A spectroscopic model for the low-lying electronic states of NO

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The rovibronic structure of A$^2\Sigma^+$, B$^2\Pi$ and C$^2\Pi$ states of nitric oxide (NO) is studied with the aim of producing comprehensive line lists for its near ultraviolet spectrum. Empirical energy levels for the three electronic states are determined using the a combination of the empirical MARVEL procedure and ab initio calculations, and the available experimental data are critically evaluated. Ab initio methods which deal simultaneously with the Rydberg-like A$^2\Sigma^+$ and C$^2\Pi$, and the valence B$^2\Pi$ state are tested. Methods of modeling the sharp avoided crossing between the B$^2\Pi$ and C$^2\Pi$ states are tested. A rovibronic Hamiltonian matrix is constructed using variational nuclear motion program DUO whose eigenvalues are fitted to the MARVEL energy levels. The matrix also includes coupling terms obtained from the refinement of the ab initio potential energy and spin-orbit coupling curves. Calculated and observed energy levels agree well with each other, validating the applicability of our method and providing a useful model for this open shell system.

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I. INTRODUCTION

Nitric oxide (NO) is one of the principle oxides of nitrogen. It plays a significant role in the nitrogen cycle of our atmosphere but also causes problems of air pollution and acid rain. Therefore, scientists are devoting increasing attention to reducing NO in combustion processes. NO is a biological messenger for both animals and plants. Apart from on Earth, NO was also observed in the interstellar environments and atmospheres of other planets.

The importance of NO has aroused the interest of academia and industry since it was prepared by van Helmont in the 17th century and then studied by Priestley in 1772. In numerous theoretical and experimental works, there are a large number of spectroscopic investigations, as spectra provide a powerful weapon to reveal the physical and chemical properties of the molecule. For instance, as a stable open shell molecule, the electronically excited Rydberg states of NO have been extensively studies, see the paper of Deller and Hogan and references therein. The spectrum of NO was also of great value to the refinement of the ab initio the theory of molecular orbitals. On one hand, excitation of inner paired electrons to higher valence orbitals leads to valence states such as B$^2\Pi$. On the other hand, the outermost unpaired electron may be excited to Rydberg orbitals, yielding a series of Rydberg states such A$^2\Sigma^+$ or C$^2\Pi$. These Rydberg states lie close in energy to the valence ones. Furthermore, as NO$^+$ has a shorter equilibrium bondlength than NO, Rydberg states tend to be lower in energy at short bondlengths, r, while valence states are lower at larger r. Thus, in NO, Rydberg-valence interactions are densely distributed in the neighbourhood of the equilibrium bond length of its ground state, where large Franck-Condon factors exist. The B$^2\Pi$ - C$^2\Pi$ interaction is the lowest one and has attracted the most attention. As described by Lagerqvist and Miescher, the two states show a strong and extended mutual perturbation. They proposed a ‘deperturbation’ method to explain the vibrational and rotational perturbation of B$^2\Pi$

Luque and Crosley have investigated spectra of diatomic molecules over a long period. Based on their works, they developed a spectral simulation program, LIFBASE, providing a database of OH, OD, CH etc., and NO as well. LIFBASE contains the positions and relative probabilities of UV transitions in four spectral systems of NO, i.e., \( \gamma (A^2\Sigma^+ \rightarrow X^2\Pi) \), \( \beta (B^2\Pi \rightarrow X^2\Pi) \), \( \delta (C^2\Pi \rightarrow X^2\Pi) \) and \( \epsilon (D^2\Sigma^+ \rightarrow X^2\Pi) \) systems. The upper vibrational energy levels for B$^2\Pi$ and C$^2\Pi$ of NO in LIFBASE are limited to below \( v = 7 \) and \( v = 1 \), respectively. However, the observed \( \beta \) and \( \delta \) transitions corresponding to higher upper vibrational energy levels are even stronger. There is a need to develop a comprehensive UV line list for NO to cover these band systems. To do this one first needs to construct a spectroscopic model which requires overcoming a number of theoretical difficulties. The purpose of this paper is to present our model and explain how we resolve these difficulties.

A major issue in generating a UV line list for NO results from the difficulty of modelling the interaction between B$^2\Pi$ and C$^2\Pi$ states, which is caused by the particular electronic structure of NO. To understand this fifteen electrons system one must analyse the electron configuration of these states from the perspective of molecular orbitals. On one hand, excitation of inner paired electrons to higher valence orbitals leads to valence states such as B$^2\Pi$. On the other hand, the outermost unpaired electron may be excited to Rydberg orbitals, yielding a series of Rydberg states such A$^2\Sigma^+$ or C$^2\Pi$. These Rydberg states lie close in energy to the valence ones. Furthermore, as NO$^+$ has a shorter equilibrium bondlength than NO, Rydberg states tend to be lower in energy at short bondlengths, r, while valence states are lower at larger r. Thus, in NO, Rydberg-valence interactions are densely distributed in the neighbourhood of the equilibrium bond length of its ground state, where large Franck-Condon factors exist. The B$^2\Pi$ - C$^2\Pi$ interaction is the lowest one and has attracted the most attention. As described by Lagerqvist and Miescher, the two states show a strong and extended mutual perturbation. They proposed a ‘deperturbation’ method to explain the vibrational and rotational perturbation of B$^2\Pi$

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II. THEORETICAL STUDY OF THE LOW-LYING ELECTRONIC STATES OF NO

Complete active space self-consistent field (CASSCF) and multireference configuration interaction (MRCI) calculations were performed in the quantum chemistry package Molpro 2015[44] to get the potential energy and spin-orbit curves of the \(X^2\Pi, A^2\Sigma^+, B^2\Pi\) and \(C^2\Pi\) states. A major issue in the calculation is achieving a balance between representations of the Rydberg, A, C, states and the valence, X and B, states. Figure 2 presents an overview of the low-lying PECs and illustrates the importance of the \(C^2\Pi - B^2\Pi\) Rydberg – Valence avoided crossing.

