

Theoretical Study of the X_2NO Systems ($X = F, Cl, Br, I$): Effects of Halogen Substitution on Structural and Spectroscopic Properties

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Abstract: Structural and spectroscopic properties of the X_2NO series of radicals, with $X = F, Cl, Br, I$, have been computed by the coupled cluster ansatz in conjunction with hierarchical series of basis sets, accounting for, in most cases, core correlation effects and extrapolation to the complete basis set limit. Namely, equilibrium structures, vibrational frequencies, and hyperfine coupling constants have been considered. Methods rooted into the density functional theory have been used to estimate anharmonic and, in conjunction with the polarizable continuum model, environmental effects. The remarkable agreement with the available experimental data, limited to the lighter member of the series, confirms the reliability of our computational approach and suggests that the data for heavier species represent reliable benchmarks for future experimental data and/or cheaper computational methods devised for larger systems.

I. Introduction

Because of their remarkable stability and strong localization of the unpaired electron on the NO moiety, nitroxides are among the most widely employed and carefully studied classes of organic free radicals (see for example refs 1 and 2). In particular, substituent effects on the geometry, electronic structure, and reactivity of nitroxides have been investigated in deep detail in a number of experimental and theoretical studies.^{3–6} However, a systematic study of halogen substituents is still lacking in spite of the remarkable interest it could have from both fundamental and application points of view.

Substituent effects on the magnetic properties of nitroxide radicals can be either direct (i.e., related to polarization or electron transfer) or indirect (i.e., related to changes of hybridization issuing from pyramidalization of the nitrogen environment). Sometimes these two effects influence the value of the magnetic properties (especially isotropic hy-

perfine couplings) in opposite directions, making more difficult the interpretation of the experimental results. For instance, the presence of halogen substituents on the nitrogen atom increases the nitrogen isotropic hyperfine coupling constants because of the effect of the electron-acceptor power of halogen groups, but this is more than compensated by the pyramidalization of the NO moiety. Analogous effects can be observed on infrared spectra since delocalization of the singly occupied molecular orbital (SOMO) leads to an increase of the NO force constant because of its antibonding nature. It is thus clear that a systematic theoretical study employing reliable quantum mechanical (QM) approaches can provide invaluable information to complement and interpret spectroscopic results.

Concerning specifically halo-nitroxides, only F_2NO is experimentally well characterized,^{7–9} which is much more pyramidal than its hydrogen (H_2NO) analogue. Also from a computational point of view, only F_2NO has been analyzed in detail and at high level of theory till now (see ref 10 and references therein). We report in the following a thorough computational study of the whole series of dihalogen substituted nitroxides, which, together with providing reference data for forthcoming experimental studies, has allowed

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also the unraveling of a number of interesting magneto-structural relationships.

II. Methodology

A. Equilibrium Structure. In the present investigation, we have thoroughly investigated the electronic ground state of the X₂NO systems, which is ²A' for all the species considered, and where X is an halogen atom, fluorine, chlorine, bromine, or iodine.

The coupled cluster (CC) method with single and double excitations with a perturbative treatment of connected triples [CCSD(T)]¹¹ has mainly been used in the present study. The variant denoted R/UCCSD(T)¹² has been employed, which is based on restricted open-shell Hartree–Fock (ROHF) orbitals but spin unrestricted in the solution of the CCSD equations. The coupled cluster model has been found to be adequate for studying these open-shell systems as test computations, carried out at the multiconfiguration self-consistent field (MCSCF)¹³ level, showed that all the species considered are well described by a single reference wave function. Furthermore, nondynamical electron correlation seems not to be particularly relevant; in fact, the coupled cluster T₁ diagnostic¹⁴ has been calculated to be in the range of 0.019–0.024 for all radicals. This is also confirmed by the D₁(ROCCSD) diagnostic,¹⁵ which has been found lower than 0.04 in all cases. For the lighter member of the series, the full CC single, doubles and triples (CCSDT)¹⁶ model, as well as the CCSDT(Q) approximation¹⁷ with a perturbative treatment of quadruples on top of a CCSDT calculation, have also been considered to test the influence of higher-order excitations.

Correlation consistent-type basis sets have been used in the present investigation. More precisely, the standard cc-pVnZ (*n* = T, Q, 5) bases¹⁸ have been employed for nitrogen, oxygen, and fluorine, the tight-d augmented valence cc-pV(*n*+d)Z basis sets¹⁹ (*n* = T, Q, 5) for the chlorine atom, and the cc-pVnZ-PP sets²⁰ (*n* = T, Q, 5) for bromine and iodine. The latter ones are series of correlation consistent basis sets in conjunction with small-core relativistic pseudopotentials that leave 25 electrons to be handled explicitly for both Br and I. On the whole, these basis sets will be denoted as VnZ (*n* = T, Q, ...) in the text. The frozen core (fc) approximation has been adopted in conjunction with the above-mentioned series of bases.

