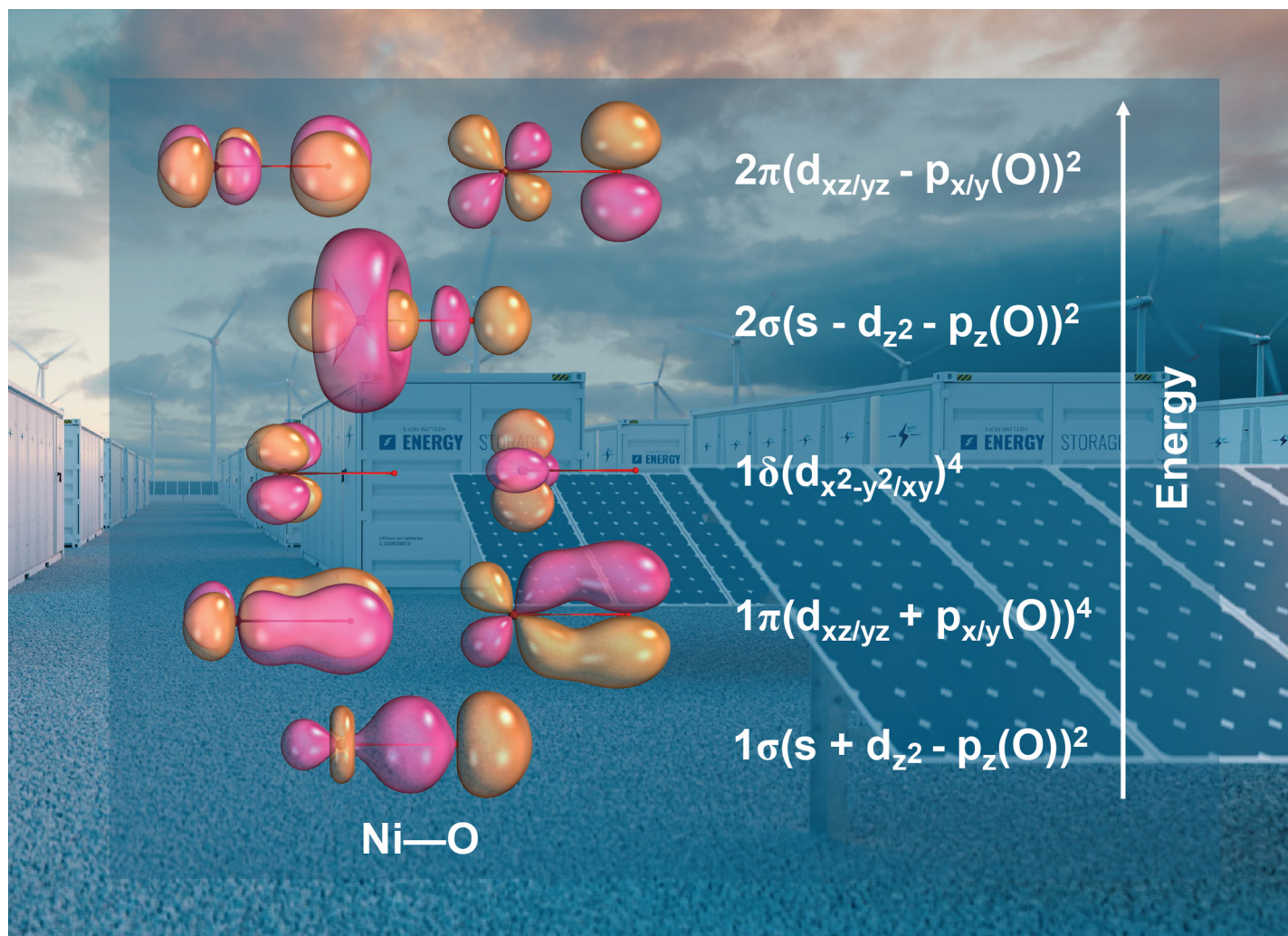




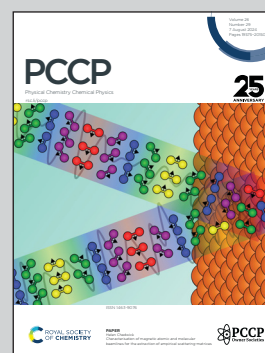
Showcasing research from Professor David Dixon's laboratory, Department of Chemistry & Biochemistry, The University of Alabama, USA.

The electronic structure of diatomic nickel oxide

The electronic structure of diatomic NiO using CASSCF, icMRCI+Q, CCSD(T), and DFT was predicted. There is significant ionic character with the  $2p_z$  of O forming a  $\sigma$  bond with the  $4s/3d_{z^2}$  of the Ni. It is difficult to calculate the vibrational frequency but icMRCI+Q provides a reliable value. The calculated FPD bond dissociation energy is in good agreement with the lower experimental value. 43 DFT functionals were benchmarked to provide guidance for describing more complex NiO systems with only 3 functionals predicting the frequency correctly.

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See David A. Dixon *et al.*,  
*Phys. Chem. Chem. Phys.*,  
2024, **26**, 19646.



Cite this: *Phys. Chem. Chem. Phys.*,  
2024, 26, 19646

# The electronic structure of diatomic nickel oxide†

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David A. Dixon \*

The nature of the Ni–O bond is relevant to catalytic and environmental applications. The vibrational frequency and electronic structure of NiO were calculated using CASSCF, icMRCI+Q, CCSD(T), and DFT. CASSCF predicted a quintet state ( $^5\Sigma^-$ ) ground state for the equilibrium bond distance with a state crossing at 1.65 Å, where the triplet ( $^3\Sigma^-$ ) state becomes of lower energy. These states arise from the  $3d^8(^3F)4s^2(^3F)$  and  $3d^9(^2D)4s^1(^3D)$  configurations of Ni. The icMRCI+Q method predicts a triplet ( $^3\Sigma^-$ ) ground state and does not predict a state crossing with the quintet. This state has significant ionic character with the  $2p_z$  of O bonding with the  $4s/3d_{z^2}$  of the Ni to form a  $\sigma$  bond. The NiO frequency at the icMRCI+Q level of  $835.0\text{ cm}^{-1}$  is in excellent agreement with experiment; the value of  $r_e$  is  $1.5992\text{ Å}$  at this computational level. CCSD(T) predicts  $\omega_e = 888.80\text{ cm}^{-1}$  when extrapolated to the complete basis set limit. Frequencies predicted using CCSD(T) deviate from experiment consistent with the calculations showing large multireference character. A wide array of density functionals were benchmarked. Of the 43 functionals tested, the ones that gave the best prediction of the frequency are  $\omega$ B97XD, CAM-B3LYP, and  $\tau$ -HCTH with respective values of  $831.8$ ,  $838.3$ , and  $837.4\text{ cm}^{-1}$  respectively. The bond dissociation energy (BDE) of NiO is predicted to be  $352.4\text{ kJ mol}^{-1}$  at the Feller–Peterson–Dixon (FPD) level in good agreement with one of the experimental values. The calculated BDEs at the DFT level are sensitive to the choice of functional and atomic asymptote. Sixteen functionals predicted the BDE within  $20\text{ kJ mol}^{-1}$  of the FPD value.

Received 30th April 2024,  
Accepted 14th June 2024

DOI: 10.1039/d4cp01796j

rsc.li/pccp

## Introduction

Solid oxide electrocatalysts (SOEC) have been a focus in recent years due to their applications in renewable energy conversion and storage,<sup>1</sup> as SOEC catalysts can selectively reduce  $\text{H}_2\text{O}$  and  $\text{CO}_2$  to achieve carbon neutral  $\text{H}_2$  generation.<sup>2–7</sup> However, with such common Ni-based catalysts,  $\text{CO}_2$  reduction is challenging.<sup>8</sup> To increase the efficiency and success of these catalysts, Ni supported on yttria stabilized zirconia (YSZ) is being developed as an SOEC catalyst that can reduce  $\text{CO}_2$  with minimal challenges. To fine tune the Ni cathode, a wide array of Ni alloys and NiO materials have been proposed, which require further exploration to understand what role these complexes play in  $\text{CO}_2$  reduction.<sup>9–11</sup> It has been established that Ni clusters on YSZ can interact with the oxygens leading to the formation of Ni–O bonds in the solid state. The current goal is to provide insights into the nature of the Ni–O bond by examining diatomic NiO.