The history of high quality CI calculation for the excited states of NO can be tracked back to 1982, when Grein and Kapur reported their work on the states with the minimum electronic energies lower than 6.58 eV[45]. Several years later, a comprehensive theoretical study on NO were presented and discussed by de Vivie and Peyerimhoff[46]. The results of this paper was further improved by Shi and East in 2006[47]. More accurate curves were obtained with extended basis set and active space in the recent works of Cheng et al.[48,49]. Although the previous work[45,46,47,48,49] provide us strong inspiration, the task is still challenging due to the interactions between Rydberg and valence states of NO.

A. Active space and basis set

For heteronuclear diatomic molecules, Molpro executes calculations in four irreducible representations \(a_1, b_1, b_2\) and \(a_2\) of the \(C_{2v}\) point group. Here, we use \([n_1, n_2, n_3, n_4] - (n'_1, n'_2, n'_3, n'_4)]\) to represent occupied orbitals excluding closed orbitals, i.e. the calculation active space. A typical active space for the lower electronic states calculation of NO is \([8, 3, 3, 0] - (2, 0, 0, 0)\], as suggested by Shi and East[47]. Although only a few of the PECs are of direct interest here, we had to include extra states to achieve correct calculation. We also adjusted the active space to get smooth curves.

A Dunning aug-cc-pV(n)Z basis set[50] was used in both CASSCF and MRCI calculation. This basis set has an additional shell of diffuse functions compare to the cc-pV(n)Z basis set, which benefits the calculation of Rydberg states. Too many diffuse functions, e.g., those of the d-aug-cc-pV(n)Z basis set, may have negative effects on the calculation because of the overemphasis of the Rydberg states relative to the valence states.

B. CASSCF calculation

Our calculations started with a \([8, 3, 3, 0] - (2, 0, 0, 0)\] active space in which the interactions between the Rydberg and valence states are inescapable. However, representing the avoided crossing points caused by \(C^2\Pi\) and the valence \(\Pi\) states proved to be a huge obstacle to obtaining satisfactory results. Panel (a) of Fig. 2 shows the terrible behavior of B - C interaction near 1.18 Å. The potential energy curve (PEC) of...
C²Π suddenly jumps to that of B²Π, producing discontinuity in the PEC of X²Π too. To get the exited states, we used the state average algorithm but the average energy of the two ²Π states changed when traversing the crossing point of C²Π and B²Π.

A valid way to smooth the curves is to increase the number of averaged states. For example, the discontinuities near 1.18 Å disappears when introducing a third ²Π state in CASSCF calculation, as shown in Panel (b) of Fig. 3. Nevertheless, similar phenomenon arises when the third state comes across L²Π. Alternatively, smooth curves can be obtained in limited active space. For example, we can get a continuos curves of C²Π in the active space \([\{(6,3,3,0)-(4,1,1,0)\}]\) from 0.9 Å to 1.28 Å.

We always started a new CASSCF iteration from the orbitals of a nearby geometry to stabilize and accelerate the calculation. The PECs in Panels (a) and (b) of Fig. 3 are obtained by increasing the internuclear distance from 0.9 Å to 1.3 Å. Interestingly, with a initial geometry at 1.3 Å, reversing the calculation direction gives a completely different result in the same active space, i.e., two smooth valence PECs of X²Π and B²Π states in Panel (c) of Fig. 3. Due to the limitation of nonlinear programming, CASSCF iterations may fall into local minima. To get the target states, the numerical optimization must be properly initialized. For the NO molecule, the iterations which begin with valence orbitals usually end with valence orbitals but it is uncertain for those begin with Rydberg orbitals. The results imply that there are at least two kinds of local minimums in the ab initio calculation of NO with Molpro: pure valence orbitals (corresponding to Panel (c) of Fig. 3) and Rydberg-valence hybrid orbitals (corresponding to Panels (a) and (b) of Fig. 3). To verify the conjecture: initializing a calculation of two ²Π states average with the CASSCF orbitals of the X²Π state in the single state calculation, one can get almost the same curves as those in Panel (c) of Fig. 3 starting from 0.9 Å.

In Section [IV], we use diabatic potentials in modeling interaction between B²Π and C²Π states. We describe the curves as ‘adiabatic’ if they contain the B - C avoided crossing feature, e.g., those in Panel (b) of Fig. 3. If not, we call the curves ‘diabatic’, e.g., those in Panel (c) of Fig. 3.

C. MRCI calculation

Although consuming many more computational resources, the MRCI calculation in Molpro is straightforward. Molpro automatically takes the CASSCF orbitals as the references and performs an internally contracted configuration interaction calculation based on single or double excitation. The spin-orbit coupling terms were also produced. To compensate the error brought by truncated configuration interaction expansion, the energies were modified by Davision correction, i.e., MRCI + Q calculation. Panel (a) of Fig. 4 demonstrates the results of CASSCF & MRCI + Q calculation of the X²Π, A²Σ⁺, B²Π, C²Π, D²Σ⁺ and L²Φ states, in \([\{(8,3,3,0)-(2,0,0,0)\}]\) active space with aug-cc-pV5Z basis set.

