



# Coupled cluster spectroscopic properties of the coinage metal nitrosyls, M–NO (M = Cu, Ag, Au)

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## Abstract

Ab initio near-equilibrium potential energy and dipole moment surfaces for the bent CuNO, AgNO, and AuNO molecules have been calculated under the Feller–Peterson–Dixon (FPD) composite framework at the coupled cluster level of theory including complete basis set extrapolation, outer-core correlation, scalar relativistic effects, and spin–orbit coupling. The Brueckner coupled cluster doubles with perturbative triples method, BCCD(T), was used to greatly improve upon CCSD(T), which was particularly problematic for CuNO. In the latter case, the BCCD(T) vibrational frequencies showed significant differences compared to CCSD(T), e.g., nearly 65 cm<sup>-1</sup> for the NO stretching frequency, and BCCD(T) also resulted in much better agreement with the available experimental frequencies. A full range of ro-vibrational spectroscopic constants are given for all three molecules of this study using the accurate composite potential energy functions and employing second-order vibrational perturbation theory.

**Keywords** FPD composite method · Ab initio spectroscopy · Brueckner coupled cluster · Coinage metal nitrosyls

## 1 Introduction

Nitric oxide, NO, is one of the most common ligands binding to a transition metal center. Particularly, nitric oxide interacting with coinage metals, [1] such as Cu, has found its application in many different areas such as NO decomposition [2], corrosion processes [2], and biochemical catalysis [3]. Since 1991, various experimental techniques have been applied to characterize the CuNO molecule. The gas-phase existence of the molecule was first identified by mass spectrometry by Sulzle et al. [4], while other experimental characterizations have included matrix FTIR [5–10] and UV–Vis spectroscopy [5].

In past studies, there have been some controversy about the ground electronic state of the CuNO molecule. In the early study of Hrušák et al. [11], the <sup>3</sup>A'' state was found to be lower in energy than the <sup>1</sup>A' state with the Hartree–Fock (HF), coupled cluster singles and doubles (CCSD), and configuration interaction (CI) methods. CCSD with perturbative triples, CCSD(T), however, gave the opposite conclusion that the singlet should be the ground state, particularly for larger basis sets. Several years later, Uzunova [12] used complete active space second-order perturbative theory (CASPT2) with unrestricted natural orbitals (UNO) and found that the triplet was the ground state, but CCSD(T) calculations again favored the singlet. Meanwhile, several density functional theory (DFT) calculations were also applied to study the CuNO molecule [5, 8, 10, 12–14], but failed to achieve consensus; the pure functionals gave a singlet ground state, while the hybrid functionals preferred a triplet ground state. In 2012, Marquardt and co-workers [13, 15] used multi-reference configuration interaction (MRCI) with several different sizes of reference spaces, as well as CCSD(T), to study this molecule. Unlike the CASPT2 study, the MRCI and CCSD(T) calculations both definitively supported a singlet ground state. Throughout the present work, a singlet ground state has been assumed for all three species.

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Since they are proposed to have similar catalytic applications as CuNO, an extension down the periodic table has included previous experimental studies of both AgNO [16, 17] and AuNO [18–23]. As with CuNO, spectroscopic investigations have been limited to observation in rare gas matrices. In addition, only limited theoretical studies have been performed on these molecules, and these have been carried out nearly exclusively at the DFT level, [16, 18, 21, 23] although Tielens et al. [18] did carry out some calculations of the binding energy of NO to Au at the CCSD(T) level of theory.

In this study, the near-equilibrium potential energy surfaces (PESs) of all three coinage metal nitrosyls (CuNO, AgNO, AuNO) have been accurately calculated using the Feller-Peterson-Dixon (FPD) coupled-cluster-based composite methodology [24] in order to determine their spectroscopic properties. In addition, the electric dipole moment surfaces have also been calculated to obtain pure rotational and infrared intensities.