There have been several computational and experimental studies of diatomic NiO. However, different values have been

obtained for the vibrational frequencies as shown in Table 1. Ram and Bernath used Fourier transform infrared emission spectroscopy of the  $A^3\Pi-X^3\Sigma^-$  band of NiO in the near-infrared region and determined the spectroscopic constants for the ground ( $X^3\Sigma^-$ ) and excited ( $A^3\Pi$ ) states by analyzing the vibration–rotation bands.<sup>12</sup> For the ground state, they chose the values of  $\omega_e$  and  $\omega_e x_e$  obtained by Srdanov and Harris in a laser-induced fluorescence (LIF) study including a rotational analysis of NiO.<sup>13</sup> Green *et al.*<sup>14</sup> measured the values of  $\omega_e$  and  $\omega_e x_e$  for NiO in an Ar matrix at 14 K and found similar values to the gas phase spectroscopic values.<sup>13</sup> Anion photoelectron spectroscopy experiments on  $\text{NiO}^-$  by Wu *et al.*<sup>15</sup> provided the adiabatic electron affinity (AEA) and harmonic vibrational frequency for the ground state of NiO. The ionization energy (IE) and other thermochemical data of NiO were reported by Watson *et al.*<sup>16</sup> in their high-temperature mass spectrometry experiments. Other experimental work on NiO includes the microwave spectrum of pure rotational transitions of the  $v = 0$  and  $v = 1$  vibrational states,<sup>17</sup> photoelectron spectroscopy of NiO and  $\text{NiO}^-$ ,<sup>18</sup> and chemiluminescent reactions of nickel with ozone and measured by mass spectrometry.<sup>19</sup> Farber and Srivastava studied the vaporization of NiO(s) and the thermodynamics of reactions of nickel metal with oxygen vapor using effusion-mass spectrometric to obtain a NiO(g) dissociation

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† Electronic supplementary information (ESI) available: Total energies in a.u. See DOI: <https://doi.org/10.1039/d4cp01796j>

Table 1 Ground state spectroscopic parameters of NiO

| Method              | $r_e$ (Å) | $\omega_e$ (cm <sup>-1</sup> )                 | $D_0$ (kJ mol <sup>-1</sup> ) | Ref.    |
|---------------------|-----------|------------------------------------------------|-------------------------------|---------|
| Experiment          | 1.62712   |                                                |                               | 12      |
| Experiment          |           | 800(50)                                        |                               | 15      |
| Experiment          | 1.627     | 839.1 ± 0.5 ( $\omega_e x_e = 5.4 \pm 0.5$ )   |                               | 13      |
| Experiment          |           | 837.61 ± 1.1 ( $\omega_e x_e = 5.92 \pm 0.6$ ) |                               | 14      |
| Experiment          |           |                                                | 349.4 ± 6.3                   | 20      |
| Experiment          |           |                                                | 373 ± 3366 ± 30               | 16      |
| GVB-CI              | 1.60      | 841                                            | 376                           | 22      |
| CISD                | 1.608     | 906                                            | 149                           | 23      |
| CISD+Q              | 1.591     | 848                                            | 254                           | 23      |
| MRCI                | 1.70      | 700                                            |                               | 24      |
| MRCI+Q              | 1.67      | 690                                            |                               | 24      |
| ICACPF              | 1.626     | 850                                            | 362                           | 26      |
| DFT/CAM-B3LYP       | 1.647     | 838.3                                          | 214.2 (BDE(1))                | Current |
| DFT/ $\tau$ -HCTH   | 1.621     | 837.4                                          | 477.6 (BDE(1))                | Current |
| DFT/ $\omega$ B97XD | 1.652     | 831.8                                          | 238.7 (BDE(1))                | Current |
| CCSD(T)/CBS         | 1.6238    | 872.1                                          | 352.4                         | Current |
| icMRCI+Q/CBS        | 1.5992    | 835.0                                          | 387.7                         | Current |

energy.<sup>20</sup> A lower limit to the dissociation energy of 250.9 ± 19.3 kJ mol<sup>-1</sup> was reported by Fisher and Armentrout based on reactions of nickel ions with cyclopropane and ethylene oxide using guided ion beam mass spectrometry.<sup>21</sup>

Computational studies of NiO range from density functional theory (DFT), Hartree–Fock, configuration interaction singles and doubles (CISD), and generalized valence bond (GVB) methods. Walch and Goddard used the GVB method to describe the Ni–O bonds in NiO, Ni<sub>2</sub>O, Ni<sub>3</sub>O, Ni<sub>4</sub>O, Ni<sub>4</sub>O<sup>+</sup>, Ni<sub>5</sub>O, and Ni<sub>5</sub>O<sup>+</sup>.<sup>22</sup> Dolg *et al.* calculated some of the spectroscopic parameters and binding energies of NiO using *ab initio* methodologies (SCF, CISD and CISD+Q) with single-electron fit (SEFIT) pseudopotentials and an active space comprising the 4s and 3d Ni atomic orbitals and 2s and 2p O orbitals.<sup>23</sup> The predicted values of the bond distance and  $\omega_e$  were highly dependent on the computational methodology. Similar behavior was found by Bauschlicher *et al.*<sup>24</sup> who compared the results from SCF, CISD, CISD+Q, MRCI, and MRCI+Q calculations. These authors noted that the large differences between the CISD and CISD+Q results show that the reference space must be larger, so that multireference CI (MRCI) calculations are necessary. They also disagreed with the description of the bonding by Walch and Goddard III, who predicted that NiO has a covalent bond.<sup>19,21</sup> DFT/B3LYP calculations of NiO have also been reported.<sup>25</sup> Bauschlicher and Maitre<sup>26</sup> have surveyed computational studies of all of the first-row transition metal oxides. They note that it is difficult to calculate the properties of NiO from single reference starting points due to localization of  $\pi^*$  singly occupied orbitals on the Ni or O. Their best values were obtained at the CASSCF/ICACPF (internally contracted average coupled pair functional) level with an extended polarized double- $\zeta$  basis set on Ni and the aug-cc-pVTZ basis set on the O without the diffuse f.

## Computational methods

The equilibrium geometry ( $r_e$ ) of NiO was initially optimized using DFT with the hybrid B3LYP exchange correlation functional<sup>27–29</sup> the correlation consistent aug-cc-pVDZ basis set for O,<sup>30,31</sup> and the aug-cc-pVDZ-PP basis set with an effective

core potential<sup>32</sup> for Ni.<sup>33,34</sup> The B3LYP geometries were used as starting points for calculations at the CCSD(T) level (coupled cluster theory with single and double excitations with perturbative triples).<sup>35–41</sup> All coupled cluster calculations were performed with the R/UCCSD(T) approach, where the restricted open-shell Hartree–Fock calculation is performed followed by a relaxation of the spin constraint at the coupled cluster level. The CCSD(T) calculations utilized the third-order Douglas–Kroll–Hess Hamiltonian (DKH3), with the aug-cc-pVNZ-DK<sup>42</sup> basis set for O and Ni. This combination of basis sets will be further denoted as aN-DK. Harmonic and anharmonic frequencies ( $\omega_e$ ,  $\omega_e x_e$ ) were obtained using a Dunham expansion at the CCSD(T) level.<sup>43</sup>

The state-averaged complete active space self-consistent field (SA-CASSCF)<sup>44–48</sup> approach was performed to account for non-dynamical correlation effects and describe the lowest spin-free states,  $\Lambda$ S. To account for the two quasi-degenerate  $^3F_g$  and  $^3D_g$  atomic states of Ni coupling with the O( $^3P_g$ ) and to improve the convergence near the equilibrium bond distance, 36  $\Lambda$ S singlet, 37  $\Lambda$ S triplet, and 39  $\Lambda$ S quintet states were optimized in the SA-CASSCF calculations. The atomic aug-cc-pVQZ-DK<sup>42</sup> basis set for O and aug-cc-pwCVQZ-DK<sup>49</sup> basis set for Ni were used, and this combination will be denoted as awQ-DK. These calculations were carried out in the highest Abelian point group available,  $C_{2v}$ . Expectation values of  $L_z^2$  were calculated to ensure that both degenerate components of each  $\Lambda$  state were correctly accounted for. The active space of NiO includes 14 electrons in nine orbitals ( $4 \times a_1$ ,  $2 \times b_1$ ,  $2 \times b_2$ ,  $1 \times a_2$  in  $C_{2v}$  symmetry), which have dominant 2p of O and 4s and 3d of Ni.