In the CASSCF routine, the projection of angular momentum of a diatomic molecule on its internuclear axis, Λ, can be assigned to specify the expected states. However, the MRCI routine does not have the option and always finds the lowest energy states of the same spin. As a result, the PECs of C²Π and L²Φ exchange with each other at their crossing point although the avoided crossing principle is not applicable for the two states, as shown by the blue curve in Panel (a) of Fig. 4. It is feasible to calculate and output the Λ quantum numbers (technically, Lz, which is defined as a non-diagonal matrix element between two degenerate components, e.g. \(\langle \Pi_v | L_z | \Pi_v \rangle \)) in MRCI calculations, which helps to distinguish the C²Π, L²Φ and L²Π states. The blue and yellow curves on the right of their crossing point were manually switched, as shown in Panel (c) of Fig. 4 according to their Λ quantum numbers shown in Panel (b). The T_e values of A²Σ⁺, B²Π and C²Π states are compared with those calculated by Shi and East in Table II.

| State   | CASSCF & MRCI + Q       | Empirical   |
|---------|--------------------------|-------------|
| A²Σ⁺    | 43538                    | 45410.2     |
|         |                          | 43965.7     |
|         |                          | 43902.99    |
| B²Π     | 44803                    | 46260.8     |
|         |                          | 45913.6     |
|         |                          | 45867.05    |
| C²Π     | 51808                    | 53709.5     |
|         |                          | 52126       |
|         |                          | 52081.97    |

a Two-state average CASSCF & MRCI + Q calculation.
b See Section [IV].

TABLE I. Comparison of T_e values of the MRCI + Q calculation
The PECs in Fig. 3 range from 1.0 Å to 1.26 Å. The curves were deliberately truncated at the right endpoint because of the C^2Π - L^2Π interaction as shown in Panel (b) of Fig. 3. On the left endpoint, the MRCI program exited with an 'INSUFFICIENT OVERLAP' error. The error is triggered by interactions with another 2Π state, H^2Π, which lies below B^2Π near the 1.06 Å and which cannot be described by the reference space. A solution to the problem is to perform MRCI calculations using a larger active space such as [(8,4,4,0) − (2,0,0,0)].

It is not quantitatively accurate to generate line lists with the \textit{ab initio} curves; however, the curves and couplings provide a suitable starting point for work. These curves and couplings need to be refined using experimental data, which is the content of the subsequent two sections.

III. MARVEL ANALYSIS OF THE ROVIBRONIC ENERGY LEVELS OF ^1^4N\textsubscript{16}O

The rovibronic energy levels of A^2Σ^+, B^2Π and C^2Π states were reconstructed by MARVEL analysis of the experimental transitions of the γ, β, δ, and Heath systems and those inside the ground state.

In the previous work by Wong \textit{et al.}\textsuperscript{[35]} 11 136 IR transitions were collected, yielding a spectroscopic network of 4106 energy levels. To retrieve the energy levels of A^2Σ^+, B^2Π and C^2Π states, we extracted a further 9861 transitions (including 3393 γ, 5103 β, 1004 δ and 361 Heath transitions) from the data sources listed in Table III. The vibronic structure of the spectroscopic network is illustrated in Fig. 5.

Although there are studies which report measured transition frequencies for the four band systems of interest, only the most reliable data sets were included in our MARVEL analysis. For example, Lagerqvist and Miescher published the line position data of 20 bands of the β and δ systems (β(5,0) to β(19,0) and δ(0,0) to δ(4,0), respectively) in 1958 (58LaMi\textsuperscript{[26]}), but half of them were replaced by more accurate line lists measured by Yoshino \textit{et al.} around 2000 (94MuYoEs\textsuperscript{[59]} 98YoEs\textsuperscript{[60]} 00ImYoEs\textsuperscript{[61]} 02ChLoL\textsuperscript{[62]} 02RuYoTh\textsuperscript{[63]} 06YoThMu\textsuperscript{[64]}).

The spectroscopic network in MARVEL\textsuperscript{[53]} is established in accordance with the upper and lower quantum numbers of the transitions. We used five quantum numbers, as shown in Table III, to uniquely label the rovibronic energy levels. The quantum numbers of some transitions were improperly assigned. New assignments plus some other comments on the sources are given below:

- In some cases (e.g. for the A^2Σ^+ state, the Q_{21} branch is indeed a copy of R_{11} branch as listed in 97DaDoK\textsuperscript{[22]} duplicate transition are provided in source data. In 27JeBaMu\textsuperscript{[6]} 58LaMi\textsuperscript{[28]} etc., A doubling fine structures of many transitions are not resolved; therefore we simply created two transitions differing in e/f parity with the same frequency in the MARVEL dataset.

- The uncertainties of the transitions of 27JeBaMu\textsuperscript{[6]} and 58LaMi\textsuperscript{[28]} were given by combination difference test, referring to the energies of X^2Π state.\textsuperscript{[25]}
FIG. 4. The PECs of the X^2Π, A^2Σ^+, B^2Π, C^2Π, D^2Σ^+ and L'^2Φ states, obtained by CASSCF & MRCI+Q calculation starting from 1.06 Å to both sides in the active space [(8, 3, 0) – (2, 0, 0)] with the aug-cc-pV5Z basis set. The third ^2Π curve and the L'^2Φ curve in Panel (a) were manually switched in Panel (c) on the right of 1 Å, according to the value of L_z, shown in Panel (b). The phase of L_z, in the Cartesian representation, is random. To distinguish different electronic states, the yellow curve in Panel (b) is smoothed for internuclear distances less than 1.1 Å. The X^2Π state is not shown in the Panel as the L_z values obtained are all –i.