## 2 Computational details

Initial calculations on the CuNO molecule were carried out at the coupled cluster singles and doubles with perturbative triples, CCSD(T) [25], level of theory with correlation consistent basis sets, [26–28] aug-cc-pVnZ ( $n = D-5$ ) for N and O and aug-cc-pVnZ-PP ( $n = D-5$ ) with a small core relativistic pseudopotential (PP) for Cu [29]. It became apparent, however, that CCSD(T) was somewhat problematic. This manifested itself in two ways: (i) after sampling the near-equilibrium PES (see below) the fitting errors were much larger than expected and (ii) the calculated N–O stretching harmonic frequency (calculated with analytical gradients and thus not subject to the possible instabilities

leading to the poor fits) was much higher than experiment. Subsequent calculations indicated that these problems were eliminated when the Brueckner coupled cluster doubles with perturbative triples method, BCCD(T) [25, 30, 31], or CCSD with full iterative triples, CCSDT [32, 33], were used. Table 1 shows the results of tests on all three molecules of this study using the aug-cc-pVDZ (N,O) and aug-cc-pVDZ-PP (Cu, Ag, Au) basis sets. These results show that CuNO is the exception, e.g., the CCSD(T) value for the N–O stretching harmonic frequency is larger than BCCD(T) and CCSDT values by more than  $70 \text{ cm}^{-1}$ . Relatively, large differences are also observed for the Cu–N bond length, nearly  $0.02 \text{ \AA}$ . For the other two molecules, the differences between CCSD(T) and BCCD(T) is nearly negligible for the vibrational frequencies although the CCSD(T) values of  $r(\text{M}-\text{N})$  appear to be too long, particularly for AgNO. In the case of CuNO, CCSDT(Q) calculations were also carried out with an increased frozen-core definition, i.e., the O 2 s was not correlated, and with just the cc-pVDZ-PP basis set on Cu and aug-cc-pVDZ on N and O. Compared to analogous CCSDT results, the equilibrium geometry was nearly unchanged ( $-0.0001 \text{ \AA}$  in  $r_e(\text{N}-\text{O})$ ,  $-0.0023 \text{ \AA}$  in  $r_e(\text{Cu}-\text{N})$ ,  $+0.4^\circ$  in the bond angle), while the NO stretching frequency decreased by just  $7 \text{ cm}^{-1}$  (about  $-2 \text{ cm}^{-1}$  in the bend and unchanged for the Cu–N stretch). Also shown in Table 1 for CuNO are two variants of how the (T) correction is included in BCCD(T). One uses a triples correction based on the assumption that canonical orbitals are used and the other does not make this assumption and thus includes all non-Brillouin terms in the determination of the (T) correction. For the properties shown in Table 1, the differences are small but are appreciable for the Cu–N bond length, nearly  $0.005 \text{ \AA}$ . In the remainder of this work, only the non-Brillouin version of BCCD(T) has been utilized. It should be noted that at its equilibrium geometry with this basis set, the

**Table 1** A comparison of coupled cluster methods for the determination of the equilibrium structure ( $\text{\AA}$  and degs.) and harmonic vibrational frequencies ( $\text{cm}^{-1}$ ). Unless indicated otherwise, the aVDZ-PP/aVDZ basis set combination was used throughout

Method	$r_e(\text{Cu}-\text{N})$	$r_e(\text{N}-\text{O})$	$\angle(\text{CuNO})$	$\omega_1(\text{N}-\text{O})$	$\omega_2(\text{bend})$	$\omega_3(\text{Cu}-\text{N})$
<i>CuNO</i>						
CCSD(T)	1.9302	1.1848	120.0	1699	404	250
BCCD(T) <sup>a</sup>	1.9124	1.1875	119.1	1623	437	268
BCCD(T) <sup>b</sup>	1.9077	1.1876	119.2	1622	439	271
CCSDT	1.9123	1.1905	119.3	1622	436	267
<i>AgNO</i>						
CCSD(T)	2.3929	1.1840	117.8	1741	289	138
BCCD(T) <sup>b</sup>	2.3839	1.1752	117.5	1743	334	138
<i>AuNO</i>						
CCSD(T)	2.0772	1.1738	117.8	1729	493	257
BCCD(T) <sup>b</sup>	2.0709	1.1711	117.7	1735	504	260