For all the species considered, geometry optimizations have been performed using numerical gradients, as implemented in MOLPRO,²¹ except those at the CCSDT and CCSDT(Q) levels, which have been carried out with the MRCC package.²² For CCSD(T) geometry optimizations, the step-sizes used were 0.0005 Å for bond lengths and 0.1 degrees for bond angles. A convergence criterion stronger than the default one has been employed: both the maximum component of the gradient and the maximum component of the step have been constrained to be lower than 1.0 × 10^{−6} a.u.

To account for basis set truncation effects, since a hierarchical sequence of bases has been considered, the systematic trend of the optimized geometrical parameters can

be exploited to estimate the complete basis set (CBS) limit. Making the assumption that the convergence behavior of the structural parameters mimics that of the energy, the consolidated 1/*n*³ extrapolation form²³ has been used to describe the convergence of the correlation contribution. To obtain extrapolated structures, the CBS limit value of the correlation contribution has then been added to the HF-SCF CBS limit, which is assumed to be reached at the HF-SCF/V6Z level

$$r(\text{CBS}) = r_{\infty}^{\text{SCF}} + \Delta r_{\infty}^{\text{corr}} \quad (1)$$

where

$$\Delta r^{\text{corr}}(n) = \Delta r_{\infty}^{\text{corr}} + An^{-3} \quad (2)$$

Even if this procedure is only empirically based, a few papers available in the literature show its reliability.²⁴

To take into account the effects of core-valence (CV) electron correlation, which are expected to be important, geometry optimizations have been carried out also including all electrons in the correlation treatment. The weighted core-valence correlation consistent cc-pwCVnZ (*n* = T, Q) basis sets²⁵ (cc-pwCVnZ-PP²⁶ for Br and I) have been used in this step. These basis sets will be denoted as wCVnZ (*n* = T, Q) in the following. Then, making use of the additivity approximation, the core correlation corrections have been added to the CBS limit of geometrical parameters

$$r(\text{CBS} + \text{CV}) = r(\text{CBS}) + r(\text{wCVnZ, all}) - r(\text{wCVnZ, valence}) \quad (3)$$

where *r*(wCVnZ,all) and *r*(wCVnZ,valence) are the geometries optimized at the R/UCCSD(T)/wCVnZ level correlating all (except the 1s electrons of Cl) and only valence electrons, respectively.

B. Spectroscopic Properties. Since electron spin resonance (ESR) spectroscopy is one of the most important experimental techniques for characterizing radicals, the magnetic hyperfine coupling has been investigated. The hyperfine interaction contains an isotropic contribution, the so-called Fermi contact term, related to the spin density at the nucleus,²⁷ and an anisotropic contribution, denoted as dipolar hyperfine coupling, which can be derived from the classical expression of interacting dipoles.²⁸ In particular, the former determines the positions of ESR lines, whereas the latter tunes spectral shapes depending on different dynamical conditions. Therefore, we focus our attention on the former.

The essential quantities to be calculated are the spin densities at the nucleus of interest, and thus, the isotropic hyperfine coupling constants (hcc) have been evaluated as expectation values of the corresponding one-electron operator²⁸ at the CCSD(T) level of theory in conjunction with core-valence basis sets of triple- and quadruple- ζ quality, possibly augmented by diffuse functions.²⁹ More precisely, computations at the CCSD(T)/CVnZ (*n* = T, Q) and CCSD(T)/aCVnZ (*n* = T) levels (where aCVnZ denotes aug-cc-pCVnZ) have been performed at our best estimated equilibrium structures (CBS + CV). For I, only pseudopotential-based basis sets have been used, whereas for Br all-electron bases,³⁰ as well as pseudopotentials, have been

employed. In all calculations, all electrons have been correlated (except the 1s electrons of Cl and Br). Only for the CVTZ basis, the frozen core approximation has also been used in order to figure out the extent of CV effects. The Cfour program package³¹ has been employed for these computations, and the unrestricted Hartree–Fock (UHF) wave function has been used as reference in CCSD(T) calculations.