FIG. 5. Vibronic structure of the MARVEL analysis. The vertical solid lines in green, blue and red illustrate the bands of γ, β and δ systems, respectively. The vertical dash line in purple represents the Heath(0, 0) band.

- The uncertainties of most validated transitions are close to the lower bounds listed in Table II (see the supplementary material).

  - The transitions of γ(3,0), β(6,0) and β(11,0) bands extracted from 02ChLoLe, 02ChLoLe and 02RuYoTh were increased by 0.083 cm⁻¹, 0.083 cm⁻¹ and 0.067 cm⁻¹, respectively, as suggested in 05ThRuYo. The uncertainties of these transitions should be 0.1 cm⁻¹ because the absolute frequencies were not calibrated. However, we used relative accuracy, i.e., 0.03 cm⁻¹, as the lower bound of uncertainty to constrain the MARVEL analysis. The uncertainties should be adjusted to 0.1 cm⁻¹ if data of higher accuracy are included in the future.

  - In the β(10,0) band of 06YoThMu, R_11(3.5) and P_{11}(3.5) were exchanged; the R_21 and P_{21} branches were exchanged.

  - In the δ(0,0) band of 94MuYoEs, P_{12}(15.5)_e and P_{12}(16.5)_f should be P_{22}(15.5)_e and P_{22}(16.5)_e, respectively.

  - In the δ(1,0) band of 00ImYoEs, the frequencies of R_{12}(15.5)_e and R_{12}(15.5)_f should be exchanged; the frequencies of P_{11}(5.5) and P_{11}(16.5)_f should be 54668.636 cm⁻¹.

  - In the δ(2,0) band of 06YoThMu, the frequencies of Q_{22}(5.5)_e and Q_{22}(6.5)_e should be 56967.72 and 56966.61 cm⁻¹, respectively.
The various measurements, but $20VeFe$ did not. Analyzing the consistency in this cycle, within the stated uncertainties of these data were excluded from our MARVEL analysis.

The combination difference analysis indicates that their data set is self-consistent within the claimed accuracy, i.e. 0.005 cm$^{-1}$ to 0.06 cm$^{-1}$. However, it is inconsistent with the ground state MARVEL energies of Wong et al$^{[26]}$. Combination difference test shows that the standard deviations of most energy levels calculated by the data set are greater than 0.1 cm$^{-1}$.

In contrast, the line list of $97DaDoKe^{[27]}$ is consistent with others. The measurements of $20VeFe$ differ from those of $97DaDoKe$ up to 0.7 cm$^{-1}$, as acknowledged by $20VeFe$. The transitions $\gamma(3,4)$ band measured by $97DaDoKe$ are consistent with the transitions in $\gamma(3,0)$ band measured by Cheung et al. ($02ChLoLe^{[28]}$). Furthermore, use of Heath band potential provides a closed loop or cycle by following $\gamma(0,0)$-Heath(0,0)-$\delta(0,0)$. The measurements of $97DaDoKe$ gave consistency in this cycle, within the stated uncertainties of the various measurements, but $20VeFe$ did not. Analyzing the ground state data and $20VeFe$ individually, we observed an average 0.43 cm$^{-1}$ shift for the lower three vibrational levels of the $A^2\Pi^+$ state; these energy differences are plotted in Fig. 6.

We were therefore forced to conclude that the measurements of $20VeFe$ are not consistent with the other measurements and these data were excluded from our MARVEL analysis.

The 20293 validated transitions (including $3141\gamma$, 4795 $\beta$, 861 $\delta$ and 360 Heath transitions) yielded 327, 1400 and 466 energy levels of the $A^2\Pi^+$, $B^2\Pi$ and $C^2\Pi$ states, respectively. These levels are plotted as a function of total angular momentum $J$ in Fig. 7. The MARVEL transitions (input) file and energies (output) file are given as part of the supplementary data.
TABLE III. Quantum numbers used in the MARVEL analysis

| Quan. No. | Meaning |
|-----------|---------|
| State     | Electronic state label, e.g., X stands for X^2Π |
| J         | Total angular momentum |
| parity    | + or - |
| v         | Vibration quantum number |
| Ω         | Projection of the total angular momentum on the internuclear axis |

Sulakshina and Borkov compared the ground state energies calculated by their RITZ code with our previous MARVEL result. The MARVEL analysis here updates the energy values of the X^2Π state by including new rovibronic transitions; as shown in Fig. 8, the energy gaps between the results of the MARVEL and RITZ analysis are narrowed as a result of this. This is especially true for high J levels belonging to the Ω = 3/2 series (see Fig. 8(b) of Sulakshina and Borkov). The majority of levels agree within the uncertainty of their determination.

IV. REFINEMENT OF CURVES FOR ^14N^16O

A. Calculation setup

The PECs of A^2Σ^+, B^2Π and C^2Π, as well as other coupling curves, were refined based on the empirical energy levels yielded by the MARVEL analysis in Section III, the PEC for the X^2Π state was left unchanged from that of Wong et al. The refinement was executed in DUO which is a general variational nuclear-motion program for calculating spectra of diatomic molecules.

DUO solves the diatomic molecular Schrödinger equation in two steps. Firstly the rotation-free radial equation of each electronic state is solved to get the vibrational energy levels, E_v, and wavefunctions, ψ_v(r):

\[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} \psi_v(r) + V_{state}(r) \psi_v(r) = E_v \psi_v(r), \]  

where \( \mu \) is the reduced mass of the molecule and \( V_{state}(r) \) is the potential energy curve. This step creates vibrational basis functions, |state, v⟩. Secondly, the fully-coupled, rovibronic Hamiltonian is diagonalized under the Hund’s case (a) rovibronic basis set defined by:

\[ | \text{state}, J, Ω, Λ, S, Σ, v \rangle = | \text{state}, Λ, S, Σ \rangle | J, Ω, M \rangle | \text{state}, v \rangle, \]  

where |state, Λ, S, Σ⟩ and | J, Ω, M⟩ represent the electronic and rotational basis functions, respectively. The quantum number M is the projection of the total angular momentum along the laboratory Z-axis.

