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

Cite as: J. Chem. Phys. 154, 074112 (2021); https://doi.org/10.1063/5.0038527
Submitted: 24 November 2020 • Accepted: 15 January 2021 • Published Online: 19 February 2021

Qianwei Qu, Bridgette Cooper, Sergei N. Yurchenko, et al.

COLLECTIONS

Paper published as part of the special topic on Quantum Dynamics with ab Initio Potentials

ARTICLES YOU MAY BE INTERESTED IN

The Molpro quantum chemistry package
The Journal of Chemical Physics 152, 144107 (2020); https://doi.org/10.1063/5.0005081

Δ-machine learning for potential energy surfaces: A PIP approach to bring a DFT-based PES to CCSD(T) level of theory
The Journal of Chemical Physics 154, 051102 (2021); https://doi.org/10.1063/5.0038301

Quantum dynamics with ab initio potentials
The Journal of Chemical Physics 155, 080401 (2021); https://doi.org/10.1063/5.0066234
A spectroscopic model for the low-lying electronic states of NO

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. But it may be harmful or even deadly as well. 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 studied (see the paper of Deller and Hogan and references therein). The spectrum of NO was also of great value in many applications, such as temperature measurements by laser induced fluorescence.

The ExoMol project computes molecular line list studies of exoplanet and (other) hot atmospheres. The ExoMol database was formally released in 2016. The most recent 2020 version covers the line lists of 80 molecules and 190 isotopologues, totaling $700 \times 10^6$ transitions. It includes an accurate infrared (IR) line list of NO, called nitoname, which contains the rovibrational transitions within the ground electronic state. The rovibrionic transitions of NO in the ultraviolet (UV) region are not included in nitoname. These bands are strong and atmospherically important and have been observed in many studies. There is no NO UV line list in well-known databases such as HITRAN (high transmission molecular absorption) and GEISA (Gestion et Etude des Informations Spectroscopiques Atmosphériques).

Luque and Crosley investigated the 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.\(^{35,36}\) 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 that 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 modeling the interaction between B\(^2\)\(\Pi\) and C\(^2\)\(\Pi\) states, which is caused by the particular electronic structure of NO. To understand this 15 electron system, one must analyze the electronic configuration of these states from the perspective of molecular orbitals. On the 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 as 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 bond length than NO,\(^{37}\) Rydberg states tend to be lower in energy at short bond lengths, \(r\), while valence states are lower at larger \(r\). Thus, in NO, Rydberg–valence interactions are densely distributed in the neighborhood 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,\(^{38}\) the two states show a strong extended mutual perturbation. They proposed a “de-perturbation” method to explain the vibrational and rotational perturbation of B\(^2\)\(\Pi\)–C\(^2\)\(\Pi\) interaction. Further analysis was made by Gal-lusser and Dressler,\(^{39}\) who set up a vibronic interaction matrix of five \(^2\)\(\Pi\) states and fitted the eigenvalues of the matrix to experimental data in the determination of Rydberg–Klein–Rees (RKR) potential curves and off-diagonal electronic energies. As a consequence, they predicted vibrational states of the B\(^2\)\(\Pi\) electronic state up to \(v = 37\).

In this paper, we propose a method based on directly diagonalizing a rovibronic matrix to resolve the energy structures of B\(^2\)\(\Pi\)–C\(^2\)\(\Pi\) coupled states. This matrix is based on the use of full variational solution of the rovibronic nuclear motion Hamiltonian rather than perturbation theory. This method is general and can be used to predict spectra, for example, at elevated temperatures.

In addition to the vibronic matrix elements (e.g., spin dou-blets) considered in the previous studies, more fine structure terms, such as \(A - doubling\) and spin–rotational coupling, are used to construct the rovibronic matrix. The eigenvalues of the matrix are fitted to rovibronic energies obtained using a MARVEL (measured active rotation-vibration energy level) procedure\(^{38,39}\) analysis of the observed NO IR/visible/UV transitions to ensure a quantitatively accurate result. Figure 1 summarizes the band systems involved in our MARVEL analysis. The objective functions were constrained with the \(ab\) \textit{initio} curves produced using Molpro\(^{40}\) to avoid over-fitting problems. The above procedures are also applied to the A\(^2\)\(\Sigma^+\) state of NO to get a self-consistent description of the doublet electronic states up to and including C\(^2\)\(\Pi\).

This work forms the foundation of our future study on the generation of the UV line list of NO. The modeling of B\(^2\)\(\Pi\)–C\(^2\)\(\Pi\) paves the way for the investigations of molecules with similar avoided crossing structures.