<sup>a</sup>BCCD(T) using the Molpro closed-shell code for the (T) contributions

<sup>b</sup>BCCD(T) using the Molpro open-shell code for the (T) contributions. Unlike the default closed-shell implementation in Molpro, this includes all non-Brillouin terms and is used throughout the current work

$T_1$  diagnostic [34] in the CCSD calculations of CuNO was rather large at 0.082, but there were no doubles amplitudes larger than 0.05, indicating multireference character was not an issue. Likewise, the  $T_1$  diagnostics for AgNO and AuNO were 0.077 and 0.065, respectively.

A full set of spectroscopic properties was derived for all 3 species from near-equilibrium potential energy surfaces (PES) of each molecule. The energy of each sampled point on the PES was obtained via the FPD composite approach [24], where in this work the total energy was expressed as:

$$E = E_{CBS} + \Delta CV + \Delta DK + \Delta SO \quad (1)$$

In Eq. (1), the first term on the right-hand side represents the frozen-core total energy extrapolated to the complete basis set limit (CBS) at the BCCD(T) level of theory [25]. Correlation consistent basis sets, aug-cc-pVnZ ( $n=D-5$ ) [26, 27] for N and O and aug-cc-pVnZ-PP ( $n=D-5$ ) [28] with small core relativistic pseudopotentials [29] (PPs) for coinage metal elements, were used. For convenience, these are abbreviated as aVnZ below. The Hartree–Fock energies were extrapolated by the formula of Karton and Martin [35],

$$E_n = E_{CBS} + A(n+1)e^{-9\sqrt{n}} \quad (2)$$

where  $E_n$  are the HF energies calculated by aVQZ and aV5Z sets ( $n=4$  and 5). The BCCD(T) correlation energies were extrapolated by a two-parameter formula, Eq. (3), also using aVQZ and aV5Z data [36, 37],

$$E_n = E_{CBS} + A \left( n + \frac{1}{2} \right)^4 \quad (3)$$

The final CBS limit for a given geometry on the PES,  $E_{CBS}$ , is the sum of the results of Eqs. (2) and (3).

The second term in Eq. (1), CV, recovers the correlation energy contribution from outer core electrons. For N and O, the core electrons include 1 s electrons, while for Cu, Ag, and Au the outer core electrons outside the PPs are 3s3p, 4s4p, and 5s5p, respectively. Both the frozen-core and outer-core correlation energies were calculated with the BCCD(T) method using aug-cc-pwCVQZ (N and O) and aug-cc-pwCVQZ-PP (Cu, Ag, Au) basis sets. The value of  $\Delta CV$  is given by the difference in these two calculations.

The third term,  $\Delta DK$ , provides the scalar relativistic contribution from the light atoms and a correction for the use of the PP for the metals. The all-electron Douglas–Kroll–Hess (DKH) scalar relativistic Hamiltonian [38–40] was used for these contributions with aug-cc-pVTZ-DK basis sets (denoted aVTZ-DK) for all atoms [28, 41] at the BCCD(T) level of theory. Second-order DKH was used for CuNO and AgNO, while the 3rd-order DKH Hamiltonian was utilized for AuNO. The energy difference between these calculations and the analogous PP-based ones using aVTZ sets yielded the  $\Delta DK$  contributions.

The final term is the spin–orbit correction,  $\Delta SO$ . In this work, two-component (2-c) DFT using the B3LYP functional [42] was used with the spin–orbit potential included with the ECP [29, 43]. Uncontracted aVDZ basis sets were used in these calculations. 2-c DFT was chosen instead of 2-c (or 4-c) CCSD(T) since a PES incorporating the latter displayed large fitting errors just as in the scalar relativistic CCSD(T) case discussed above.