Users are asked to set up some super-parameters to get the correct solution. The calculation setup for the refinement of ^14N^16O is summarized below. More details can be found in the DUO input file which is given as supplementary material and includes the PEC parameters.

- Equation (1) was solved by the Sinc-DVR method.
- The calculation range was from 0.6 to 4.0 Å.
- The number of grids points was 701, uniformly spaced.
- The numbers of vibrational basis sets for X^2Π, A^2Σ^+, B^2Π and C^2Π were 10, 10, 30 and 10, respectively.
- The maximum total angular momentum considered here was 52 1/2.
• The upper bound of the total energy was 65 000 cm⁻¹.

B. Refinement results of the A²Σ⁺ state

The PEC of A²Σ⁺ state represented by a fourth-order Extended Morse Oscillator (EMO) function\[20\]. The EMO is defined as a function of internuclear distance, r:

\[ V(r) = T_e + (D_e - T_e)[1 - \exp(-\beta_{EMO}(r)(r - r_e))]^2, \quad (3) \]

where the distance-dependent coefficient \( \beta_{EMO} \) is expressed as

\[ \beta_{EMO}(r) = \sum_{i=0}^{N} b_i y_p^{eq}(r)^i. \quad (4) \]

The reduced variable \( y_p^{eq}(r) \) has the formula:

\[ y_p^{eq}(r) \equiv \frac{r - (r_e)^p}{r + (r_e)^p}, \quad (5) \]

where \( p \) controls the shape of \( y_p^{eq}(r) \). The programmed EMO function in DUO is not exactly the same as defined by Eq.\[3\], A reference point \( R_{ref} \) (usually the equilibrium internuclear distance) divides the curve into left and right parts. The numbers of terms \( N \), as well as \( p \), for the left and right parts can be assigned different values, i.e., \( N_l, N_R, p_L \) and \( p_R \). The unknown dissociation energy of the state is regarded as a dummy parameter in the refinement. The initial guess of \( D_e \) was given by a pure Morse function and the value was fine-tuned in each iteration. The optimal parameters of the EMO function is listed in Table IV. The \textit{ab initio} and refined PECs of the A²Σ⁺ state are compared in Panel (a) of Fig.\[7\].

In addition, our model of the A²Σ⁺ state contains a spin-rotational term. In DUO, the nonzero diagonal and off-diagonal matrix elements of spin-rotational operator \( \hat{H}_{SR} \)\[68\] are given by

\[ \langle A, S, \Sigma \mid \hat{H}_{SR} \mid A, S, \Sigma \rangle = \frac{\hbar^2}{2\mu r^2} \gamma_{SR}^{A}(r) \left[ \Sigma^2 - S(S + 1) \right], \quad (6) \]

\[ \langle A, S, \Sigma \mid \hat{H}_{SR} \mid A, S, \Sigma \pm 1 \rangle = \frac{\hbar^2}{4\mu r^2} \gamma_{SR}^{A}(r) \sqrt{S(S + 1) - \Sigma(\Sigma \pm 1)} \times \sqrt{J(J + 1) - \Omega(\Omega \pm 1)}. \quad (7) \]

The dimensionless spin-rotational coefficient \( \gamma_{SR}^{A}(r) \) of A²Σ⁺ state was modeled as a constant whose value is

\[ \gamma_{SR}^{A}(r) = -2.08043004478781 \times 10^{-3}. \quad (8) \]

C. Refinement results of the B²Π - C²Π coupled states

1. Deperturbation of the B²Π - C²Π interaction

For this work we only consider coupling between two electronic states. The interaction between two electronic states belong to the same irreducible representation of the molecular point group directly depends on the avoided crossing of their diabatic PECs. Thus, it is possible to model the coupled states by introducing two adiabatic potentials\[21\]. This could be accomplished by diagonalizing the matrix:

\[ \begin{pmatrix} V_1(r) & W(r) \\ W(r) & V_2(r) \end{pmatrix}, \quad (9) \]

where \( V_1(r) \) and \( V_2(r) \) are two diabatic potentials and \( W(r) \) is the coupling curves. The adiabatic PECs, \textit{i.e.} the eigenvalues of the matrix, are

\[ V_{low}(r) = \frac{V_1(r) + V_2(r)}{2} - \frac{\sqrt{(V_1(r) - V_2(r))^2 + 4W^2(r)}}{2}, \quad (10) \]

\[ V_{upp}(r) = \frac{V_1(r) + V_2(r)}{2} + \frac{\sqrt{(V_1(r) - V_2(r))^2 + 4W^2(r)}}{2}. \quad (11) \]

EMO potential functions are used to model \( V_1(r) \) and \( V_2(r) \) in Eqs.\[10\] and \[11\] while \( W(r) \) is given by:

\[ W(r) = \sum_{i=0}^{N} w_i (r - r_0)^i \cosh(b(r - r_0)). \quad (12) \]

The function rapidly decreases to \( W_0 \) when \( r \) moves away from \( r_0 \).