**FIG. 1.** The band systems of NO involved in this work and their names. The \(\gamma\), \(\beta\), and \(\delta\) systems mainly cover the UV transitions of NO. Jenkins \textit{et al.} recorded many visible lines from the B\(^2\)\(\Pi\) state to higher vibrational levels of X\(^2\)\(\Pi\), e.g., those of the \(\beta(3, 16)\) band.\(^{41}\) The high-accuracy IR transitions of the Heath (0, 0) band were measured by Amiot and Verges.\(^{42}\) For a comprehensive band system diagram, see the work of Cartwright \textit{et al.}\(^{43}\)

**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 and C, states and the valence, X and B, states. Figure 2 presents an overview of the low-lying potential energy curve (PECs) and illustrates the importance of the C\(^2\)\(\Pi\)–B\(^2\)\(\Pi\) Rydberg–valence avoided crossing.

The history of high quality configuration interaction (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 was presented and discussed by de Vivie and Peyerimhoff.\(^{46}\) The results of this paper were 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 \textit{et al.}\(^{48,49}\) Although the previous works\(^{45–48,50–53}\) 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\(_{2v}\)
The states of interest are plotted by solid curves. Here, $^2\Sigma^+$ is the $^2\Pi$ to $^2\Pi$ PEC, while $^2\Pi$ is the $^2\Pi$ to $^2\Pi$ PEC.

A Dunning aug-cc-pV(n)Z basis set\(^1\) was used in both CASSCF and MRCI calculations. This basis set has an additional shell of diffuse functions compared 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 $^2\Pi$ and the valence $^4\Pi$ states proved to be a huge obstacle to obtaining satisfactory results. Panel (a) of Fig. 3 shows the terrible behavior of B–C interaction near 1.18 Å. The potential energy curve (PEC) of $^2\Pi$ suddenly jumps to that of $^2\Pi$, producing discontinuity in the PEC of $^2\Pi$. To get the exited states, we used the state average algorithm, but the average energy of the two $^2\Pi$ states changed when traversing the crossing point of $^2\Pi$ and $^2\Pi$.

A valid way to smooth the curves is to increase the number of averaged states. For example, the discontinuities near 1.18 Å disappear when introducing a third $^2\Pi$ state in CASSCF calculation, as shown in panel (b) of Fig. 3. Nevertheless, similar phenomenon arises when the third state comes across L$^2\Pi$. Alternatively, smooth curves can be obtained in limited active space. For example, we can get a continuous curves of $^2\Pi$ 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 an...
The Journal of Chemical Physics

ARTICLE

FIG. 4. The PECs of the $X^2Π$, $A^2Σ^+$, $B^2Π$, $C^2Π$, $D^2Σ^+$, and $L^2Φ$ states, obtained by CASSCF and MRCI + Q calculation starting from 1.06 Å to both sides in the active space [(8, 3, 3, 0) − (2, 0, 0, 0)] with the aug-cc-pV5Z basis set. The third $^3Π$ curve and the $L^2Φ$ curve in panel (a) were manually switched in panel (c) on the right of 1.2 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 shown in the panel as the $L_z$ values obtained are all $L_z$.

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 $X^2Π$ and $B^2Π$ 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 that begin with valence orbitals usually end with valence orbitals, but it is uncertain for those beginning with Rydberg orbitals. The results imply that there are at least two kinds of local minima 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 $Π$ states average with the $Σ$ states, 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 Sec. IV, we use diabatic potentials in modeling the interaction between $B^2Π$ and $C^2Π$ 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 (SOC) terms were also produced. To compensate the error brought by the 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 and MRCI + Q calculation of the $X^2Π$, $A^2Σ^+$, $B^2Π$, $C^2Π$, $D^2Σ^+$, and $L^2Φ$ states, in [(8, 3, 3, 0) − (2, 0, 0, 0)] active space with the aug-cc-pV5Z basis set.

In the CASSCF routine, the projection of angular momentum of a diatomic molecule on its internuclear axis, $A$, 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 $C^2Π$ and $L^2Φ$ 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 $A$ quantum numbers (technically, $L_z$, which is defined as a non-diagonal matrix element between two degenerate components, e.g., $⟨Π_x | L_z | Π_y⟩$) in MRCI calculations, which helps to distinguish the $C^2Π$, $L^2Φ$, and $L^2Π$ 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 $A$ quantum numbers shown in panel (b). The $T_e$ values of $A^2Σ^+$, $B^2Π$, and $C^2Π$ states are compared with those calculated by Shi and East in Table I.

<table>
<thead>
<tr>
<th>State</th>
<th>Shi and east</th>
<th>This work</th>
<th>Huber and herzberg</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A^2Σ^+$</td>
<td>43 558</td>
<td>43 410.2</td>
<td>43 965.7</td>
<td>43 902.99</td>
</tr>
<tr>
<td>$B^2Π$</td>
<td>44 803</td>
<td>46 260.3</td>
<td>45 913.6</td>
<td>45 867.05</td>
</tr>
<tr>
<td>$C^2Π$</td>
<td>51 808</td>
<td>53 709.5</td>
<td>52 126</td>
<td>52 081.97</td>
</tr>
</tbody>
</table>

aSee Sec. IV.

bTwo-state average CASSCF and MRCI + Q calculation.