The potential energy functions for each molecule were defined by fits to 84 FPD energies that covered the geometry ranges  $-0.3a_0 \leq R(\text{MN}) - R_e(\text{MN}) \leq +0.5a_0$ ,  $-0.3a_0 \leq r(\text{NO}) - r_e(\text{NO}) \leq +0.5a_0$ , and  $-30^\circ \leq \theta(\text{MNO}) - \theta_e(\text{MNO}) \leq +30^\circ$  to functions of the form

$$V(Q_1, Q_2, Q_3) = \sum_{ijk} C_{ijk} (Q_1)^i (Q_2)^j (Q_3)^k \quad (4)$$

where  $Q_1 = R(\text{M-N}) - R_e(\text{M-N})$ ,  $Q_2 = r(\text{N-O}) - r_e(\text{N-O})$ , and  $Q_3 = A_0 \Delta\theta + A_1 \Delta\theta^2 + A_2 \Delta\theta^3$  where  $\Delta\theta = \theta(\text{MNO}) - \theta_e(\text{MNO})$  [44]. For the bending coordinate, the parameters  $A_1$  and  $A_2$  were chosen to satisfy the boundary conditions at linearity of  $Q_3 = 1$  and  $dQ_3/d\theta = 0$ . The value of  $A_0$  was roughly optimized in the fitting procedure. The expansion coefficients are given explicitly in Table S1 of the Supplementary Information (SI). Using Eq. (4), the calculated energies were reproduced with root-mean-square errors of less than  $1 \text{ cm}^{-1}$  and maximum errors of no more than  $2.3 \text{ cm}^{-1}$ . The derivatives from Eq. (4) were transformed by the usual L-tensor algebra [45] to a quartic forcefield in dimensionless normal coordinates, and these were then used in standard second-order perturbation theory treatments [45] of the spectroscopic constants. Both the fitting of the surfaces and the latter spectroscopic constant analyses were carried out with the Surfit program of Senekowitsch [46].

The electric dipole moment surfaces are calculated at the BCCD(T) level of theory with the aVTZ basis sets for each molecule at the same 84 geometries as the potential energy surfaces described above. A finite field approach was used with field strengths of  $\pm 0.001$  a.u. The resulting dipole moment surfaces were first rotated into an Eckart frame [47] and the resulting  $a$  and  $b$  principal axes components were then fit to fourth-order polynomials in simple displacement coordinates. The expansion coefficients  $D_{ijk}^a$  and  $D_{ijk}^b$  are given in Table S2 of the SI. The derivatives of the dipole moments corresponding to each vibrational normal coordinate were then obtained via the Surfit program and were used to calculate the intensities for each mode using [48]

$$I_i (\text{cm}^{-2} \text{atm}^{-1} \text{ at } 300 \text{ K}) = 65.785 \times \omega_i \times \frac{\left( \mu'_{i,a} \right)^2 + \left( \mu'_{i,b} \right)^2}{2} \quad (6)$$

where  $\omega_i$  is the harmonic frequency (in  $\text{cm}^{-1}$ ) for each mode and  $\mu'_{i,a}$  and  $\mu'_{i,b}$  are the first derivatives of dipole moments

(in a.u.) along the  $a$  and  $b$  principal axes, respectively, for the  $i$ th normal mode.

Except for the spin–orbit calculations, which utilized the DIRAC program [49], all other calculations were carried out using the MOLPRO suite of ab initio programs [50].

### 3 Results and discussion

#### 3.1 Potential energy surfaces and spectroscopic properties

Tables 2, 3 and 4 summarize the basis set convergence, individual FPD contributions, and final composite results for the equilibrium geometries and harmonic frequencies for CuNO, AgNO, and AuNO, respectively. In each case, these properties were derived from separate potential energy functions accurately fit via Eq. (4) to 84 energies representing the

**Table 2** Equilibrium bond lengths (Å), bond angles (deg.) and harmonic frequencies<sup>a</sup> (cm<sup>-1</sup>) of the CuNO molecule calculated from the fitted potentials with respect to the basis set and contributions of different FPD terms. All calculations except  $\Delta$ SO correspond to the BCCD(T) method. See the text