The coupled PECs of X¹Σg⁺ and B¹Σg⁺ states of C₂ were represented by adiabatic potential in our previous work\[22\], producing accurate line list. Nevertheless, this method is not optimal for NO where the avoided crossing between the B and C states is very sharp. Thus, for example, the adiabatic B – X and C – X transition dipole moment curves (TDMCs) change dramatically around the crossing point making them hard to use in any reliable calculation of transition intensities and a slight shift of the crossing point, \( r_0 \), during refinement may significantly change the intensities of nearby lines. We therefore adopt the following procedure for the generating line lists involving these coupled electronic states:

1. Solve the radial equations set up with diabatic PECs of different electronic states to get vibrational basis.
2. Construct rovibronic Hamiltonian matrix with all necessary elements, including the electronic interaction terms.
3. Diagonalize the matrix under rovibronic basis set to get the rovibronic energy levels and the corresponding wavefunctions.
4. Refine the diabatic PECs, electronic interaction terms and other coupling curves by fitting the energies to observed energy levels.
5. Calculate the Einstein A coefficient with the diabatic TDMCs and let the wavefunctions determine the weights of TDMCs for each rovibronic state at different geometries.
TABLE IV. The optimized EMO parameters of the PECs of $A^2\Sigma^+$, $B^2\Pi$, $C^2\Pi$ states and the spin-orbit (SO) coupling within the $B^2\Pi$ state. The parameters are given electronically in the DUO input which is given in the supplementary information.

| Parameter | $A^2\Sigma^+$ | $B^2\Pi$ | $C^2\Pi$ | $\langle B^2\Pi|\hat{\sigma}_{SO}|B^2\Pi\rangle$ |
|-----------|---------------|-----------|-----------|-------------------------------------|
| $T_e$ [cm$^{-1}$] | 4.390299 27730943 $\times 10^4$ | 4.586704 506676095 $\times 10^4$ | 5.208197 35839884 $\times 10^4$ | 8.497424 00431892 |
| $r_c$, $r_{ref}$ [Å] | 1.063666 00836862 | 1.416673 77245069 | 1.063704 70837254 | 1.1 |
| $D_e$ [cm$^{-1}$] | 1.292051 39030394 $\times 10^5$ | 7.1627 $\times 10^4$ | 1.271773 18888436 $\times 10^5$ | 5.774077 92042591 $\times 10^1$ |
| $p$ | 4 | 4 | 2 | 4 |
| $N_r$ | 2 | 4 | 2 | 4 |
| $b_0$ [Å$^{-1}$] | 2.704913 98179678 | 2.150144 13975452 | 2.863985 60325524 | 2.015987 55938854 |
| $b_1$ [Å$^{-1}$] | 2.073903 44060448 $\times 10^{-2}$ | 9.835900 99793413 $\times 10^{-2}$ | 5.525725 33543132 $\times 10^{-1}$ | 0 |
| $b_2$ [Å$^{-1}$] | 8.14901009782977 $\times 10^{-2}$ | 4.118983 73004704 $\times 10^{-1}$ | 3.452639 96521417 | 11.0 |
| $b_3$ [Å$^{-1}$] | $-9.539702 898683$ $\times 10^{-1}$ | 0 | $-3.788700$ 19311205 $\times 10^1$ | 0 |
| $b_4$ [Å$^{-1}$] | $-2.050677 38507637$ | $-4.436396 50588521$ $\times 10^{-1}$ | 8.286371 43949508 $\times 10^1$ | 6.672511 52788665 |
| $b_5$ [Å$^{-1}$] | $1.215719$ 27232752 | 0 | 0 | 0 |
| $b_6$ [Å$^{-1}$] | $-1.784795$ 35777777 | $\times 10^1$ | 0 | 0 |
| $b_7$ [Å$^{-1}$] | 3.127784 54452573 | 0 | 0 | 0 |
| $b_8$ [Å$^{-1}$] | 5.403077 72958800 | 0 | 0 | 0 |

FIG. 9. The ab initio and refined PECs of the $A^2\Sigma^+$, $B^2\Pi$ and $C^2\Pi$ states as well as the refined B - C interaction term $W(r)$. (a) diabatic and (b) adiabatic representations. The refined potential curves in Panel (b) is calculated using Eqs. (10) and (11). The ab initio curves are shifted using empirical $T_e$ values.
TABLE V. Optimized Lorentz parameters for the B - C interaction curve.

| Parameter     | Value                      |
|---------------|----------------------------|
| \( b [\text{Å}^{-1}] \) | 2.21707630646740 \times 10^{-3} |
| \( r_0 [\text{Å}] \)     | 1.18808573722698             |
| \( w_0 [\text{cm}^{-1}] \) | 1.40173178754200 \times 10^{-5} |

TABLE VI. Optimized values of the spin-orbit (SO) and spin-rotation (SR) coupling terms.

| Term                        | Value                          |
|-----------------------------|--------------------------------|
| \( \langle \Sigma_2 \Pi | \hat{H}_{\text{SO}} | \Sigma_2 \Pi \rangle \text{[cm}^{-1}] \) | 2.8206375746938                |
| \( \langle \Sigma_2 \Pi | \hat{H}_{\text{SO}} | B^2 \Pi \rangle \text{[cm}^{-1}] \) | 1.8176677228787                |
| \( \gamma_{\text{SR}}^{C} \)   | 2.70593061789197 \times 10^{-3} |

The method not only rescues us from the dilemma of constructing adiabatic TDMCs but also improves the flexibility of our program. For instance, it is convenient to model the \( B^2 \Pi \) - \( C^2 \Pi \) - \( L^2 \Pi \) coupled states of NO by adding new definitions of the potential of \( L^2 \Pi \) and coupled term between \( C^2 \Pi \) and \( L^2 \Pi \) in the input file of DUO, without changing its code.