TABLE I. Comparison of $T_e$ values of the MRCI + Q calculation.

© Author(s) 2021
The PECs in Fig. 4 range from 1.0 Å–1.26 Å. The curves were deliberately truncated at the right endpoint because of the C2II–L2II interaction, as shown in panel (b) of Fig. 3. On the left endpoint, the MRCl program exited with an "INSUFFICIENT OVERLAP" error. The error is triggered by interactions with another 2I state, H11–I1, which lies below B1 near the 1.06 Å and which cannot be described by the reference space. A solution to the problem is to perform MRCl 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 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 Secs. III and IV.

III. MARVEL ANALYSIS OF THE ROVIBRONIC ENERGY LEVELS OF 14N16O

The rovibronic energy levels of $A^3\Sigma^+$, B1, and C1 states were reconstructed by MARVEL analysis of the experimental transitions of the γ, β, and δ systems and states inside the ground state. In the previous work by Wong et al., 25 1136 IR transitions were collected, yielding a spectroscopic network of 4106 energy levels. To retrieve the energy levels of $A^3\Sigma^+$, B1, and C1 states, we extracted further 9861 transitions (including 3393 γ, 5103 β, 1004 δ, and 361 Heath transitions) from the data sources listed in Table II. The vibronic structure of the spectroscopic network is illustrated in Fig. 5.

Although there are studies that report measured transition frequencies for the four band systems of interest, only the most reliable datasets 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 (58LaMi26), but half of them were replaced by more accurate line lists measured by Yoshino et al. around 2000 (94MuYoEs25, 98YeYoEsPa35, 00ImYoEs36, 02ChLoLe58, 02Ru YoTh39, and 06YoThMu38).

### TABLE II. Data sources used in the final MARVEL analysis.

<table>
<thead>
<tr>
<th>Source</th>
<th>Band</th>
<th>$J''_{\text{min}}$</th>
<th>$J''_{\text{max}}$ (cm$^{-1}$)</th>
<th>Uncertainty</th>
<th>Trans.</th>
<th>Trans.</th>
</tr>
</thead>
<tbody>
<tr>
<td>97DaDoKe27</td>
<td>γ(0, 0)</td>
<td>0.5</td>
<td>41.5</td>
<td>0.04–0.15</td>
<td>304</td>
<td>277</td>
</tr>
<tr>
<td>97DaDoKe</td>
<td>γ(0, 1)</td>
<td>0.5</td>
<td>40.5</td>
<td>0.04–0.15</td>
<td>277</td>
<td>245</td>
</tr>
<tr>
<td>97DaDoKe</td>
<td>γ(0, 2)</td>
<td>1.5</td>
<td>39.5</td>
<td>0.04–0.15</td>
<td>339</td>
<td>317</td>
</tr>
<tr>
<td>97DaDoKe</td>
<td>γ(0, 3)</td>
<td>1.5</td>
<td>38.5</td>
<td>0.04–0.1</td>
<td>289</td>
<td>279</td>
</tr>
<tr>
<td>97DaDoKe</td>
<td>γ(0, 4)</td>
<td>1.5</td>
<td>42.5</td>
<td>0.04–0.1</td>
<td>294</td>
<td>283</td>
</tr>
<tr>
<td>97DaDoKe</td>
<td>γ(0, 5)</td>
<td>1.5</td>
<td>37.5</td>
<td>0.04–0.1</td>
<td>266</td>
<td>249</td>
</tr>
<tr>
<td>97DaDoKe</td>
<td>γ(0, 6)</td>
<td>1.5</td>
<td>31.5</td>
<td>0.04–0.1</td>
<td>158</td>
<td>142</td>
</tr>
<tr>
<td>97DaDoKe</td>
<td>γ(1, 0)</td>
<td>0.5</td>
<td>30.5</td>
<td>0.04–0.15</td>
<td>302</td>
<td>275</td>
</tr>
<tr>
<td>97DaDoKe</td>
<td>γ(1, 4)</td>
<td>0.5</td>
<td>41.5</td>
<td>0.04–0.15</td>
<td>295</td>
<td>277</td>
</tr>
<tr>
<td>97DaDoKe</td>
<td>γ(1, 5)</td>
<td>1.5</td>
<td>39.5</td>
<td>0.04–0.15</td>
<td>142</td>
<td>135</td>
</tr>
<tr>
<td>97DaDoKe</td>
<td>γ(2, 6)</td>
<td>1.5</td>
<td>40.5</td>
<td>0.04–0.15</td>
<td>277</td>
<td>246</td>
</tr>
<tr>
<td>97DaDoKe</td>
<td>γ(2, 7)</td>
<td>2.5</td>
<td>41.5</td>
<td>0.04–0.15</td>
<td>160</td>
<td>155</td>
</tr>
<tr>
<td>02ChLoLe58</td>
<td>γ(3, 0)</td>
<td>0.5</td>
<td>24.5</td>
<td>0.03–0.05</td>
<td>227</td>
<td>205</td>
</tr>
</tbody>
</table>

Note: Number of measured (A) and validated (V) Transitions.