Dynamic correlation effects were accounted for by using the internally contracted multireference configuration interaction (icMRCI) method taking the SA-CASSCF wavefunctions as a reference, as implemented in MOLPRO.<sup>50–52</sup> The relaxed Davidson correction (+Q)<sup>53</sup> was included as an estimate of missing quadruple excitations. Only the ground state ( $^3\Sigma^-$ ) was optimized and a potential energy curve (PEC) was calculated around the bond distance but keeping the nine  $A_2$   $\Lambda$ S triplet states as a reference. The same approach was done using second-order perturbation theory (CASPT2)<sup>54,55</sup> in order to recover dynamical correlation effects; however, some points on the ground state

PEC did not fit on the curve well enough to calculate the vibrational properties. The harmonic, and anharmonic frequencies ( $\omega_e$ ,  $\omega_e x_e$ ) were obtained using a Durham expansion<sup>43</sup> in the same interval used in the UCCSD(T)/aD-DK calculation, but at the icMRCI+Q/awQ-DK level. Certain points did not fall on the curves and were not included in the calculation of the frequencies. Inclusion of these points resulted in a large sum of squares of residuals in the fitting procedure, a large deviation in the fitted minimum energy, and yielded a value of  $\omega_e x_e > 15 \text{ cm}^{-1}$ . For the icMRCI+Q calculation, even small errors in the energies used in the fit had a significant impact on the predicted  $\omega_e x_e$  for the ground state. Thus, only  $\omega_e$  was calculated from the fit for the icMRCI+Q. Spectroscopic properties produced by the CASSCF, icMRCI+Q, and CCSD(T) calculations were then extrapolated to the complete basis set limit (CBS) using awCnZ-DK (where n = D, T and Q) using the eqn (1) for the energies.

$$E_n = E_{\text{CBS}} + A \exp[-(n-1)] + B \exp[-(n-1)^2] \quad (1)$$

The bond dissociation energy (BDE) of NiO was predicted at the Feller–Peterson–Dixon (FPD) composite thermochemistry level,<sup>56–59</sup> including spin–orbit corrections and the zero-point energies calculated at the icMRCI+Q/awn-DK level.

For the DFT benchmark study, the 43 selected functionals are given in Table 2 and consist of a mix of local spin density approximation (LSDA), general gradient approximations (GGA), meta GGA (mGGA), hybrid GGA (HGGA), and hybrid meta GGA (HmGGA) functionals. The optimization and frequency analysis conducted with the given functionals started with the B3LYP optimized geometry. The DFT calculations were done with the aug-cc-pVDZ basis set on O and the aug-cc-pVDZ-PP basis set on Ni (10 electron pseudopotential on Ni). The DFT calculations were performed at the unrestricted spin level.

A bonding analysis of NiO was performed based on the natural population analysis (NPA) results based on the Natural Bond Orbitals (NBOs)<sup>101,102</sup> using NBO7<sup>103,104</sup> with the MOL-PRO program package at the awQ-DK level.

Table 2 DFT exchange–correlation functionals

| Method                          | Exchange                            | Correlation                         | Type  |
|---------------------------------|-------------------------------------|-------------------------------------|-------|
| B1B95 <sup>60</sup>             | Becke 96                            | Becke 95                            | HmGGA |
| B1LYP <sup>30,61</sup>          | Becke 96                            | Lee–Yang–Parr                       | HGGA  |
| B3LYP <sup>27,28</sup>          | Becke 93                            | Lee–Yang–Parr                       | HGGA  |
| B3P86 <sup>28,65</sup>          | Becke 93                            | Perdew 86                           | HGGA  |
| B3PW91 <sup>28</sup>            | Becke 93                            | Perdew–Wang 91                      | HGGA  |
| B971 <sup>64</sup>              | Handy–Tozer’s modified B97          | Handy–Tozer’s modified B97          | HGGA  |
| B972 <sup>65</sup>              | Wilson–Bradley–Tozer’s modified B97 | Wilson–Bradley–Tozer’s modified B97 | HGGA  |
| B98 <sup>66</sup>               | Becke 98                            | Becke 98                            | HGGA  |
| BP86 <sup>62,67</sup>           | Becke 88                            | Perdew 86                           | GGA   |
| BMK <sup>68</sup>               | Boese–Martin                        | Perdew 86                           | HGGA  |
| CAM-B3LYP <sup>69</sup>         | Becke 88                            | Lee–Yang–Par                        | HGGA  |
| HSE06 <sup>70–74</sup>          | Heyd–Scuseria–Ernzerhof             | Perdew–Burke–Ernzerhof              | HGGA  |
| HS06 <sup>70–74</sup>           | Heyd–Scuseria–Ernzerhof             | Perdew–Burke–Ernzerhof              | HGGA  |
| HSE03 <sup>70–74</sup>          | Heyd–Scuseria–Ernzerhof             | Perdew–Burke–Ernzerhof              | HGGA  |
| LC- $\omega$ PBE <sup>75</sup>  | Perdew–Burke–Ernzerhof              | Perdew–Burke–Ernzerhof              | HGGA  |
| M052X <sup>76</sup>             | Minnesota 05                        | Minnesota 05                        | HmGGA |
| M05 <sup>77</sup>               | Minnesota 05                        | Minnesota 05                        | HmGGA |
| M062X <sup>78</sup>             | Minnesota 062x                      | Minnesota 062X                      | HmGGA |
| M06 <sup>78</sup>               | Minnesota 06                        | Minnesota 06                        | HmGGA |
| M06HF <sup>79,80</sup>          | Minnesota 06HF                      | Minnesota 06HF                      | HmGGA |
| M08HX <sup>81</sup>             | Minnesota 08HX                      | Minnesota 08HX                      | HmGGA |
| M11 <sup>82</sup>               | Minnesota 11                        | Minnesota 11                        | HmGGA |
| MN12SX <sup>83</sup>            | Minnesota 12SX                      | Minnesota 12SX’                     | HmGGA |
| MN15 <sup>84</sup>              | Minnesota 15                        | Minnesota 15                        | HmGGA |
| mPW1LYP <sup>27,85</sup>        | Barone’s modified PW91              | Lee–Yang–Par                        | HGGA  |
| mPW1PBE <sup>85–87</sup>        | Barone’s modified PW91              | Perdew–Burke–Ernzerhof              | HGGA  |
| mPW1PW91 <sup>63,85</sup>       | Barone’s modified PW91              | Perdew–Wang 91                      | HGGA  |
| mPW3PBE <sup>85–87</sup>        | Barone’s modified PW91              | Perdew–Burke–Ernzerhof              | HGGA  |
| N12SX <sup>83</sup>             | N12SX                               | N12SX’                              | HmGGA |
| O3LYP <sup>27,88</sup>          | Handy’s OPTX                        | Lee–Yang–Par                        | HGGA  |
| PBE1PBE <sup>86,89</sup>        | Perdew–Burke–Ernzerhof              | Perdew–Burke–Ernzerhof              | HGGA  |
| PBEh1PBE <sup>86,90</sup>       | 98 Revised PBE                      | Perdew–Burke–Ernzerhof              | HGGA  |
| PBE <sup>86</sup>               | Perdew–Burke–Ernzerhof              | Perdew–Burke–Ernzerhof              | GGA   |
| PBE0 <sup>89</sup>              | Perdew–Burke–Ernzerhof              | Perdew–Burke–Ernzerhof              | HGGA  |
| PW91 <sup>63,91</sup>           | Perdew–Wang 1991                    | Perdew–Burke–Ernzerhof              | GGA   |
| SOGGA11X <sup>92</sup>          | SOGGA11X                            | SOGGA11X                            | HmGGA |
| SVWN5 <sup>93,94</sup>          | Slater                              | VWN Functional V                    | LSDA  |
| $\tau$ -HCTH <sup>95</sup>      | $\tau$ -Dependent of HCTH           | $\tau$ -Dependent of HCTH           | mGGA  |
| TPSSH <sup>96</sup>             | Tao–Perdew–Staroverov–Scuseria      | Tao–Perdew–Staroverov–Scuseria      | HmGGA |
| $\omega$ B97 <sup>97</sup>      | Becke 97                            | Becke 97                            | HGGA  |
| $\omega$ B97X <sup>97</sup>     | Becke 97                            | Becke 97                            | HGGA  |
| $\omega$ B97XD <sup>98,99</sup> | Becke 97                            | Becke 97                            | HGGA  |
| X3LYP <sup>27,100</sup>         | Becke 97                            | Becke 97                            | HGGA  |

The DFT calculations were done using the Gaussian 16 program.<sup>105</sup> All CCSD(T), CASSCF, CASPT2, and MRCI+Q calculations were performed in the MOLPRO 2021<sup>50–52</sup> computational chemistry program on computers at The University of Alabama, and the Alabama Supercomputing Authority (Dense Memory Cluster).