	$R_e(\text{Cu-N})$	$r_e(\text{N-O})$	$\theta_e$	$\omega_1$	$\omega_2$	$\omega_3$
AVDZ	1.9077	1.1876	119.24	1621.6	438.7	270.8
AVTZ	1.8847	1.1774	119.48	1618.2	463.5	283.5
AVQZ	1.8787	1.1740	119.45	1630.9	469.6	286.7
AV5Z	1.8789	1.1732	119.32	1631.9	469.5	286.7
CBS[Q5]	1.8792	1.1727	119.22	1632.6	469.2	286.5
$\Delta$ CV	-0.0019	-0.0021	0.0	9.7	5.5	2.9
$\Delta$ DK	0.0030	-0.0003	-0.1	0.2	1.2	-0.1
$\Delta$ SO	-0.0001	0.0000	0.0	-0.1	0.0	0.0
Composite	1.8802	1.1704	119.11	1642	476	289

<sup>a</sup>1 = NO stretch, 2 = bend, 3 = Cu–N stretch

**Table 3** Equilibrium bond lengths (Å), bond angles (deg.), and harmonic frequencies (cm<sup>-1</sup>) of the AgNO molecule calculated from the fitted potentials with respect to the basis set and contributions of different FPD terms. All calculations except  $\Delta$ SO correspond to the BCCD(T) method. See the text

	$R_e(\text{Ag-N})$	$r_e(\text{N-O})$	$\theta_e$	$\omega_1$	$\omega_2$	$\omega_3$
AVDZ	2.3839	1.1752	117.49	1742.6	334.0	138.1
AVTZ	2.3052	1.1657	117.80	1720.8	356.8	158.5
AVQZ	2.2912	1.1622	117.74	1731.4	362.9	163.5
AV5Z	2.2903	1.1614	117.63	1733.1	364.1	163.7
CBS[Q5]	2.2900	1.1608	117.56	1734.5	364.7	163.7
$\Delta$ CV	-0.0450	-0.0013	0.1	-2.1	+15.5	+14.0
$\Delta$ DK	+0.0070	-0.0002	-0.1	+0.6	-0.9	-1.2
$\Delta$ SO	+0.0009	+0.0001	0.0	-0.3	-0.5	-0.2
Composite	2.2529	1.1593	117.64	1733	379	176

<sup>a</sup>1 = NO stretch, 2 = bend, 3 = Ag–N stretch

**Table 4** Equilibrium bond lengths (Å), bond angles (deg.), and harmonic frequencies (cm<sup>-1</sup>) of the AuNO molecule calculated from the fitted potentials with respect to the basis set and contributions of different FPD terms. All calculations except  $\Delta$ SO correspond to the BCCD(T) method. See the text

	$R_e(\text{Au-N})$	$r_e(\text{N-O})$	$\theta_e$	$\omega_1$	$\omega_2$	$\omega_3$
AVDZ	2.0709	1.1711	117.70	1735.4	504.0	259.5
AVTZ	2.0370	1.1608	117.97	1732.8	527.9	277.0
AVQZ	2.0320	1.1571	117.95	1748.2	531.5	279.2
AV5Z	2.0298	1.1563	117.88	1749.7	532.6	280.0
CBS[Q5]	2.0284	1.1558	117.83	1751.0	533.4	280.5
$\Delta$ CV	-0.0170	-0.0018	+0.1	+7.7	+14.2	+11.6
$\Delta$ DK	-0.0031	0.0000	0.0	-1.6	+1.2	+1.2
$\Delta$ SO	-0.0052	+0.0005	+0.2	-3.2	-1.3	+2.4
Composite	2.0031	1.1545	118.16	1754	547	296

<sup>a</sup>1 = NO stretch, 2 = bend, 3 = Au–N stretch

stated basis set or FPD contribution, e.g., the  $\Delta CV$  values were derived as the difference between spectroscopic constants calculated from the BCCD(T)/CBS[Q5] PES and the BCCD(T)/CBS[Q5] +  $\Delta CV$  PES, where  $\Delta CV$  in this latter context is the contribution due to outer-core correlation at each of the 84 points as described in the previous section. As seen in these tables, the BCCD(T) geometries and harmonic frequencies are well converged even with the aVQZ basis sets. Further extensions and extrapolation to the CBS limits changes the bond lengths by only a few thousandths of an Angstrom and the frequencies by no more than  $3\text{ cm}^{-1}$ .