The spectroscopic network in MARVEL35 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 $A^3\Sigma^+$ state, the $Q_{21}$ branch is indeed a copy of the $R_{11}$ branch as listed in 97DaDoKe\textsuperscript{25}), duplicate transition is provided in source data. In 27JeBaMu\textsuperscript{41}, 58LaMi\textsuperscript{26}, etc., $\Lambda$-doubling fine structures of many transitions are not resolved; therefore, we simply created two transitions differing in $\epsilon/\eta$ parity with the same frequency in the MARVEL dataset.

The uncertainties of the transitions of 27JeBaMu\textsuperscript{41} and 58LaMi\textsuperscript{26} were given by the combination difference test, referring to the energies of the $X^2\Pi$ state.

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

The transitions of $\gamma(3,0)$, $\beta(6,0)$, and $\beta(11,0)$ bands extracted from 02ChLoLe\textsuperscript{58}, 02ChLoLe\textsuperscript{56}, and 02RuYoTh\textsuperscript{29} were increased by $+0.083$ cm\textsuperscript{-1}, $+0.083$ cm\textsuperscript{-1}, and $+0.067$ cm\textsuperscript{-1}, respectively, as suggested in 05ThRuYo\textsuperscript{64}. The uncertainties of these transitions should be $0.1$ cm\textsuperscript{-1} because the absolute frequencies were not calibrated. However, we used relative accuracy, i.e., $0.03$ cm\textsuperscript{-1}, as the lower bound of uncertainty to constrain the MARVEL analysis. The uncertainties should be adjusted to $0.1$ cm\textsuperscript{-1} if data of higher accuracy are included in the future.

- In the $\beta(10,0)$ band of 06YoThMu\textsuperscript{28}, $R_{13}(3.5)$ and $P_{13}(3.5)$ were exchanged; the $R_{21}$ and $P_{21}$ branches were exchanged.
- In the $\delta(0, 0)$ band of 94MuYoEs\textsuperscript{30}, $P_{12}(15.5)$, and $P_{12}(16.5)$ should be $P_{22}(15.5)$, and $P_{22}(16.5)$, respectively.
- In the $\delta(1, 0)$ band of 00lmYoEs\textsuperscript{31}, the frequencies of $R_{13}(15.5)$, and $R_{13}(15.5)$ should be exchanged; the frequencies of $P_{15}(5.5)$ and $P_{15}(16.5)$ should be $54.668.636$ cm\textsuperscript{-1}.
- In the $\delta(2, 0)$ band of 06YoThMu\textsuperscript{28}, the frequencies of $Q_{22}(5.5)$ and $Q_{22}(6.5)$ should be $56.967.72$ cm\textsuperscript{-1} and $56.966.61$ cm\textsuperscript{-1}, respectively.
- The transitions, $R_{22}(0.5)_{\beta R}, Q_{22}(0.5)_{\beta R}$, $R_{12}(0.5)_{\epsilon R}$ of 97DaDoKe\textsuperscript{27} and $R_{22}(0.5)$ of 02ChLoLe\textsuperscript{26} are related to unknown lower states ($J = 0.5$ and $\Omega = 1.5$). Those transitions were not validated.

The most serious issue we encountered concerned the 2020 measurements of Ventura and Fellows (20VeFe\textsuperscript{32}) who published a new line list for the $\gamma$ system containing 6436 transitions. The transitions of 20VeFe disagree with those measured by Daniel et al. (97DaDoKe).\textsuperscript{2} MARVEL and combination difference analysis indicate that their dataset is self-consistent within the claimed accuracy, i.e., $0.005$ cm\textsuperscript{-1}--$0.06$ cm\textsuperscript{-1}. However, it is inconsistent with the ground state MARVEL energies of Wong et al.\textsuperscript{15} The combination difference test shows that the standard deviations of most energy levels calculated by the dataset are greater than $0.1$ cm\textsuperscript{-1}.

In contrast, the line list of 97DaDoKe\textsuperscript{2} is consistent with others. The measurements of 20VeFe differ from those of 97DaDoKe by up to $0.7$ cm\textsuperscript{-1}, as acknowledged by 20VeFe. The transitions in the $\gamma(3, 4)$ band measured by 97DaDoKe are consistent with the transitions in the $\gamma(3, 0)$ band measured by Cheung et al. (02ChLoLe).\textsuperscript{15} Furthermore, the 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\textsuperscript{-1} shift for the lower three vibrational levels of the $A^3\Sigma^+$ 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.