As clear from the type of bases used, core correlation effects have been directly taken into account. On the other hand, to estimate the effect caused by basis set truncation, the two-parameter CBS extrapolation formula proposed by Bartlett and co-workers in ref 32 has been employed

$$A_n^{(K)} = A_\infty^{(K)} + Be^{-(n-1)} \quad (4)$$

where $A_n^{(K)}$ and $A_\infty^{(K)}$ denote the hcc of the K -th nucleus,

$$A_n^{(K)} = \frac{8\pi g_e}{3 g_0} g_K \beta_K \sum_{\mu,\nu} P_{\mu,\nu}^{\alpha-\beta} \langle \phi_\mu | \delta(r_{nK}) | \phi_\nu \rangle \quad (5)$$

computed with the CVnZ basis and extrapolated to the CBS limit, respectively.

According to the notation of ref 32, this extrapolation will be denoted as CBS2. This extrapolation function, which is an approximation of the exponential/Gaussian 3-parameter equation by Peterson, Woon, and Dunning,³³ has been chosen as well-tested for the property under consideration by Bartlett and co-workers (see ref 32).

Since vibrational and environmental effects may significantly affect the hcc's,⁵ to provide reliable predictions for experimental values, they have also been estimated in the present investigation. The vibrational effects have been accounted for by adding to the CCSD(T) results the difference between equilibrium and zero-point averaged values computed at the B3LYP/EPRIII level. The vibrational averaging is based on a perturbative approach, and we refer interested readers to ref 34 for all computational details. It is noteworthy that the EPRIII basis set (12s8p2d1f/8s5p2d1f)³⁵ has been chosen because it was purposely developed and widely validated for calculations of hyperfine coupling constants.

Environmental (argon matrix) effects have been estimated by means of the polarizable continuum model (PCM)³⁶ and a dielectric constant of 1.43 at the B3LYP/EPRIII level, as well. This approach is expected to provide at least semi-quantitative results as, while non electrostatic contributions play a significant role in determining thermodynamic characteristics in nonpolar solvents, local spectroscopic properties are sensitive only to electrostatic contributions.

The Gaussian03 program package³⁷ has been used for calculations of both vibrational and environmental effects.

Other useful information on radicals come from IR spectroscopy. The theoretical prediction of infrared harmonic and anharmonic vibrational frequencies requires the evaluation of harmonic and anharmonic force fields, respectively. These have been computed for the main isotopic species of the X₂NO radicals. More precisely, the harmonic part of the force field has been obtained at the CCSD(T)/VTZ as well as CCSD(T)/aVTZ (aVTZ denoting aug-cc-pVTZ²⁹) levels of

theory (in the fc approximation) by means of analytic second derivatives of the energy, as described in ref 38 and as implemented in the Cfour program package.³¹ To account for the anharmonic part, a mixed approach has been considered, i.e., anharmonic effects have been analyzed by a second-order perturbative treatment based on third and fourth energy derivatives computed at the B3LYP/EPRIII level,³⁴ as implemented in Gaussian03.³⁷ A number of studies have shown that addition of DFT anharmonic contributions to CCSD(T) harmonic frequencies allows a reliable reproduction of experimental fundamentals.^{10,39–42}

III. Results and Discussion

A. Molecular Structure. The equilibrium geometries and energies of the X₂NO systems, with X = F, Cl, Br, and I, obtained at the CCSD(T) level using different basis sets are summarized in Table 1. The extrapolation to the CBS limit has been carried out as explained in the methodology section (eqs 1–2), and the results obtained are listed in Table 1, together with best estimated equilibrium structures provided by inclusion of the core correlation corrections (eq 3). It has to be noted that the results for F₂NO come from a previous study by the same authors.¹⁰

As evident from Table 1, the convergence to the CBS limit is practically reached at the CCSD(T)/V5Z level for bond distances involving only first-row atoms, whereas for bond lengths involving heavier atoms deviations as large as ~0.01 Å between the CCSD(T)/VQZ and CCSD(T)/V5Z levels are observed. Unfortunately, computations in conjunction with the V6Z basis have been found to be too costly. For Cl₂NO, a non-monotonic trend has been observed for the NO distance and the angle; since we essentially perform a 2-point extrapolation and the SCF trend is monotonic, the CBS limit for them can be obtained. As far as CV corrections are concerned, it should be noted that in general they are relevant for bond lengths, whereas they are less important for angles. As pointed out in ref 10 and as is evident from the results of Table 1, these corrections are well estimated using both the wCVQZ and wCVTZ bases. For this reason, they have been computed at the CCSD(T)/wCVTZ level for the species with X = Cl, Br, and I, for which the wCVQZ basis is hardly applicable. Concerning scalar relativistic effects, they are expected to be relevant only for Br₂NO and I₂NO, and they are assumed to be completely recovered by the use of pseudopotentials.