## Results and discussion

### Vibrational frequency

In the multiconfiguration and multireference calculations, the two lowest atomic states arising from the  $3d^8(^3F)4s^2(^3F)$  and  $3d^9(^2D)4s(^3D)$  configurations of Ni were correlated because their associated spin-orbit states are very close in energy. This resulted in a high density of molecular electronic states around the minimum bond distance of the ground state up to  $20\,000\text{ cm}^{-1}$  relative to the ground state for the SA-CASSCF calculations. A quintet state ( $^5\Sigma^-$ ) was predicted as the ground state, followed by a triplet ( $^3\Sigma^-$ ) state close in energy, with bond distances of about  $1.77\text{ \AA}$  and  $1.69\text{ \AA}$ , respectively. Fig. 1 shows this behavior at the SA-CASSCF level.

The inclusion of dynamic correlation effects by icMRCI+Q dramatically changed the description of electronic molecular states of NiO. Spin-orbit effects were also included to check whether possible avoided crossings could change the description of the potential energy curves. However, this did not happen for the  $\Omega$  states resulting from the  $\Lambda S^5\Sigma^-$  ( $\Omega = 0, 1, 2$ ) and  $^3\Sigma^-$  ( $\Omega = 0, 1$ ) states. The spin-orbit splitting was  $107\text{ cm}^{-1}$  for the ground

Table 3 Low-lying states of NiO at the icMRCI+Q/awQ-DK + SO level

| State          | $\Omega$ | $\Delta E$ (eV) | $\Lambda S$ composition       |
|----------------|----------|-----------------|-------------------------------|
| $^3\Sigma_0^-$ | 0        | 0.000           | 98% $^3\Sigma^-$ + 2% $^3\Pi$ |
| $^3\Sigma_1^-$ | 1        | 0.006           | 99% $^3\Sigma^-$ + 1% $^3\Pi$ |
| $^5\Sigma_2^-$ | 2        | 0.560           | 95% $^5\Sigma^-$ + 4% $^3\Pi$ |
| $^5\Sigma_1^-$ | 1        | 0.560           | 99% $^5\Sigma^-$ + 1% $^3\Pi$ |
| $^5\Sigma_0^-$ | 0        | 0.560           | 100% $^5\Sigma^-$             |

state  $^3\Sigma^-$  ( $\Omega = 0$ ) and the first excited state  $^3\Sigma^-$  ( $\Omega = 1$ ). Table 3 presents the composition of the spin-orbit states that correlate to the  $^5\Sigma^-$  and  $^3\Sigma^-$  states. Fig. 2 shows the spin-orbit icMRCI+Q/awQ-DK potential energy curves up to  $8000\text{ cm}^{-1}$ . The ground state at the icMRCI+Q level was predicted to be the  $^3\Sigma_0^-$  and lies more than  $4000\text{ cm}^{-1}$  below the  $^5\Sigma_2^-$  state; thus, there is no crossing between the triplet and quintet states as was found at the SA-CASSCF level. There is no significant change in the shape of the PECs and the energy splitting due to the spin-orbit effects is small for NiO, so the following analysis will focus on the  $\Lambda S$  states. Table 4 presents the spectroscopic parameters calculated for the ground state ( $^3\Sigma^-$ ) of NiO using the awT-DK and awQ-DK basis sets, and the extrapolation to the complete basis set (CBS) limit. The basis set has very little effect on the bond distance, which shows a small shortening as more functions are included in the basis set, as well as a small decrease in the  $\omega_e$  and  $\omega_e x_e$ . The inclusion of spin-orbit coupling lowers the energy of the ground state by  $111\text{ cm}^{-1}$  relative to the value without spin orbit and has no significant impact on the bond distance. In the spin-orbit calculation, a small change in the shape of the PECs around the bond distance decreases the  $\omega_e$  and  $\omega_e x_e$  for the  $\Omega$  states associated with the  $\Lambda S^3\Sigma^-$  state.

Coupled cluster theory at the CCSD(T) level was used as the benchmark of the single reference methods as shown in Table 4. There is a modest basis set effect from aD to aT with the overall bond distance decreasing by  $0.01\text{ \AA}$ , and the  $\omega_e$  increasing by  $20\text{ cm}^{-1}$ . However, there is little effect of increasing the basis set from aT to aQ on the bond distance and frequency. When correlating the outer core electrons in the system, the bond distance is very similar to the calculations correlating only the valence electrons. The effect on the  $\omega_e$  is modest with the frequencies being roughly  $10\text{ cm}^{-1}$  less than valence only calculations. There are large  $T_1$  values for the CCSD(T) calculations showing substantial multi-reference character which arises from the  $3d^8(^3F)4s^2(^3F)$  and  $3d^9(^2D)4s(^3D)$  configurations as described above. The quintet state is  $149\text{ kJ mol}^{-1}$  above the triplet at the awcTZ-DK level of theory.

The potential energy curve calculated at the CCSD(T)/awCQ-DK level is given in Fig. 3. Potential energy curves calculated at the CCSD(T) level were obtained at intervals of  $0.01\text{ \AA}$  as the frequency of NiO is highly sensitive to  $R_e$ , and to appropriately model the  $^5\Sigma^-$  ( $\Omega = 0, 1, 2$ ) and  $^3\Sigma^-$  ( $\Omega = 0$ ) state crossing that occurs at approximately  $1.62\text{ \AA}$  in the multi-reference calculations. When compared to the results from the multireference and multiconfigurational calculations, icMRCI+Q and CASSCF, respectively, CCSD(T) consistently overestimates  $\omega_e$ . Fig. 3 shows an overlay of the potential energy curves from the

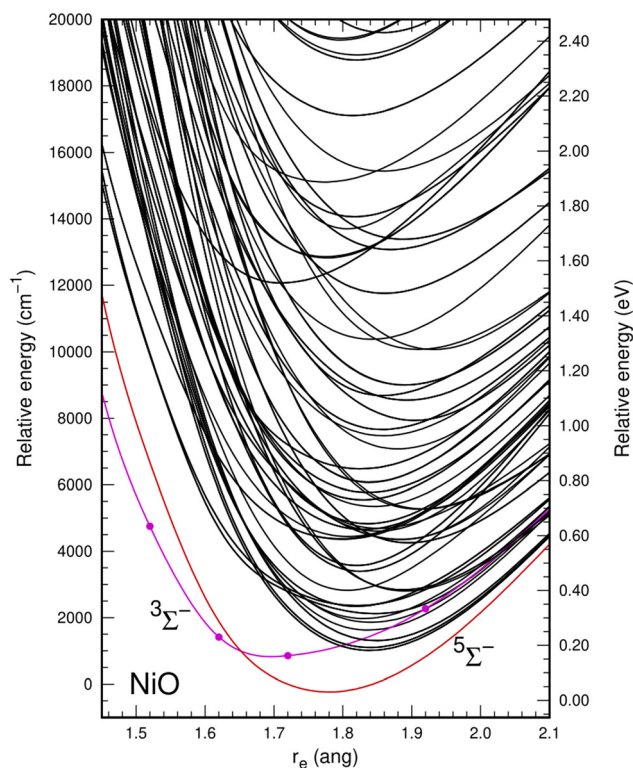


Fig. 1 Potential energy curves of the low-lying  $\Lambda S$  singlet, triplet, and quintet SA-CASSCF states.

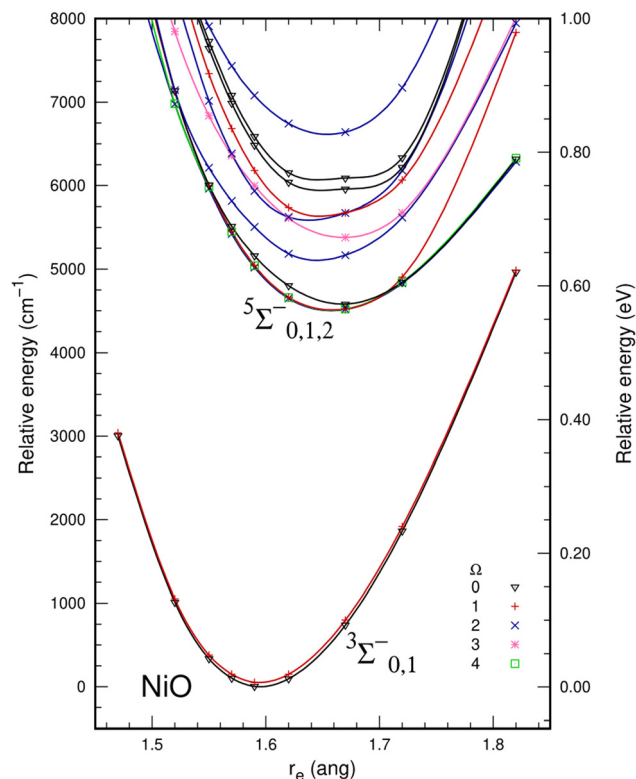


Fig. 2 Potential energy curves of the low-lying  $\Omega$  states using the spin-orbit icMRCI+Q energies.