![FIG. 5. Vibronic structure of the MARVEL analysis. The vertical solid lines in green, blue, and red illustrate the bands of $\gamma$, $\beta$, and $\delta$ systems, respectively. The vertical dashed line in purple represents the Heath (0, 0) band.](image-url)

### TABLE III. Quantum numbers used in the MARVEL analysis.

<table>
<thead>
<tr>
<th>Quan. No.</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J$</td>
<td>Total angular momentum</td>
</tr>
<tr>
<td>Parity</td>
<td>$+$ or $-$</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Vibration quantum number</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>Projection of the total angular momentum on the internuclear axis</td>
</tr>
</tbody>
</table>

![FIG. 6. The differences between the $A^3\Sigma^+$ state MARVEL energies corresponding to 20VeFe and those obtained from the sources of Table II. The average energy shift is $0.43$ cm$^{-1}$.](image-url)
The 20 293 validated transitions (including 3141 γ, 4795 β, 861 δ, and 360 Heath transitions) yielded 327, 1400, and 466 energy levels of the $A^2\Sigma^+$, $B^2\Pi$, 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 material.

Sulakshina and Borkov compared the ground state energies calculated by their RITZ code with our previous MARVEL result. The majority of levels agree within the uncertainty of their determination.

IV. REFINEMENT OF CURVES FOR $^{14}\text{N}^{16}\text{O}$

A. Calculation setup

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

Dvo solves the diatomic molecular Schrödinger equation in two steps. First, the rotation-free radial equation of each electronic state is solved to get the vibrational energy levels, $E_v$, and wavefunctions, $\psi_v(r)$,

$$\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} \psi_v(r) + V_{\text{state}}(r) \psi_v(r) = E_v \psi_v(r), \quad (1)$$

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

$$|\text{state}, J, \Omega, S, \Sigma, \Omega, \Omega, \nu\rangle = |\text{state}, \Lambda, S, \Sigma|J, \Omega, M|\text{state}, \nu\rangle, \quad (2)$$

where $|\text{state}, \Lambda, S, \Sigma|J, \Omega, M\rangle$ 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 $^{14}\text{N}^{16}\text{O}$ is summarized below. More details can be found in the Dvo input file, which is given as the supplementary material and includes the PEC parameters.

- Equation (1) was solved by the Sinc-DVR (discrete variable representation) method.
- The calculation range was from 0.6 Å to 4.0 Å.
- The number of grid points was 701, uniformly spaced.
- The numbers of vibrational basis sets for $X^2\Pi$, $A^2\Sigma^+$, $B^2\Pi$, and $C^2\Pi$ were 60, 15, 30, and 10, respectively.
- The maximum total angular momentum considered here was 52$^1\frac{1}{2}$.
- The upper bound of the total energy was 65 000 cm$^{-1}$.

B. Refinement results of the $A^2\Sigma^+$ state

The PEC of the $A^2\Sigma^+$ state is represented by a fourth-order Extended Morse Oscillator (EMO) function. The EMO is defined as a function of internuclear distance, $r$,

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

where the distance-dependent coefficient $\beta_{\text{EMO}}$ is expressed as

$$\beta_{\text{EMO}}(r) = \sum_{n=0}^{N} \beta_n \psi_n^2(r). \quad (4)$$
The reduced variable $y_{p}^{\text{S3}}(r)$ has the formula

$$y_{p}^{\text{S3}}(r) = \frac{p - (r_{p})^{p}}{p^{p} + (r_{p})^{p}},$$  

(5)

where $p$ controls the shape of $y_{p}^{\text{S3}}(r)$. The programmed EMO function in DUO is not exactly the same as defined by Eq. (3). A reference point $R_{\text{ref}}$ (usually the equilibrium internuclear distance) divides the curve into left and right parts. The numbers of terms $N_{L}$, 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 $D_{c}$ 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 ab initio and refined PECs of the $A^{3}\Sigma^{+}$ state are compared in panel (a) of Fig. 9.