On the basis of equilibrium structure evaluations for radicals performed following an approach analogous to that carried out in the present work (see, for instance, refs 10, 24, 41, and 42), an accuracy of about 0.001–0.005 Å is expected for the CBS + CV equilibrium distances derived in the present investigation, where the smaller uncertainty is referred to bond lengths involving first-row atoms and the larger to those for which the convergence to the CBS limit is slower.

From the results collected in Table 1, one may note that the NO distance decreases along the series, that is, when going from F₂NO to I₂NO, by about 0.03 Å. This is clearly related to the decrease of electronegativity from fluorine to

Table 1. Equilibrium Structure and Energy of X₂NO (X = F, Cl, Br, I)

RHF/UCCSD(T) ^a	X-N (Å)	N-O (Å)	∠XNO (deg.)	∠XNOX (deg.)	Energy (E _h)
F ₂ NO ^b					
aVTZ	1.4470	1.1693	117.14	121.24	−329.0874340
aVQZ	1.4379	1.1674	117.18	121.46	−329.1728545
VTZ	1.4349	1.1730	117.24	121.83	−329.0560601
VQZ	1.4345	1.1684	117.20	121.64	−329.1604408
V5Z	1.4345	1.1673	117.17	121.50	−329.1964277
CBS	1.4345	1.1667	117.15	121.40	
wCVTZ(fc)	1.4358	1.1711	117.20	121.69	−329.0788772
wCVTZ(all)	1.4330	1.1699	117.24	121.79	−329.2921954
wCVQZ(fc)	1.4339	1.1683	117.19	121.65	−329.1701498
wCVQZ(all)	1.4309	1.1669	117.21	121.70	−329.4087740
CBS+CV(CQ) ^c	1.4315	1.1653	117.17	121.45	
CBS+CV(CT) ^d	1.4317	1.1655	117.19	121.50	
Cl ₂ NO					
aVTZ	1.9967	1.1513	117.69	133.89	−1049.1366472
aVQZ	1.9764	1.1501	117.75	133.22	−1049.2086088
VTZ	1.9968	1.1514	117.62	134.11	−1049.1164283
VQZ	1.9766	1.1497	117.74	133.34	−1049.2020942
V5Z	1.9658	1.1506	117.72	132.94	−1049.2292431
CBS	1.9565	1.1514	117.71	132.60	
wCVTZ(fc)	1.9952	1.1494	117.61	134.16	−1049.1322261
wCVTZ(all)	1.9866	1.1495	117.65	133.94	−1049.7523524
CBS+CV	1.9479	1.1515	117.75	132.38	
Br ₂ NO					
aVTZ	2.2184	1.1432	118.11	144.07	−961.0783449
VTZ	2.2521	1.1392	117.87	149.98	−961.0479344
VQZ	2.2178	1.1384	118.06	144.05	−961.1351502
V5Z	2.2073	1.1380	118.03	143.30	−961.1609242
CBS	2.1963	1.1377	118.02	142.51	
wCVTZ(fc)	2.2463	1.1378	117.89	149.45	−961.0738369
wCVTZ(all)	2.2193	1.1375	117.81	148.07	−962.6724172
CBS+CV	2.1693	1.1374	117.94	141.16	
I ₂ NO					
aVTZ	2.4571	1.1463	119.33	154.84	−723.3562812
VTZ	2.5105	1.1418	118.85	180.02	−723.3348060
VQZ	2.4672	1.1404	119.11	158.43	−723.4136048
V5Z	2.4605	1.1394	119.08	160.51	−723.4413458
CBS	2.4545	1.1387	119.07	162.59	
wCVTZ(fc)	2.5004	1.1404	118.97	169.39	−723.3081629
wCVTZ(all)	2.4773	1.1389	118.87	169.10	−724.8908209
CBS+CV	2.4266	1.1362	118.94	162.30	

^a According to the text, the standard cc-pVnZ basis sets for first-row elements, the cc-pV(n+d)Z bases for Cl, and the cc-pVnZ-PP pseudopotential-based sets for Br and I have been used. ^b Ref 10. ^c CV(CQ) means CV corrections at the CCSD(T)/wCVQZ level. ^d CV(CT) means CV corrections at the CCSD(T)/wCVTZ level.