Table 4 Spectroscopic parameters for the ground state ( $^3\Sigma^-$ ) of NiO calculated at the icMRCI+Q/awn-DK ( $n = T, Q$ ) level

| Method   | Basis set | $r_e/\text{\AA}$ | $\omega_e/\text{cm}^{-1}$ | $\omega_e x_e$ | $T_1$  |
|----------|-----------|------------------|---------------------------|----------------|--------|
| icMRCI+Q | awT-DK    | 1.6023           | 838.5                     | <sup>a</sup>   |        |
| icMRCI+Q | awQ-DK    | 1.6003           | 836.1                     | <sup>a</sup>   |        |
| icMRCI+Q | CBS       | 1.5992           | 835.0                     | <sup>a</sup>   |        |
| CCSD(T)  | aD-DK     | 1.63628          | 865.6                     | 1.87           | 0.129  |
| CCSD(T)  | aT-DK     | 1.62481          | 889.08                    | 2.08           | 0.126  |
| CCSD(T)  | aQ-DK     | 1.62276          | 889.40                    | 1.93           | 0.126  |
| CCSD(T)  | CBS       | 1.62177          | 888.80                    | 1.82           |        |
| CCSD(T)  | awT-DK    | 1.62496          | 876.09                    | 2.29           | 0.1029 |
| CCSD(T)  | awQ-DK    | 1.62425          | 873.54                    | 1.94           | 0.1029 |
| CCSD(T)  | CBS       | 1.62384          | 872.07                    | 1.74           |        |

<sup>a</sup>  $\omega_e x_e$  was not calculated. See Computational section for discussion.

CCSD(T), MRCI, MRCI+Q, and CASSCF calculations. Therefore, as a benchmark, methods other than CCSD(T) should be used due to the highly multireference character of the Ni–O bond.

### Thermochemistry

The bond dissociation energies (BDEs) of NiO calculated at CCSD(T)/awn-DK and icMRCI+Q/awn-DK levels are given in Table 5. Spin-orbit (SO) constants were calculated at the icMRCI+Q/awn-DK level and these numbers were used to estimate the final BDE values in both cases. Due to the excessive number of singlet, triplet, and quintet electronic molecular states correlating to the two lowest dissociation

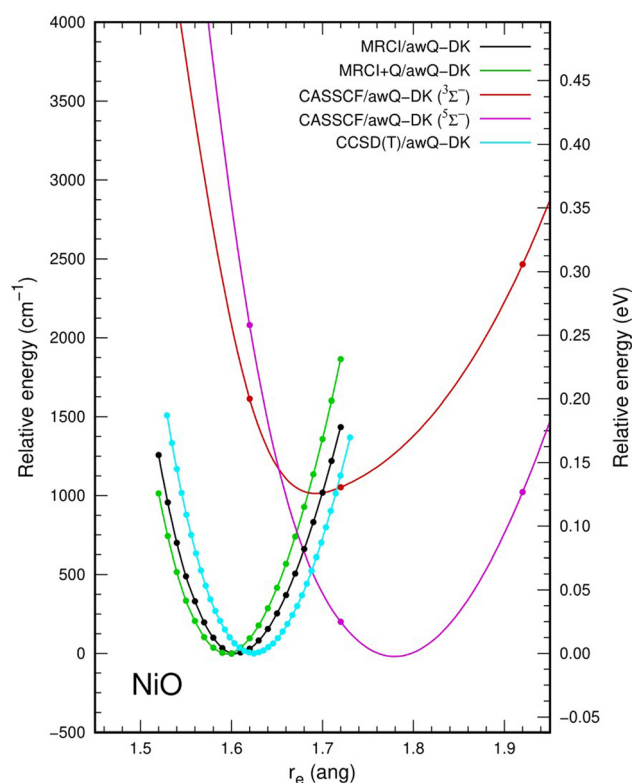


Fig. 3 Potential energy curves of the ground  $^3\Sigma^-$  state calculated at the CCSD(T)/awQ-DK level (light blue), the potential energy curve of the  $^3\Sigma^-$  state calculated at the icMRCI+Q/awQ-DK level (black), the potential energy curve of the  $^3\Sigma^-$  state calculated at the icMRCI+Q/awQ-DK level (green), the potential energy curve of the  $^5\Sigma^-$  state calculated at the CASSCF/awQ-DK level (red), and the potential energy curve of the  $^3\Sigma^-$  state calculated at the CASSCF/awQ-DK level (purple).

channels,  $\text{Ni}(^3F_g) + \text{O}(^3P_g)$  and  $\text{Ni}(^3D_g) + \text{O}(^3P_g)$ , the icMRCI+Q did not converge properly at the dissociation limit. Therefore, only the NiO triplet states ( $9 A_1, 9 B_1, 9 B_2, 9 A_2$ ) were optimized in the SA-CASSCF, and these states were taken as a reference for the ground state optimization in the icMRCI+Q. The  $L_z^2$  numbers confirmed the correct convergence in the asymptotic limit at  $r(\text{Ni–O}) = 6 \text{ \AA}$ .

For the CCSD(T) calculations, the BDE was calculated relative to separate atomic energies, instead of using the supermolecule approximation used for icMRCI+Q. Due to the multi-reference nature of the triplet ground state, the BDE at the FPD/CCSD(T) level was first calculated relative to the excited quintet state where the  $T_1$  values are much smaller showing less multi-reference character. The BDE of the ground triplet state was then obtained by using the icMRCI+Q adiabatic energy difference between the triplet ground state and the excited quintet state.

We have previously found that the CCSD(T) energies can be improved by using orbitals from density functional theory.<sup>106–108</sup> Thus, another approach to the prediction of the BDE of NiO is to use orbitals generated at the DFT level using the PW91 functional for the triplet state. This approach led to reasonable values of the  $T_1$  diagnostic<sup>109</sup> on the order of 0.015. The BDE for the triplet state was substantially improved over

**Table 5** BDE (kJ mol<sup>−1</sup>) including the spin–orbit and zero-point energy (ZPE) corrections calculated at the CCSD(T)/awn-DK and icMRCI+Q/awn-DK levels

| Calculation                                    | awT-DK | awQ-DK | CBS (awn-DK) |
|------------------------------------------------|--------|--------|--------------|
| CCSD(T) Quintet                                | 238.0  | 235.6  | 234.2        |
| icMRCI+Q                                       | 388.8  | 398.7  | 404.3        |
| SO constant (Ni)                               | 12.0   | 12.0   | 12.0         |
| SO constant (O)                                | 0.9    | 1.0    | 1.0          |
| SO constant (NiO <sup>3</sup> Σ <sup>−</sup> ) | 1.3    | 1.3    | 1.3          |
| SO constant (NiO <sup>5</sup> Σ <sup>−</sup> ) | 7.2    | 3.3    | 1.0          |
| ZPE correction <sup>3</sup> Σ <sup>−</sup>     | 5.0    | 5.0    | 5.0          |
| ZPE correction <sup>5</sup> Σ <sup>−</sup>     | 3.2    | 3.3    | 3.3          |
| FPD/CCSD(T) <sup>5</sup> Σ <sup>−</sup>        | 229.1  | 222.6  | 218.9        |
| FPD/CCSD(T) <sup>3</sup> Σ <sup>−</sup>        | 362.6  | 356.1  | 352.4        |
| Final icMRCI+Q <sup>3</sup> Σ <sup>−</sup>     | 372.2  | 382.1  | 387.7        |
| Watson <i>et al.</i> <sup>16</sup>             |        |        | 373.2        |
| Farber and Srivastava <sup>20</sup>            |        |        | 349.4 ± 6.3  |

that using the HF orbitals for the CCSD calculations and is within 10 kJ mol<sup>−1</sup> of the value from the quintet state.