In addition, our model of the $A^{3}\Sigma^{+}$ state contains a spin–rotational term. In DUO, the nonzero diagonal and off-diagonal matrix elements of the spin–rotational operator $H_{\text{SR}}^{\text{S3}}$ are given by

$$\langle A, S, \Sigma | H_{\text{SR}}^{\text{S3}} | A, S, \Sigma \rangle = \frac{\hbar^{2}}{2 \mu r^{2}} y_{\text{SR}}^{\text{S3}}(r) \left[ \Sigma^{2} - S(S + 1) \right],$$  

(6)

$$\langle A, S, \Sigma | H_{\text{SR}}^{\text{S3}} | A, S, \Sigma \pm 1 \rangle = \frac{\hbar^{2}}{4 \mu r^{2}} y_{\text{SR}}^{\text{S3}}(r) \sqrt{S(S + 1) - \Sigma(S \pm 1)} \times \sqrt{J(J + 1) - \Omega(\Omega \pm 1)}. $$  

(7)

The dimensionless spin–rotational coefficient $y_{A}^{\text{SR}}(r)$ of the $A^{3}\Sigma^{+}$ state was modeled as a constant whose value is

$$y_{A}^{\text{SR}}(r) = -2.080 \times 10^{-3}.$$  

(8)

C. Refinement results of the $B^{2}\Pi$–$C^{2}\Pi$ coupled states

1. Deperturbation of the $B^{2}\Pi$–$C^{2}\Pi$ interaction

For this work, we only consider coupling between two electronic states. The interaction between two electronic states belonging 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. This could be accomplished by diagonalizing the matrix

$$\begin{pmatrix} V_{1}(r) & W(r) \\ W(r) & V_{2}(r) \end{pmatrix},$$  

(9)

where $V_{1}(r)$ and $V_{2}(r)$ are two diabatic potentials and $W(r)$ is the coupling curves. The adiabatic PECs, i.e., the eigenvalues of the matrix, are

$$V_{\text{low}}(r) = \frac{V_{1}(r) + V_{2}(r)}{2} = \frac{\sqrt{[V_{1}(r) - V_{2}(r)]^{2} + 4W^{2}(r)}}{2},$$  

(10)

$$V_{\text{upp}}(r) = \frac{V_{1}(r) + V_{2}(r)}{2} + \frac{\sqrt{[V_{1}(r) - V_{2}(r)]^{2} + 4W^{2}(r)}}{2}.$$  

(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

$$W(r) = \sum_{i \neq 0} w_{i}(r - r_{0}) \cosh(b(r - r_{0})).$$  

(12)

The function rapidly decreases to $W_{0}$ when $r$ moves away from $r_{0}$. The coupled PECs of $X^{1}\Sigma^{+}$ and $B^{1}\Sigma^{+}$ states of $C_{2}$ were represented by adiabatic potential in our previous work, producing the accurate line list. Nevertheless, this method is not optimal for

| Parameter | $A^{3}\Sigma^{+}$ | $B^{2}\Pi$ | $C^{2}\Pi$ | $(B^{2}\Pi|H_{\text{SR}}^{\text{S3}}|B^{2}\Pi)$ |
|-----------|-----------------|-----------|-----------|----------------------------------|
| $T_{c}$ (cm$^{-1}$) | 4.390 299 277 309 43 × 10$^{4}$ | 4.586 704 505 95 × 10$^{4}$ | 5.208 197 358 898 84 × 10$^{4}$ | 8.497 424 004 318 92 × 10$^{4}$ |
| $r_{0}$, $r_{\text{ref}}$ (Å) | 1.063 666 008 368 62 | 1.416 639 772 450 69 | 1.063 704 708 372 54 | 1.1 |
| $D_{1}$ (cm$^{-1}$) | 1.292 051 390 303 94 × 10$^{5}$ | 7.162 7 × 10$^{4}$ | 1.271 773 188 884 36 × 10$^{5}$ | 5.774 077 920 425 91 × 10$^{5}$ |
| $P$ | 4 | 4 | 4 | 4 |
| $N_{1}$ | 2 | 4 | 2 | 4 |
| $N_{2}$ | 4 | 8 | 4 | 4 |
| $b_{0}$ (Å$^{-1}$) | 2.704 913 981 796 78 × 10$^{-1}$ | 2.150 144 139 754 52 × 10$^{-1}$ | 2.683 985 603 255 24 × 10$^{-1}$ | 2.015 987 559 388 54 × 10$^{-1}$ |
| $b_{1}$ (Å$^{-1}$) | 2.073 903 440 604 48 × 10$^{-2}$ | 9.835 900 997 934 13 × 10$^{-2}$ | 5.525 275 335 431 32 × 10$^{-1}$ | 0 |
| $b_{2}$ (Å$^{-1}$) | 8.149 010 097 829 77 × 10$^{-2}$ | 4.118 983 730 047 04 × 10$^{-1}$ | 3.452 639 965 214 17 × 10$^{-1}$ | 214 17 × 10$^{-1}$ |
| $b_{3}$ (Å$^{-1}$) | 2.399 702 892 896 83 × 10$^{-1}$ | 0 | 3.768 976 845 482 42 × 10$^{-1}$ | 0 |
| $b_{4}$ (Å$^{-1}$) | 2.050 677 385 076 37 × 10$^{-1}$ | 0 | 3.768 976 845 482 42 × 10$^{-1}$ | 0 |
| $b_{5}$ (Å$^{-1}$) | 1.215 719 272 327 52 × 10$^{-1}$ | 0 | 3.768 976 845 482 42 × 10$^{-1}$ | 0 |
| $b_{6}$ (Å$^{-1}$) | −1.784 955 357 577 77 × 10$^{-1}$ | 0 | 3.768 976 845 482 42 × 10$^{-1}$ | 0 |
| $b_{7}$ (Å$^{-1}$) | 3.127 784 544 525 73 × 10$^{-1}$ | 0 | 3.768 976 845 482 42 × 10$^{-1}$ | 0 |
| $b_{8}$ (Å$^{-1}$) | 5.403 077 729 588 00 × 10$^{-1}$ | 0 | 3.768 976 845 482 42 × 10$^{-1}$ | 0 |
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 the 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.