The effects of correlating the outer-core electrons are nearly negligible for CuNO in regard to the equilibrium structure although the frequencies increase by  $3\text{--}10\text{ cm}^{-1}$ . Correlation of the outer-core has the largest effect on AgNO, decreasing the Ag–N bond length by  $0.045\text{ \AA}$  and increasing the bending and Ag–N harmonic frequencies by  $15.5$  and  $14.0\text{ cm}^{-1}$ , respectively. The CV effect on these properties in AuNO are intermediate between the Cu and Ag cases, but as in AgNO the largest changes were a decrease in the Au–N bond length and increases in  $\omega_2$  and  $\omega_3$ . The two remaining modifications to the PESs,  $\Delta DK$  and  $\Delta SO$ , resulting in only small changes to these properties, particularly in regard to  $\Delta SO$ . The largest effect from using the PP is calculated for AgNO where the Ag–N bond length is increased with DK calculations by  $0.007\text{ \AA}$ . The analogous changes for CuNO and AuNO were just  $+0.003\text{ \AA}$  and  $-0.003\text{ \AA}$ , respectively. In all cases the harmonic frequencies changed by less than  $2\text{ cm}^{-1}$ . Not surprisingly the effects of SO coupling was nearly negligible for these closed-shell molecules. The largest SO effect was for AuNO where  $R_e(\text{Au–N})$  decreased by  $0.005\text{ \AA}$  with a concomitant increase in the Au–N harmonic frequency by  $2.4\text{ cm}^{-1}$ .

Using the final FPD composite PESs, a large number of spectroscopic constants were calculated via second-order vibrational perturbation theory for all three molecules. The rotational and ro-vibrational constants are shown in Table 5 while the pure vibrational constants are given in Table 6. The bond lengths of Table 5 are expected to be accurate to within about  $0.005\text{ \AA}$  while the harmonic frequencies of Table 6 have expected accuracies on the order of  $15\text{ cm}^{-1}$ . No significant resonances were identified for these molecules, so it is expected that vibrational perturbation theory should be very reliable in these cases. In regard to previous calculations, DFT methods have tended to yield bond lengths for both the M–N and N–O bonds that are too long, by as much as  $0.09$  and  $0.02\text{ \AA}$ , respectively, but with a lot of variation depending on the functional and basis set employed [8, 16, 18, 23]. In regard to the vibrational data of Table 6, the largest variations between the current harmonic frequencies and previous DFT results is in the NO stretching vibration. Consistent with predicting too short NO bond lengths, B3LYP tended to yield values for the NO stretching frequency that

**Table 5** Calculated rotational and ro-vibrational constants<sup>a</sup> obtained with the final composite PESs for CuNO, AgNO, and AuNO (most abundant isotopomers)