The calculated FPD/CCSD(T) and icMRCI+Q BDEs of the triplet ground state of NiO are not in particularly good agreement with each other, differing by 37 kJ mol<sup>−1</sup>. The experimental results Farber and Srivastava<sup>20</sup> and Watson *et al.*<sup>16</sup> differ by 24 kJ mol<sup>−1</sup> so they cannot be used to help in distinguishing between the two calculated values. The FPD value is consistent with the lower value of 349.4 ± 6.3 kJ mol<sup>−1</sup><sup>20</sup> within the error bars. The icMRCI+Q value is 14 kJ mol<sup>−1</sup> greater than the larger experimental value of 372.2 kJ mol<sup>−1</sup>.<sup>16</sup>

## Electronic structure

The orbital populations and the charges (*q*) from NBO analysis for NiO are shown in Table 6. The NBO analysis in Table 7 shows that NiO has significant ionic interactions with a highly polarized σ bond that is predominantly composed of the 2p<sub>z</sub> on O and the 4s on Ni. Two α unpaired electrons associated with the dπ non-bonding orbitals on nickel result in the <sup>3</sup>Σ<sup>−</sup> ground state. Fig. 4 also shows the SA-CASSCF natural orbitals at the awQ-DK level associated with the nine electrons correlated in the 14 orbitals of the active space. The icMRCI+Q wavefunction for the ground state indicates a strong multireference character. The corresponding major contributions are given in eqn (2)

$$0.71 |1\sigma^2 1\delta^4 2\sigma^2 1\pi^4 2\pi^2\rangle - 0.39 |1\sigma^2 1\delta^4 2\sigma^1 3\sigma^1 1\pi^4 2\pi^2\rangle \quad (2)$$

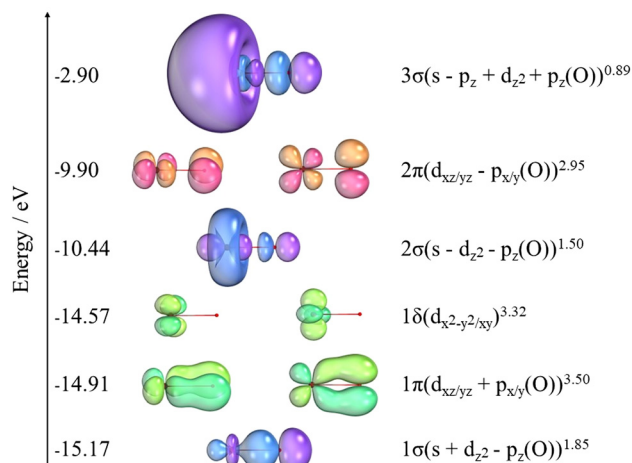
There are 10 additional configurations whose coefficients range from 0.10 to 0.20. The triplet state is comprised of two α unpaired electrons associated with the dπ non-bonding orbitals on Ni. Further NBO analysis shows that NiO has significant

**Table 6** NPA charges (*q*) and population for NiO at awQ-DK level

| Property       | NiO ( <sup>3</sup> Σ <sup>−</sup> ) |
|----------------|-------------------------------------|
| <i>q</i> (Ni)  | 1.405                               |
| <i>q</i> (O)   | −1.405                              |
| 4s (4sα/4sβ)   | 0.49 (0.24/0.24)                    |
| 3d (3dα/3dβ)   | 8.07 (4.96/3.11)                    |
| O 2p (2pα/2pβ) | 5.39 (2.76/2.63)                    |

**Table 7** NBOs of NiO at the awQ-DK level

| NBO      | Symmetry | occ   | Ni%q | Ni%s | Ni%d | O%q  | O%s  | O%p  |
|----------|----------|-------|------|------|------|------|------|------|
| Ni–O     | σ        | 2.000 | 23.7 | 96.3 | 3.3  | 76.3 | 6.1  | 93.6 |
| LP(Ni)   | δ        | 4.000 | 100  | 0.0  | 100  |      |      |      |
| LP(Ni)   | σ        | 1.998 | 100  | 3.2  | 96.8 |      |      |      |
| LP(Ni) α | π        | 1.994 | 100  | 0.0  | 99.9 |      |      |      |
| LP(O)    | σ        | 1.998 |      |      |      | 100  | 94.1 | 5.9  |
| LP(O)    | π        | 3.982 |      |      |      | 100  | 0.0  | 100  |

**Fig. 4** Natural orbitals (SA-CASSCF/awQ-DK) energies and composition for the 14 electrons correlated in the active space. Unlabeled orbitals are on Ni. Ni on the left and O on the right. 80% of the surfaces were accounted for.

ionic interactions and a σ bond that is mostly a p<sub>z</sub> of oxygen combined with the 4s of nickel.

## Benchmarking DFT functionals: frequency

Table 8 shows  $\omega_e$  and  $r_e$  calculated using 43 DFT functionals benchmarked against the best multireference value and experiment. Of the functionals tested, 3 functionals predicted  $\omega_e$  in reasonable agreement with experiment and the icMRCI+Q calculations. The three best functionals were CAM-B3LYP,  $\tau$ -HCTH, and  $\omega$ B97xd, which predicted  $\omega_e$  within 5 cm<sup>−1</sup> of experiment and of the icMRCI+Q calculations. CAM-B3LYP is a long-range corrected form of B3LYP utilizing the Coulomb-attenuating method (CAM). CAM-B3LYP overestimates the Ni–O bond length by approximately 0.02 Å from the experimental value<sup>12</sup> of 1.62712 Å and 0.04 Å from the icMRCI+Q value. The CAM-B3LYP result differs from experiment<sup>13</sup> by 7.3 cm<sup>−1</sup> and from icMRCI+Q calculations by 3.3 cm<sup>−1</sup>. The  $\omega$ B97XD functional which also includes long range interactions differs from experiment by 0.8 cm<sup>−1</sup> and by 3.2 cm<sup>−1</sup> from the best calculated value. The  $\tau$ -HCTH meta GGA functional differs by 1.7 cm<sup>−1</sup> from experiment and 2.4 cm<sup>−1</sup> from icMRCI+Q. In comparison to the best functionals, commonly used functionals such as B3LYP, PBE, and M06 predict  $\omega_e$  values that are not in agreement with experiment. The B3LYP value is ~ 50 cm<sup>−1</sup> larger than experiment and similar to the CCSD(T)

**Table 8** Spectroscopic parameters for the ground state ( $^3\Sigma^-$ ) of NiO calculated at the DFT/aD level

| Functional       | $r_e$ (Å) | $\omega_e$ (cm $^{-1}$ ) | $\Delta\text{Expt}$ (cm $^{-1}$ ) | $\Delta\text{icMRCI+Q}$ (cm $^{-1}$ ) |
|------------------|-----------|--------------------------|-----------------------------------|---------------------------------------|
| B1B95            | 1.605     | 900.8                    | 61.7                              | 65.8                                  |
| B1LYP            | 1.612     | 892.2                    | 53.1                              | 57.2                                  |
| B3LYP            | 1.611     | 888.5                    | 49.4                              | 53.5                                  |
| B3P86            | 1.601     | 908.8                    | 69.7                              | 73.8                                  |
| B3PW91           | 1.605     | 901.5                    | 62.4                              | 66.5                                  |
| B971             | 1.651     | 743.1                    | 96.0                              | 91.9                                  |
| B972             | 1.608     | 884.4                    | 45.3                              | 49.4                                  |
| B98              | 1.650     | 743.1                    | 96.0                              | 91.9                                  |
| BP86             | 1.616     | 866.6                    | 27.5                              | 31.6                                  |
| BMK              | 1.603     | 945.6                    | 106.5                             | 110.6                                 |
| CAM-B3LYP        | 1.647     | 838.3                    | 0.8                               | 3.3                                   |
| HSE06            | 1.602     | 910.4                    | 71.3                              | 75.4                                  |
| HS06             | 1.602     | 910.2                    | 71.1                              | 75.2                                  |
| HSE03            | 1.603     | 911.3                    | 72.2                              | 76.3                                  |
| LC- $\omega$ PBE | 1.590     | 959.2                    | 120.1                             | 124.2                                 |
| M052X            | 1.621     | 911.3                    | 72.2                              | 76.3                                  |
| M05              | 1.623     | 887.0                    | 47.9                              | 52.0                                  |
| M062X            | 1.625     | 875.6                    | 36.5                              | 40.6                                  |
| M06              | 1.599     | 913.4                    | 74.3                              | 78.4                                  |
| M06HF            | 1.673     | 797.2                    | 41.9                              | 37.8                                  |
| M08HX            | 1.632     | 884.0                    | 44.9                              | 49.0                                  |
| M11              | 1.618     | 919.8                    | 80.7                              | 84.8                                  |
| MN12SX           | 1.595     | 938.3                    | 99.2                              | 103.3                                 |
| MN15             | 1.624     | 873.8                    | 34.7                              | 38.8                                  |
| mPW1LYP          | 1.611     | 893.2                    | 54.1                              | 58.2                                  |
| mPW1PBE          | 1.605     | 911.9                    | 72.8                              | 76.9                                  |
| mPW1PW91         | 1.602     | 910.5                    | 71.4                              | 75.5                                  |
| mPW3PBE          | 1.603     | 903.9                    | 64.8                              | 68.9                                  |
| N12SX            | 1.645     | 801.9                    | 37.2                              | 33.1                                  |
| O3LYP            | 1.616     | 858.9                    | 19.8                              | 23.9                                  |
| PBE1PBE          | 1.602     | 910.0                    | 70.9                              | 75.0                                  |
| PBEh1PBE         | 1.602     | 912.0                    | 72.9                              | 77.0                                  |
| PBE              | 1.617     | 862.4                    | 23.3                              | 27.4                                  |
| PPE0             | 1.600     | 917.0                    | 77.9                              | 82.0                                  |
| PW91             | 1.617     | 866.4                    | 27.3                              | 31.4                                  |
| SOGGA11X         | 1.663     | 758.4                    | 80.7                              | 76.6                                  |
| SVWN5            | 1.586     | 925.9                    | 86.8                              | 90.9                                  |
| $\tau$ -HCTH     | 1.621     | 837.4                    | 1.7                               | 2.4                                   |
| TPSSH            | 1.611     | 889.3                    | 50.2                              | 54.3                                  |
| $\omega$ B97     | 1.596     | 947.6                    | 108.5                             | 112.6                                 |
| $\omega$ B97X    | 1.644     | 853.9                    | 14.8                              | 18.9                                  |
| $\omega$ B97XD   | 1.652     | 831.8                    | 7.3                               | 3.2                                   |
| X3LYP            | 1.610     | 892.0                    | 52.9                              | 57.0                                  |