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 \( D_{\text{NO}} \), without changing its code.

### TABLE V. Optimized Lorentz parameters for the B–C interaction curve.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( b (\text{Å}^{-1}) )</td>
<td>2.217 076 306 467 40 \times 10^1</td>
</tr>
<tr>
<td>( r_0 (\text{Å}) )</td>
<td>1.188 083 737 226 98</td>
</tr>
<tr>
<td>( w_0 (\text{cm}^{-1}) )</td>
<td>1.401 731 787 542 00 \times 10^3</td>
</tr>
</tbody>
</table>
by fitting to constants. The spin–rotational coefficient of the C\textsuperscript{2}Π state was also model on a constant. The values of these terms are listed in Table VI.

The \(\Lambda\) – doubling fine structures of \(\beta\) and \(\delta\) system bands were observed in most of the work listed in Table II. Due to the \(\Lambda\) – doubling matrix elements, i.e., \(<\Lambda'\Sigma'\Omega'|\hat{H}_{ld}|\Lambda\Sigma\Omega>\), according to the terms given by Brown and Merer,\textsuperscript{7} the coefficients of the C\textsuperscript{2}Π state were also model on a constant. The values of these terms are listed in Table VI.

### Table VI. Optimized values of the spin–orbit (SO) and spin–rotation (SR) coupling terms.

<table>
<thead>
<tr>
<th>Term</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\langle C^2\Pi</td>
<td>\hat{H}_{SO}</td>
</tr>
<tr>
<td>(\langle C^2\Pi</td>
<td>\hat{H}_{SO}</td>
</tr>
<tr>
<td>(\gamma_{\text{CR}}^\text{SR})</td>
<td>2.705 930 617 891 97 \times 10^-3</td>
</tr>
</tbody>
</table>

### Table VII. Optimized polynomial parameters of the \(\Lambda\) – doubling curves of the B\textsuperscript{2}Π and C\textsuperscript{2}Π states.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>B\textsuperscript{2}Π</th>
<th>C\textsuperscript{2}Π</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p_v + 2q_v)</td>
<td>(q_v)</td>
<td>(p_v + 2q_v)</td>
</tr>
<tr>
<td>(r_0) (Å)</td>
<td>1.416 504 703 523 37 \times 10^-10</td>
<td>1.416 504 703 523 37 \times 10^-10</td>
</tr>
<tr>
<td>(a_0) (cm(^{-1}))</td>
<td>1.065 516 703 466 50 \times 10^-2</td>
<td>6.453 326 916 333 86 \times 10^-3</td>
</tr>
<tr>
<td>(a_1) (cm(^{-1})Å(^{-1}))</td>
<td>-2.921 142 813 629 27 \times 10^-1</td>
<td>-1.189 741 089 831 74 \times 10^-2</td>
</tr>
<tr>
<td>(a_2) (cm(^{-1})Å(^{-2}))</td>
<td>5.095 170 164 836 91 \times 10^-1</td>
<td>3.040 771 809 152 39 \times 10^-2</td>
</tr>
</tbody>
</table>
observed rovibronic levels. The vibronic residues given by Gallusser and Dressler\textsuperscript{37} are greater than our rovibronic residues. Unlike Gallusser and Dressler, we did not include higher electronic states, such as L\textsuperscript{2}Π and K\textsuperscript{2}Π, in our model, which reduces its range of applicability where the state energy is greater than 63 000 cm\textsuperscript{-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 numbers, 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, \( v \), and \( \Omega \) 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 the B (\( v = 13 \))–C (\( v = 2 \)) 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.