Constant	CuNO	AgNO	AuNO
$R_e(\text{M–N}, \text{\AA})$	1.8802	2.2529	2.0031
$r_e(\text{N–O}, \text{\AA})$	1.1704	1.1593	1.1545
$\theta_e(\text{deg.})$	119.11	117.64	118.16
$A_e(\text{MHz})$	97,321	87,645	93,300
$B_e(\text{MHz})$	4682	3112	3388
$C_e(\text{MHz})$	4467	3006	3270
$\tau_{AAAA}(\text{MHz})$	– 55.66	– 43.31	– 31.62
$\tau_{BBBB}(\text{MHz})$	– 0.0201	– 0.0170	– 0.0076
$\tau_{CCCC}(\text{MHz})$	– 0.0150	– 0.0143	– 0.0062
$\tau_{AABB}(\text{MHz})$	0.484	0.256	0.207
$\tau_{BBCC}(\text{MHz})$	– 0.0172	– 0.0155	– 0.0068
$\tau_{CCAA}(\text{MHz})$	0.323	0.188	0.154
$\tau_{ABAB}(\text{MHz})$	– 0.0856	– 0.0611	– 0.0359
$\alpha_{1A}(\text{MHz})$	1932	1368	1259
$\alpha_{2A}(\text{MHz})$	– 2137	– 2071	– 1649
$\alpha_{3A}(\text{MHz})$	– 710	– 224	– 531
$\alpha_{1B}(\text{MHz})$	– 8.6	– 29.7	– 4.1
$\alpha_{2B}(\text{MHz})$	41.4	21.9	20.6
$\alpha_{3B}(\text{MHz})$	10.4	34.1	13.1
$\alpha_{1C}(\text{MHz})$	– 4.0	– 26.2	– 2.4
$\alpha_{2C}(\text{MHz})$	41.3	24.0	21.8
$\alpha_{3C}(\text{MHz})$	14.3	33.0	13.4

<sup>a</sup> 1 = NO stretch, 2 = bend, 3 = M–N stretch

**Table 6** Calculated vibrational constants<sup>a</sup> obtained with the final composite PESs for CuNO, AgNO, and AuNO (most abundant isotopomers)

Constant	CuNO	AgNO	AuNO
$\omega_1(\text{cm}^{-1})$	1642.5	1732.8	1753.9
$\omega_2(\text{cm}^{-1})$	475.9	378.8	547.5
$\omega_3(\text{cm}^{-1})$	289.3	176.4	295.8
$X_{11}(\text{cm}^{-1})$	– 15.9	– 19.8	– 15.7
$X_{22}(\text{cm}^{-1})$	– 4.7	– 3.0	– 3.7
$X_{33}(\text{cm}^{-1})$	– 0.8	– 3.2	– 0.1
$X_{12}(\text{cm}^{-1})$	6.0	3.3	2.8
$X_{13}(\text{cm}^{-1})$	– 0.8	5.5	0.3
$X_{23}(\text{cm}^{-1})$	– 6.5	0.7	– 7.4
$\nu_1(\text{cm}^{-1})$	1613	1698	1724
$\nu_2(\text{cm}^{-1})$	466	375	538
$\nu_3(\text{cm}^{-1})$	284	173	292

<sup>a</sup> 1 = NO stretch, 2 = bend, 3 = M–N stretch

are too high by up to  $60\text{ cm}^{-1}$  (CuNO) [8]. The BP86 or BPW91 functionals yielded results much closer to the current BCCD(T)-based values, although the NO stretch for

**Table 7** Comparison of the composite FPD anharmonic vibrational frequencies ( $\text{cm}^{-1}$ ) with the available experimental values

Molecule	Source	$\nu_1$	$\nu_2$	$\nu_3$
CuNO	FPD, this work	1613	466	284
	Exp [5]. (Ar)	1587.4	452.6	278.2
	Exp [8]. (Ne)	1602.2		
AgNO	Exp [6]. (Ar)	1610.5		
	FPD, This work	1698	375	173
	Exp [16]. (Ar)	1680.3		
AuNO	Exp [16]. (Ne)	1711.8/1707.3		
	FPD, This work	1724	538	292
	Exp. [23]. (Ne)	1710.4	523.8	
	Exp. [23]. (Ar)	1701.9	517.6	

<sup>a</sup>1 = NO stretch, 2 = bend, 3 = M–N stretch

AgNO resulting from BPW91 was smaller by about  $60 \text{ cm}^{-1}$ . [16] Last, in the matrix isolation spectroscopy work of Krim et al. [5] values were evaluated for the  $X_{11}$  and  $X_{22}$  anharmonicity constants,  $-16.5$  and  $-4.8 \text{ cm}^{-1}$ , respectively. These are in excellent agreement with the results obtained from the current composite PES,  $-15.9$  and  $-4.7 \text{ cm}^{-1}$ .