2. Refined curves

The diabatic PECs of \( B^2 \Pi \) and \( C^2 \Pi \) states were modeled using EMO functions whose optimal parameters are listed in Table IV. The \textit{ab initio} and refined PECs of \( B^2 \Pi \) and \( C^2 \Pi \) states are compared in Panel (a) Fig. 9. Its optimal parameters of the function are listed in Table VI. Although not used in this work, the adiabatic curves were calculated as defined by Eqs. (10) and (11). They are compared with the \textit{ab initio} adiabatic PECs in Panel (b) of Fig. 9. The dissociation energy of \( C^2 \Pi \) state is also a dummy parameter. The refined PECs of \( A^2 \Sigma^+ \) and \( C^2 \Pi \) states are physically meaningless outside the our calculation range (i.e., when energy is greater than \( 75000 \text{ cm}^{-1} \)).

The spin-orbit coupling function (SOC) of \( B^2 \Pi \) state was also fitted to an EMO function whose optimal parameters were listed in the last column of Table IV. Figure 10 compares the \textit{ab initio} and refined SOCs. The diagonal spin-orbital term of \( C^2 \Pi \) state and the off-diagonal term between \( B^2 \Pi \) and \( C^2 \Pi \) were determined empirically by fitting to constants. The spin-rotational coefficient of \( C^2 \Pi \) state was also model on a constant. The values of these terms are listed in Table VII.

The \( \Lambda \) - doubling fine structures of \( \beta \) and \( \delta \) system bands were observed in most of the work listed in Table IV. DUO calculates the \( \Lambda \) - doubling matrix elements, i.e., \( \langle \Lambda' \Sigma' \Omega' | \hat{H}_{\text{LD}} | \Lambda \Sigma \Omega \rangle \), according to the terms given by Brown and Merer.

\[
\langle \pm 1, \Sigma \pm 2, J, \Omega | \hat{H}_{\text{LD}} | \pm 1, \Sigma, J, \Omega \rangle = \frac{1}{2} (p_v + q_v + q_r) \times  \\
\sqrt{S(S+1) - \Sigma(S+1)] | [S(S+1) - (\Sigma \pm 1)(\Sigma \pm 2)]}, \]

(13)

\[
\langle \pm 1, \Sigma \pm 1, J, \Omega \mp 1 | \hat{H}_{\text{LD}} | \pm 1, \Sigma, J, \Omega \rangle = -\frac{1}{2} (p_v + q_v) \times  \\
\sqrt{S(S+1) - \Sigma(S \pm 1)] | [J(J+1) - \Omega(\Omega \mp 1)]}, \quad (14)
\]

\[
\langle \pm 1, \Sigma, J, \Omega \mp 2 | \hat{H}_{\text{LD}} | \pm 1, \Sigma, J, \Omega \rangle = \frac{1}{2} q_v \times  \\
\sqrt{[J(J+1) - \Omega(\Omega \mp 1)] | [J(J+1) - (\Omega \mp 1)(\Omega \mp 2)]}. \quad (15)
\]

For \( B^2 \Pi \) and \( C^2 \Pi, \Sigma = \mp 1/2 \). Therefore, the matrix elements described in Eq. (13) are zero and only the coefficients of Eqs. (14) and (15) were fitted to polynomials, i.e.,

\[
P(r) = a_0 + \sum_{i=0}^3 a_i (r - r_0)^i. \quad (16)
\]

The optimized parameters of the \( \Lambda \) - doubling terms are listed in Table VII.

3. Fitting residues of the rovibronic energy levels

The fitting residues of the \( A^2 \Sigma^+ \) state are shown in Panel (a) of Fig. 11. The high-\( J \) energies of \( v = 3 \) vibrational levels are mainly determined by blended lines of 97DaDoKe.NG[2]. The fitting residues of the \( B^2 \Pi \) and \( C^2 \Pi \) states are shown in Panel (b) of Fig. 11 where the cold colors represent the \( B^2 \Pi \) state and the warm ones represent the \( C^2 \Pi \) state. The \( F_1 \) (i.e., \( \Omega = \frac{1}{2} \)) and \( F_2 \) (i.e., \( \Omega = \frac{3}{2} \)) levels are also distinguishable. The residue distributions indicate \( J \)-dependent systematic er-
we did not include higher electronic states, such as L than our rovibronic residues. Unlike Gallusser and Dressler, bronic residues given by Gallusser and Dressler 37 network and energy levels. On the other hand, our model (MARVEL et al. 38) helped us reconstruct reliable spectroscopic orror of our model, which may result from some off-diagonal couplings, e.g., the coupling between C\(^2\Pi\) and D\(^2\Sigma^+\) states 25.

The residues of all rovibronic energy levels are plotted against their corresponding uncertainties. The root-mean-square and average value of uncertainties and residues are compared in Table VIII.

The accuracy of our model is definitely higher than those of Lagerqvist and Miescher 25, or Gallusser and Dressler 37. On one hand, the most recent measurements (e.g., the works of Yoshino et al. 28) and spectroscopic analysis techniques (MARVEL 25) helped us reconstruct reliable spectroscopic network and energy levels. On the other hand, our model was directly fitted to the observed rovibronic levels. The rovibronic residues given by Gallusser and Dressler 37 are greater than our rovibronic residues. Unlike Gallusser and Dressler, we did not include higher electronic states, such as L\(^2\Pi\) and K\(^2\Pi\), in our model, which reduces its range of applicability where the state energy is greater than 63000 cm\(^-1\). However, thanks to diabatic coupling strategy of DUO, the model can easily be updated in a future study.