values. Furthermore, PBE and M06 are 70 cm $^{-1}$  and 80 cm $^{-1}$  larger than experiment, respectively.

### Benchmarking DFT functionals: Ni–O BDE

The Ni–O BDEs with different functionals are given in Table 9. We derive BDE(1) and BDE(2) from eqn (3) and (4) respectively,



For BDE(1) (eqn (3)), the correction to the ground triplet state of the Ni is taken from experiment<sup>110,111</sup> based on the electronic configuration found by the NBO analysis of the atom. The ground state of Ni is  ${}^3\text{F}$  ( $3\text{d}^8 4\text{s}^2$ ) with the  ${}^3\text{D}$  ( $3\text{d}^9 4\text{s}^1$ ) excited state 204.787 cm $^{-1}$  higher in energy. BDE(2) (eqn (4)) arising from singlet Ni can be corrected to the ground state Ni using a similar approach. There are two open shell singlet  ${}^1\text{D}$  states corresponding to the  $3\text{d}^9 \text{s}^1$  configuration at 3409.937 cm $^{-1}$  and

the  $3\text{d}^8 4\text{s}^2$  configuration at 13 521.347 cm $^{-1}$ . The closed shell  ${}^1\text{S}$  state corresponding to the  $3\text{d}^{10}$  configuration is at 14 728.840 cm $^{-1}$ .

In contrast to the issues with the frequency calculations, 16 DFT functionals predicted BDE(1) value within 20 kJ mol $^{-1}$  of the FPD BDE, with 4 functionals, HS06, HSE03, MN15, and PBE1PBE, predicting the BDE within 4 kJ mol $^{-1}$  of the FPD value. A majority of the functionals predicted the  ${}^3\text{D}$  excited state of Ni as the ground state instead of the  ${}^3\text{F}$  state, although this corresponds to only a small energy correction of 2.5 kJ mol $^{-1}$ . The top three performing functionals for the frequency calculations, CAM-B3LYP,  $\tau$ -HCTH, and  $\omega$ B97XD all performed poorly, with  $\Delta\text{BDE}(1)$  values of 138.2,  $-125.2$ , and 113.7 kJ mol $^{-1}$ , respectively. Calculating the Ni–O BDE with respect to a singlet Ni and correcting the energy with the singlet–triplet splitting of Ni giving BDE(2) does improve many of the poorly performing functionals including CAM-B3LYP and  $\tau$ -HCTH. The PBE0 functional is in essentially exact agreement with the FPD value. A limitation on the BDE(2) values is the state of the Ni as taken from the NBO analysis as most of the atomic singlet Ni DFT calculations go to an open shell  $\text{s}^1\text{d}^9$  singlet rather than the closed shell  $\text{d}^{10}$  configuration which introduces additional errors.

## Conclusions

The vibrational frequency, bond dissociation energy, and electronic structure of NiO were calculated using a range of methodologies including CASSCF, icMRCI+Q, CCSD(T), and DFT. CASSCF predicted a quintet state ( ${}^5\Sigma^-$ ) ground state for the equilibrium bond distance with a state crossing occurs at 1.65 Å, where the triplet ( ${}^3\Sigma^-$ ) state becomes lower energy. icMRCI+Q predicts a triplet ( ${}^3\Sigma^-$ ) state as the ground state and does not predict a state crossing. The ground state results from the ionic interaction of the O  $2\text{p}_z$  bonding with the  $4\text{s}/3\text{d}_{z^2}$  of Ni to form a  $\sigma$  bond. The inclusion of dynamic correlation effects at the icMRCI+Q level altered the electronic structure predicted by CASSCF. At the icMRCI+Q level, the ground state is  ${}^3\Sigma^-$  in agreement with experiment.<sup>12,13</sup> The frequency calculated at the icMRCI+Q/CBS level is within 4.1 cm $^{-1}$  of experiment,<sup>13</sup> and the bond distance is within 0.028 Å of experiment.<sup>12</sup> The calculated values show little effect of increasing basis set size, with frequencies deviating from the complete basis set level by 3 cm $^{-1}$  for the triple zeta basis set, and 1 cm $^{-1}$  for the quadruple basis set.

To benchmark the accuracy of non-multireference methods for the frequency, CCSD(T) and DFT were used. CCSD(T) predicts vibrational frequencies that are  $\sim 50$  cm $^{-1}$  too high due to the multireference character of the ground triplet state. Correlation of the outer core electrons of Ni improves the calculated frequency but the value still differs by  $\sim 40$  cm $^{-1}$  from experiment. An array of 43 DFT functionals was benchmarked. The 3 best functionals out of the 43 tested are  $\omega$ B97XD, CAM-B3LYP, and  $\tau$ -HCTH which gave frequencies within  $<10$  cm $^{-1}$  of experiment.

The BDE of NiO was calculated at the FPD/CCSD(T) and icMRCI+Q levels as well as with the 43 DFT functionals. The

**Table 9** Bond dissociation energies (BDE) in  $\text{kJ mol}^{-1}$  for NiO calculated at the DFT/aD level with different functionals