Table 7 compares the calculated anharmonic vibrational frequencies of this work as derived from the final composite PESs with the available experimental values obtained in rare gas matrices. In every case the present *ab initio* values are higher than the values from the matrix IR experiments. As anticipated, the present results do agree better overall with the Ne matrix results, generally within less than 1% for the NO stretch ( $\nu_1$ ). Larger matrix shifts, at least on a percentage basis, are observed for the lower frequency  $\nu_2$  and  $\nu_3$  modes.

### 3.2 Dipole moment surfaces and normal mode intensities

The expansion coefficients for the Eckart frame dipole moment functions of CuNO, AgNO, and AuNO are shown in Table S2. In these cases the molecules at equilibrium are oriented with the N–O bond nearly aligned along the *a*-axis with the O atom in the positive *ab* quadrant (origin at the molecular center of mass). A positive sign of an equilibrium dipole moment component implies the positive end of the dipole vector lies along the positive *a* or *b* axis. In all cases, the equilibrium values are relatively small:  $\mu_a = -0.408 \text{ D}$ ,  $\mu_b = -0.132 \text{ D}$  (CuNO);  $\mu_a = 0.041 \text{ D}$ ,  $\mu_b = 0.004 \text{ D}$  (AgNO);  $\mu_a = 0.741 \text{ D}$ ,  $\mu_b = -0.088 \text{ D}$  (AuNO). The corresponding total equilibrium values are given in Table 8. With such small magnitudes, these molecules are expected to have relatively weak pure rotational spectra and AgNO will be particularly challenging to observe. The infrared intensities of the fundamental vibrational normal modes for each molecule are

**Table 8** Calculated BCCD(T)/aVTZ equilibrium dipole moments  $\mu_e$  (in Debye) and infrared intensities  $I_i$  (in  $\text{cm}^{-2} \text{ atm}^{-1}$ ). The latter are calculated within the double harmonic approximation for the *i*th vibrational mode<sup>a</sup>

	$\mu_e$	$I_1$	$I_2$	$I_3$
CuNO	0.428	7026	77.3	27.6
AgNO	0.042	5272	65.1	19.4
AuNO	0.746	3536	63.7	18.3

<sup>a</sup>1 = NO stretch, 2 = bend, 3 = M–N stretch

also listed in Table 8. The N–O stretching modes have the largest intensities by far, followed by the bending modes and then the M–N stretching modes. The intensity of  $\nu_1$  decreases along the series from CuNO to AuNO. Based on the relatively small magnitudes of the dipole moment second derivatives with respect to dimensionless normal coordinates shown in Table S3, most of the overtones are not expected to have unusually large intensities. An exception may be the bending mode since the second derivative terms  $\mu''_{22}$  are larger (CuNO and AgNO) or nearly as large (AuNO) as the corresponding first derivatives.

## 4 Conclusions

Accurate near-equilibrium potential energy functions have been calculated for the coinage metal nitrosyl molecules CuNO, AgNO, and AuNO using the Feller–Peterson–Dixon (FPD) composite methodology that included CBS extrapolations and contributions from outer-core correlation, all-electron relativistic corrections, and spin–orbit coupling. The present work also found that the BCCD(T) level of theory was much more reliable compared to CCSD(T), particularly for CuNO. This correlated with the relatively large value for the T1 diagnostic in CuNO but otherwise the apparent lack of multideterminantal character. A large set of spectroscopic constants, both rotational and vibrational, was determined for all three molecules which will hopefully facilitate their observation by experiment in the gas phase. Full three-dimensional dipole moment functions were also determined in this work at the BCCD(T) level of theory. The pure rotational spectra are predicted to be relatively weak for all three molecules, particularly AgNO. In agreement with the available IR experiments, the  $\nu_1$  stretch is predicted to be much more intense than the bend or M–N stretch.

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