308	0.619266	0.96139			0.685270

[a] Values calculated using Dunham coefficients of Ref. [1].

Unfortunately, no experimental or theoretical results can be found in the literature about the D_υ of the $NO^+(X^1\Sigma^+, a^3\Sigma^+)$ and no experimental and theoretical data exist anywhere about the B_υ and D_υ of the $A^1\Pi$ state when $\upsilon \neq 3$ either. Thus, we cannot make any direct comparison between them. However, according to the excellent agreement between the present spectroscopic parameters and the measurements and the good accordance between the present $G(\upsilon)$ and B_υ values and the experimental findings, we have reasons to believe that the results collected in Tables 4 and 5 are reliable and accurate.

3.3. APEFs and classical turning points

Based on the PECs obtained by the *ab initio* calculations, we fit the APEFs of these three states for the NO^+ to the Murrell–Sorbie (M–S) function. The M–S function can analytically describe the interaction potential of diatomic molecules and ions well. In recent years, we have used this function to accurately deduce the APEFs for a number of diatomic molecules.[40–42] The common M–S function is expressed as follows:[43]

$$V(\rho) = -D_e\left(1 + \sum_{i=1}^{n} a_i\rho^i\right)\exp(-a_1\rho), \qquad (1)$$

where $\rho = r - R_e$, with r and R_e denoting the diatomic internuclear distance and its equilibrium internuclear distance, respectively. D_e is the dissociation energy and a_i ($i = 1, 2, \ldots, n$) are the fitting parameters. The number of parameter a_i is different for different molecules. In this work, we employ $n = 6$ for the fitting action of these three states. The fitting results are collected in Table 6.

Table 6. Parameters of the M–S APEFs for $NO^+(X^1\Sigma^+, a^3\Sigma^+, A^1\Pi)$ at the MRCI/aug-cc-pV6Z level of theory.

States	a_1/nm^{-1}	a_2/nm^{-2}	a_3/nm^{-3}	a_4/nm^{-4}	a_5/nm^{-5}	a_6/nm^{-6}	$\Delta E_{RMSE}/eV$
$X^1\Sigma^+$	37.0486	–29.0896	1079.554	–1228.035	246259.37	–955413.92	0.0205
$a^3\Sigma^+$	32.4828	–6.5649	2474.300	23785.334	–348002.12	1025405.25	0.00655
$A^1\Pi$	33.4690	–764.4386	1159.509	105854.104	–839934.25	1806488.49	0.0122

To evaluate the fitting quality of the PEC, we calculate the root-mean-square error ($\Delta E_{\rm RMSE}$) in the fitting process,

$$\Delta E_{\rm RMSE} = \sqrt{\frac{1}{N}\left\{\sum_{i=1}^{N}[V_{\rm APEF}(i) - V_{ab\ initio}(i)]^2\right\}}, \quad (2)$$

where $V_{\rm APEF}(i)$ and $V_{ab\ initio}(i)$ are energies attained by the fitting and by the *ab initio* calculations, respectively and N is the number of the fitting points. For the M–S APEFs, the present $\Delta E_{\rm RMSE}$ are only 0.0205 eV for the $X^1\Sigma^+$, 0.00655 eV for the $a^3\Sigma^+$, and 0.0122 eV for the $A^1\Pi$ electronic states. It shows that the present M–S functions are suited well for reproducing the PECs of these electronic states and the fitting is of high quality. Therefore, the present APEFs collected in Table 6 should be reliable and can be accurately used to perform the classical turning points.

For the vibrational levels of these electronic states, we calculate their corresponding classical turning points using the APEFs in Table 6. Only in that way can it be clearly demonstrated whether the present APEFs can accurately describe the PECs for the $NO^+(X^1\Sigma^+,\ a^3\Sigma^+,\ A^1\Pi)$. We tabulate the classical turning points $R_{\rm min}$ and $R_{\rm max}$ of the $NO^+(X^1\Sigma^+,\ a^3\Sigma^+,\ A^1\Pi)$ ion in Tables 2, 3, and 4, respectively.

It should be noted that these classical turning points tabulated in Ref. [13] were calculated by the Rydberg–Klein–Rees (RKR) method at the experimentally observed vibrational levels. For the ground state, the differences between the present $R_{\rm min}$ and the RKR data[13] are only 0.196%, 0.191%, 0.256%, 0.312%, 0.199%, 0.244%, 0.310%, and 0.356% when $\upsilon = 0, 1, 2, \ldots, 7$. The deviations between the present $R_{\rm max}$ and the RKR data[13] are also only 0.180%, 0.122%, 0.094%, 0.092%, 0.074%, 0.105%, 0.056%, and 0.039% when $\upsilon = 0, 1, 2, \ldots, 7$, respectively. From Table 3, we can see that the $R_{\rm min}$ results from Ref. [13] are anomalistic. Therefore, we cannot make any direct comparisons between them. But the present results accord very well with the Palmieri's results. For the $A^1\Pi$ states, the percent errors of $R_{\rm min}$ from the experiments[13] are only 0.236%, 0.306%, 0.339%, 0.446%, 0.432%, 0.494%, 0.604%, and 0.725% when $\upsilon = 0, 1, 2, \ldots, 7$. And the percentage errors between the present $R_{\rm max}$ values and the measurements[13] also are only 0.056%, 0.062%, 0.097%, 0.219%, 0.358%, 0.505%, 0.708%, and 0.992% when $\upsilon = 0, 1, 2, \ldots, 7$, respectively. According to these, we deduce that the results for the remaining classical turning points when $\upsilon \geq 7$ for the three different electronic states of the NO^+ ion are reliable and accurate. Furthermore, we conclude that the M–S APEFs in Table 6 must be reliable and accurate.

4. Conclusions

The PECs of the $NO^+(X^1\Sigma^+,\ a^3\Sigma^+,\ A^1\Pi)$ ion are obtained using the CASSCF approach followed by the MRCI method and aug-cc-pV6Z basis set for the N and O atom. The present spectroscopic constants, which are determined by the PECs obtained here, are in agreement with the experimental data. The first 20 vibrational levels, the classical turning points and the inertial rotation and centrifugal distortion constants are also calculated when $J = 0$ for the first time. Compared with the available measurements, the present calculations are reliable and accurate. As a whole, the present results provide more accurate and complete investigations on the molecular parameters of the $NO^+(X^1\Sigma^+,\ a^3\Sigma^+,\ A^1\Pi)$ ion than those given by the previous theoretical studies

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