![FIG. 11. Fitting residues of (a) \( \text{A}^2\Sigma^+ \) state and (b) \( \text{B}^2\Pi–\text{C}^2\Pi \) coupled states.](image)

![FIG. 12. Residues against uncertainties of (a) \( \text{A}^2\Sigma^+ \) state and (b) B–C coupled states with vibrational states given in the bars.](image)

---

**TABLE VIII.** Overall comparison of the uncertainty and residue.

<table>
<thead>
<tr>
<th></th>
<th>( \text{A}^2\Sigma^+ )</th>
<th>( \text{B}^2\Pi–\text{C}^2\Pi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>RMS uncertainty</td>
<td>0.042 84</td>
<td>0.079 27</td>
</tr>
<tr>
<td>RMS residue</td>
<td>0.033 90</td>
<td>0.272 17</td>
</tr>
<tr>
<td>Average uncertainty</td>
<td>0.024 53</td>
<td>0.057 53</td>
</tr>
<tr>
<td>Average absolute residue</td>
<td>0.015 99</td>
<td>0.18603</td>
</tr>
</tbody>
</table>
FIG. 13. Calculated and observed energy levels of the B(\(v = 13\))–C(\(v = 2\)) coupled series. The right-hand side 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.

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

<table>
<thead>
<tr>
<th>DUO</th>
<th>Assigned</th>
<th>MARVEL</th>
<th>DUO</th>
<th>Residue</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N)</td>
<td>(N)(^a)</td>
<td>(J)</td>
<td>Parity</td>
<td>(E_{\text{DUO}})</td>
<td>(\Lambda)</td>
</tr>
<tr>
<td>39</td>
<td>39</td>
<td>1.5</td>
<td>+</td>
<td>52.349.0418 52,349.0274</td>
<td>0.0144</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>1.5</td>
<td>+</td>
<td>52.373.2372 52,373.3626</td>
<td>-0.1255</td>
</tr>
<tr>
<td>41</td>
<td>41</td>
<td>1.5</td>
<td>+</td>
<td>52.380.1912 52,380.1101</td>
<td>0.9810</td>
</tr>
<tr>
<td>42</td>
<td>42</td>
<td>1.5</td>
<td>+</td>
<td>52,392.3000 52,392.3172</td>
<td>-0.0165</td>
</tr>
<tr>
<td>64</td>
<td>64</td>
<td>2.5</td>
<td>-</td>
<td>59,217.4976 59,217.9730</td>
<td>-0.4754</td>
</tr>
<tr>
<td>65</td>
<td>65</td>
<td>2.5</td>
<td>-</td>
<td>59,250.3720 59,250.8248</td>
<td>-0.4528</td>
</tr>
<tr>
<td>66</td>
<td>66</td>
<td>2.5</td>
<td>-</td>
<td>59,654.3005 59,654.8551</td>
<td>-0.5846</td>
</tr>
<tr>
<td>67</td>
<td>67</td>
<td>2.5</td>
<td>-</td>
<td>59,692.2845 59,692.6292</td>
<td>-0.3447</td>
</tr>
</tbody>
</table>

\(^a\)The counting numbers \((N)\) were manually assigned to match the corresponding MARVEL energy level.

\(^b\)In these columns, “3” and “4” indicate the B(\(v = 13\)) and C(\(v = 2\)) states, respectively.

V. CONCLUSION

In this paper, potential energy curves and coupling for the low-lying electronic state of NO are calculated using the quantum chemistry package Molpro. The strong interaction between Rydberg and valence states makes the \textit{ab initio} calculation challenging. We obtain both adiabatic and diabatic PECs and SOCs for the \(A^2\Sigma^+\), \(B^2\Pi\), and \(C^2\Pi\) states. The curves were refined by fitting the rovibrionic energy levels calculated by the variational nuclear motion program DUO to those reconstructed by MARVEL analysis. The rms error of the \(A^2\Sigma^+\) state fitting and \(B^2\Pi–C^2\Pi\) coupled state fitting are 0.033 90 cm\(^{-1}\) and 0.272 17 cm\(^{-1}\), respectively, which energies were determined by our use of a MARVEL procedure and the best available measurements. The success of \(B^2\Pi–C^2\Pi\) coupled state fitting validates our deperturbation method for treating the coupled electronic state. This work, when combined with the earlier \(X^2\Pi\) study of Wong et al., provides a comprehensive spectroscopic model for the lowest for electronic states of NO and thus a good start point for...
SUPPLEMENTAL MATERIAL

Three text files are provided as the supplemental material to the article: MARVEL.txt: input transitions file used with MARVEL. NO.model.txt: a Duo input file that fully specifies our spectroscopic model including the associated potential energy and coupling curves.

ACKNOWLEDGMENTS

We are indebted to Dr. Rafal Hakalla (University of Rzeszów) for valuable discussions. Qianwei Qu acknowledges the financial support from University College London and the China Scholarship Council. This work was supported by STFC Project Nos. ST/M001334/1 and ST/R000476/1 and ERC Advanced Investigator Project No. 883830. The authors acknowledge the use of the UCL Myriad, Grace and Kathleen High Performance Computing Facilities and associated support services in the completion of this work.

DATA AVAILABILITY

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

REFERENCES