| Functional       | BDE(1) | $\Delta\text{BDE}(1)$ | Ni config BDE(1) <sup>a</sup>     | BDE(2) | $\Delta\text{BDE}(2)$ | Ni config BDE(2) <sup>a</sup>     |
|------------------|--------|-----------------------|-----------------------------------|--------|-----------------------|-----------------------------------|
| B1B95            | 347.5  | 4.9                   | [Ar]s <sup>1</sup> d <sup>9</sup> | 372.4  | −20.0                 | [Ar]d <sup>10</sup>               |
| B1LYP            | 334.9  | 17.5                  | [Ar]s <sup>1</sup> d <sup>9</sup> | 455.6  | −103.2                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| B3LYP            | 367.0  | −14.6                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 475.1  | −122.7                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| B3P86            | 383.7  | −31.3                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 551.1  | −198.7                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| B3PW91           | 363.3  | −10.9                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 500.5  | −148.1                | [Ar]d <sup>10</sup>               |
| B971             | 309.7  | 42.7                  | [Ar]s <sup>2</sup> d <sup>8</sup> | 457.0  | −104.6                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| B972             | 379.3  | −26.9                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 466.2  | −113.8                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| B98              | 304.0  | 48.4                  | [Ar]s <sup>1</sup> d <sup>9</sup> | 376.9  | −24.5                 | [Ar]d <sup>10</sup>               |
| BP86             | 463.0  | −110.6                | [Ar]s <sup>1</sup> d <sup>9</sup> | 545.1  | −192.7                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| BMK              | 389.5  | −37.1                 | [Ar]s <sup>2</sup> d <sup>8</sup> | 565.9  | −213.5                | [Ar]d <sup>10</sup>               |
| CAM-B3LYP        | 214.2  | 138.2                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 380.2  | −27.8                 | [Ar]s <sup>1</sup> d <sup>9</sup> |
| HSE06            | 191.3  | 161.1                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 323.7  | 28.7                  | [Ar]s <sup>1</sup> d <sup>9</sup> |
| HS06             | 348.5  | 3.9                   | [Ar]s <sup>1</sup> d <sup>9</sup> | 480.0  | −128.5                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| HSE03            | 349.8  | 2.6                   | [Ar]s <sup>1</sup> d <sup>9</sup> | 482.6  | −130.2                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| LC- $\omega$ PBE | 368.2  | −15.8                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 507.2  | −154.8                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| M052X            | 307.2  | 45.2                  | [Ar]s <sup>1</sup> d <sup>9</sup> | 337.6  | 14.8                  | [Ar]d <sup>10</sup>               |
| M05              | 374.0  | −21.6                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 328.0  | 24.4                  | [Ar]d <sup>10</sup>               |
| M062X            | 262.4  | 90.0                  | [Ar]s <sup>1</sup> d <sup>9</sup> | 294.0  | 58.4                  | [Ar]d <sup>10</sup>               |
| M06              | 364.6  | −12.2                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 451.5  | −99.1                 | [Ar]s <sup>1</sup> d <sup>9</sup> |
| M06HF            | 189.5  | 162.9                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 307.4  | 45.0                  | [Ar]d <sup>10</sup>               |
| M08HX            | 291.6  | 60.8                  | [Ar]s <sup>1</sup> d <sup>9</sup> | 459.5  | −107.1                | [Ar]d <sup>10</sup>               |
| M11              | 326.1  | 26.3                  | [Ar]s <sup>2</sup> d <sup>8</sup> | 438.8  | −86.4                 | [Ar]s <sup>1</sup> d <sup>9</sup> |
| MN12SX           | 251.9  | 100.5                 | [Ar]s <sup>2</sup> d <sup>8</sup> | 384.9  | −32.5                 | [Ar]s <sup>2</sup> d <sup>8</sup> |
| MN15             | 353.7  | −1.3                  | [Ar]s <sup>1</sup> d <sup>9</sup> | 288.5  | 63.9                  | [Ar]d <sup>10</sup>               |
| mPW1LYP          | 342.7  | 9.7                   | [Ar]s <sup>1</sup> d <sup>9</sup> | 461.3  | −108.9                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| mPW1PBE          | 342.3  | 10.1                  | [Ar]s <sup>1</sup> d <sup>9</sup> | 393.8  | −41.4                 | [Ar]d <sup>10</sup>               |
| mPW1PW91         | 338.7  | 13.7                  | [Ar]s <sup>1</sup> d <sup>9</sup> | 390.3  | −37.9                 | [Ar]d <sup>10</sup>               |
| mPW3PBE          | 371.5  | −19.1                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 489.6  | −137.2                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| N12SX            | 264.4  | 88.0                  | [Ar]s <sup>2</sup> d <sup>8</sup> | 444.7  | −92.3                 | [Ar]s <sup>1</sup> d <sup>9</sup> |
| O3LYP            | 385.3  | −32.9                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 466.7  | −114.3                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| PBE1PBE          | 349.4  | 3.0                   | [Ar]s <sup>1</sup> d <sup>9</sup> | 479.8  | −127.4                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| PBEh1PBE         | 347.8  | 4.6                   | [Ar]s <sup>1</sup> d <sup>9</sup> | 479.9  | −127.5                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| PBE              | 469.5  | −117.1                | [Ar]s <sup>1</sup> d <sup>9</sup> | 546.7  | −194.3                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| PPE0             | 245.9  | 106.5                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 352.2  | 0.2                   | [Ar]d <sup>10</sup>               |
| PW91             | 469.8  | −117.4                | [Ar]s <sup>1</sup> d <sup>9</sup> | 549.4  | −197.0                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| SOGGA11X         | 464.6  | −112.2                | [Ar]s <sup>1</sup> d <sup>9</sup> | 512.8  | −160.4                | [Ar]d <sup>10</sup>               |
| SVWN5            | 587.6  | −235.2                | [Ar]s <sup>1</sup> d <sup>9</sup> | 636.1  | −283.7                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| $\tau$ -HCTH     | 477.6  | −125.2                | [Ar]s <sup>1</sup> d <sup>9</sup> | 358.9  | −6.5                  | [Ar]s <sup>2</sup> d <sup>8</sup> |
| TPSSH            | 396.0  | −43.6                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 499.3  | −146.9                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| $\omega$ B97     | 374.5  | −22.1                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 620.5  | −268.1                | [Ar]s <sup>1</sup> d <sup>9</sup> |
| $\omega$ B97X    | 240.4  | 112.0                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 358.6  | −6.2                  | [Ar]d <sup>10</sup>               |
| $\omega$ B97XD   | 238.7  | 113.7                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 283.7  | 68.7                  | [Ar]d <sup>10</sup>               |
| X3LYP            | 362.4  | −10.0                 | [Ar]s <sup>1</sup> d <sup>9</sup> | 473.9  | −121.5                | [Ar]s <sup>1</sup> d <sup>9</sup> |

<sup>a</sup> Ni atom configuration from the NBO analysis.

available experimental data<sup>16,20</sup> are not in good enough agreement to distinguish between the FPD/CCSD(T) and icMRCI+Q BDE values for the NiO BDE. The FPD/CCSD(T) value of  $352 \text{ kJ mol}^{-1}$  is consistent with the experimental<sup>20</sup> BDE of  $349.4 \pm 6.3 \text{ kJ mol}^{-1}$  whereas the icMRCI+Q BDE of  $388 \text{ kJ mol}^{-1}$  is larger than the largest experimental<sup>16</sup> value by  $14 \text{ kJ mol}^{-1}$ . The results show that further experimental investigation of the thermodynamics of the NiO bond is needed. The DFT values for 16 functionals are in agreement within  $20 \text{ kJ mol}^{-1}$  of the FPD/CCSD(T) value using the BDE(1) expression but these do not include the 3 best functionals for the frequency predictions. The 3 best frequency functionals have errors ranging from  $−125$  to  $138 \text{ kJ mol}^{-1}$  using the BDE(1) expression. Use of the state splitting corrected BDE(2) expression substantially improved the BDE values for the CAM-B3LYP and  $\tau$ -HCTH functionals, especially the latter value. Note that the use of the BDE(2) expression resulted in worse agreement for most functionals. It is important to calculate the electronic state of the Ni atom used in the BDE equation with

each functional so an appropriate experimental correction for the excited state-ground state splitting can be applied.

Comparison of the multireference and single reference results shows that the MRCI approach gives a bond distance for the  $^3\Sigma^-$  ground state that is a bit too short but has the right curvature; in contrast, the single reference based CCSD(T) method with a large  $T_1$  value demonstrating multireference character yields a good bond distance, but the predicted curvature is too tight. The CCSD(T) method predicts a good bond energy if the energy of the excited  $^5\Sigma^-$  state which is dominated by a single configuration. The BDE for the ground  $^3\Sigma^-$  state can then be obtained by the energy difference between the  $^3\Sigma^-$  and  $^5\Sigma^-$  states. The MRCI approach predicts a BDE that is likely to be too large and this can be attributed to the difficulty in calculating the energy at large  $R$ . Selected DFT functionals can predict the bond distance and vibrational frequency with some reliability but fail in predicting the BDE unless a carefully selected set of atomic states is chosen.

The current work demonstrates that the vibrational frequency and BDE of NiO can be reliably calculated using advanced correlated molecular orbital theory approaches. If one starts with a single reference-based method such as CCSD(T), the  $T_1$  values should be carefully checked for the presence of multi-reference character. When using DFT, it is important to be careful about the choice of the functional as commonly used functionals such as PBE and B3LYP perform poorly when calculating both the spectroscopic properties and BDE of NiO. In addition, care must be taken to examine the electronic state of the bare metal atom as it may not be the ground state. For more complex NiO based systems, it will be important to carefully choose the functional and compromise may need to be made for getting the best functional in terms of vibrational spectroscopy predictions and reaction energies.

## Data availability

The data supporting this article have been included as part of the Supplementary Information.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences by UNCAGE-ME, an Energy Frontier Research Center funded by the United States Department of Energy, Office of Science, Basic Energy Sciences under Award DE-SC0012577. D. A. D. thanks the Robert Ramsay Fund at The University of Alabama.

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