We note that some of the assignments to B or C electronic states differ between DUO and our MARVEL analysis. DUO uses three good quantum number, namely the total angular momentum \( J \), the total parity and the counting number of the levels with the same values of \( J \) and parity. The other quantum numbers such as state, \( \nu \), \( \Omega \), are estimated using the contribution of the basis functions to a given wavefunction. It is to be anticipated that in regions of heavily mixed wavefunctions this may lead to differences compared to other assignment methods. The MARVEL and DUO energy levels of B (\( \nu = 13 \)) - C (\( \nu = 2 \)) coupled series are plotted in Fig. 13 Table IX lists some energy levels in the output .en file of DUO. Both of them demonstrate the differences between the quantum numbers of MARVEL and DUO results.

V. CONCLUSION

In this paper, potential energy curves and coupling for the low-lying electronic state of NO are calculated using quantum chemistry package Molpro. The strong interaction between Rydberg and valence states makes the \( ab\ initio \) calculation challenging. We obtain both adiabatic and diabatic PECs and SOCIs for the \( \Lambda^2\Sigma^+, \ \Pi^2\Pi\) and \( \Pi^2\Pi\) states. The curves were refined by fitting the rovibronic energy levels calculated by variational nuclear motion program DUO to those reconstructed by MARVEL analysis. The RMS error of the \( \Pi^2\Pi - \Sigma^2\Pi\) state fitting and \( \Pi^2\Pi - \Pi^2\Pi\) coupled states fitting are 0.03390 cm\(^-1\) and 0.2722 cm\(^-1\), respectively, which energies were determined by our use of a MARVEL procedure and the best available measurements. The success of \( \Pi^2\Pi - \Pi^2\Pi\) coupled states fitting validates our deperturbation method for treating the coupled electronic state. This work, when combined with the earlier X\(^2\Pi\) study of Wang et al. 25 provides a comprehensive spectroscopic model four the lowest for electronic states of NO and thus a good start point for the generation of a NO UV line list. This line list will be presented elsewhere.

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DATA AVAILABILITY

The data that supports the findings of this study are available within the article and its supplementary material.

SUPPLEMENTARY MATERIAL

Three text files are provided as supplementary material to the article:
FIG. 11. Fitting residues of (a) $A^2\Sigma^+$ state and (b) $B^2\Pi$ - $C^2\Pi$ coupled states.

TABLE IX. Sample lines extracted from the output .en file of DUO.

| DUO | Assigned | MARVEL | DUO | DUO | MARVEL |
|-----|----------|--------|-----|-----|--------|
| $N$ | $N'$ | $J$ | Parity | Energy | Energy | Residue | Weight | state | $v$ | $\Lambda$ | $\Sigma$ | $\Omega$ | state | $v$ | $\Lambda$ | $\Sigma$ | $\Omega$ |
| 39 | 39 | 1.5 | + | 52349.0418 | 52349.0274 | 0.0144 | 9.50E-05 | 3 | 7 | 1 | -0.5 | 0.5 | 3 | 7 | 1 | -0.5 | 0.5 |
| 40 | 40 | 1.5 | + | 52373.2372 | 52373.3626 | -0.1255 | 1.40E-03 | 4 | 0 | 1 | -0.5 | 1.5 | 3 | 7 | 1 | 0.5 | 1.5 |
| 41 | 41 | 1.5 | + | 52380.1912 | 52380.1101 | 0.0810 | 1.30E-03 | 4 | 0 | 1 | -0.5 | 0.5 | 4 | 0 | 1 | -0.5 | 0.5 |
| 42 | 42 | 1.5 | + | 52392.3007 | 52392.3172 | -0.0165 | 1.30E-03 | 3 | 7 | 1 | 0.5 | 1.5 | 4 | 0 | 1 | 0.5 | 1.5 |
| 64 | 64 | 2.5 | - | 59217.4976 | 59217.3626 | -0.4754 | 9.50E-05 | 3 | 15 | -1 | 0.5 | -0.5 | 4 | 3 | -1 | 0.5 | -0.5 |
| 65 | 65 | 2.5 | - | 59250.3720 | 59250.8248 | -0.4528 | 9.50E-05 | 4 | 3 | -1 | -0.5 | -1.5 | 4 | 3 | -1 | 0.5 | -1.5 |
| 66 | 66 | 2.5 | - | 59654.3005 | 59654.8551 | -0.5546 | 3.70E-06 | 4 | 3 | -1 | 0.5 | -0.5 | 3 | 15 | -1 | 0.5 | 0.5 |
| 67 | 67 | 2.5 | - | 59692.2845 | 59692.6292 | -0.3447 | 4.80E-06 | 3 | 15 | -1 | -0.5 | -1.5 | 3 | 15 | -1 | -0.5 | -1.5 |

a The counting numbers ($N$) were manually assigned to match the corresponding MARVEL energy level.
b In these columns, ‘3’ and ‘4’ indicate the $B^2\Pi$ and $C^2\Pi$ states, respectively.

MARVEL_Transitions.txt: input transitions file used with MARVEL.
MARVEL_Energies.txt: energy levels file generated by MARVEL using the file MARVEL_Transitions.txt.
NO_XABC.model.txt: a Duo input file which fully specifies our spectroscopic model including the associated potential energy and coupling curves.

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FIG. 12. Residues against uncertainties of (a) \( \Delta^{2}\text{Li}^+ \) state and (b) B - C coupled states with vibrational states given in the bars.
FIG. 13. Calculated and observed energy levels of the B\((v = 13)\) - C\((v = 2)\) coupled series. The right hand panel is a blow up of the avoided crossing between the states which gives a clearer view of the \(\Lambda\) - doubling splitting and the difference between the quantum numbers given by MARVEL and DUO.

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