iodine, and thus to corresponding decrease of σ -withdrawing ability. At the same time the nominally singly occupied orbital (SOMO) is more delocalized for larger and more polarizable substituents and this leads to a shortening of the NO bond in view of the antibonding character of this orbital (π^*) in the NO moiety. On the other hand, steric effects on the XNO angle are not so marked; in fact, it increases only by less than 1°. It is more interesting to observe how the dihedral XNOX angle varies from X = F to X = I. It is evident that this angle enlarges by about 10 degrees from one element of the series to the another, a little bit more when going from Br₂NO to I₂NO. In fact, while F₂NO is strongly pyramidal, I₂NO is close to being planar with a dihedral INOI angle of about 168°. Actually, the geometry optimization employing the VTZ basis fails in finding the minimum structure and converges to an approximately planar structure close to the transition state for the inversion motion. Transition states governing nitrogen inversion have been optimized for all X₂NO species employing the aVTZ basis set. The geometries, the corresponding equilibrium and

Table 2. Structure of the Planar Transition States and Barriers to Planarity

UCCSD(T)/aVTZ ^b	X-N (Å)	N-O (Å)	∠XNO (deg)	ΔE ₀ (kcal/mol)	ΔE ₀ ^a (kcal/mol)
X = F	1.3624	1.2119	126.52	11.30	12.70
X = Cl	1.7359	1.2290	123.07	11.67	12.61
X = Br	1.9100	1.2246	122.67	6.52	7.54
X = I	2.4794	1.1435	119.42	0.07	0.39

^a ZPV corrections computed at the UCCSD(T)/aVTZ level within harmonic approximation. ^b According to the text, the aug-cc-pVTZ basis set for first-row elements, the aug-cc-pV(T+d)Z basis for Cl, and the aug-cc-pVTZ-PP pseudopotential-based set for Br and I have been used.

ground-state (at the harmonic approximation) energy barriers are collected in Table 2. The energy barriers clearly reflect the decreasing along the series of the displacement of nitrogen out of the plane defined by the atoms directly bonded to it.

As mentioned in the Methodology section, the effect of high-order excitations on molecular structure has been investigated for the lighter member of the series, F₂NO. More

Table 3. Equilibrium Structure of F₂NO: Higher-Order Excitations and Other Contributions

	X–N (Å)	N–O (Å)	∠XNO (deg)	∠XNOX (deg)
V5Z	1.4345	1.1673	117.17	121.50
Δ <i>r</i> (CBS) ^a	0.0	−0.0006	−0.02	−0.10
Δ <i>r</i> (CV) ^b	−0.0030	−0.0014	+0.02	+0.05
Δ <i>r</i> (diff) ^c	+0.0034	−0.0010	−0.02	−0.18
Δ <i>r</i> (full-T) ^d	−0.0003	−0.0001	−0.02	−0.02
Δ <i>r</i> (Q) ^e	+0.0033	+0.0012	−0.01	−0.03
Best estimate	1.4379	1.1654	117.12	121.22

^a *r*(CBS) − *r*(V5Z). ^b *r*(wCVQZ, all) − *r*(wCVQZ, valence).
^c *r*(aVQZ) − *r*(VQZ). ^d According to eq 6. ^e According to eq 7.

Table 4. Equilibrium Structure of X₂NO (X = F, Cl, Br, I) at the B3LYP/EPRIII Level

	X–N (Å)	N–O (Å)	∠XNO (deg)	∠XNOX (deg)
X = F	1.4581	1.1616	117.01	128.99
X = Cl	2.0806	1.1468	117.95	141.99
X = Br	2.2655	1.1318	118.29	147.85
X = I	2.4914	1.1304	118.84	151.70

precisely, full triples corrections have been obtained with the VTZ basis as

$$\Delta r(\text{full} - \text{T}) \cong r(\text{CCSDT}) - r(\text{CCSD(T)}) \quad (6)$$

whereas the VDZ set has been used for quadruples corrections

$$\Delta r(\text{Q}) \cong r(\text{CCSDT(Q)}) - r(\text{CCSDT}) \quad (7)$$

From the results collected in Table 3, it is first of all evident that higher-order corrections are quite small, being on the order of 0.0001–0.001 Å for distances and 0.01–0.03° for angles. In particular, as expected, full triples corrections are almost negligible, while those caused by quadruples excitations are larger. From Table 3 it is furthermore clear that the effect of diffuse functions is non-negligible for F₂NO; this finding is essentially related to the strong electronegativity of fluorine. In Table 3, an equilibrium structure that account for all the contributions considered is provided: this should be considered as the best estimates obtainable at the moment. Since higher-order excitations are found to be quite small, we can claim that the CBS + CV structures given in Table 1 might be considered as the best estimated structures for X₂NO, with X = Cl, Br, and I.

As far as the comparison with literature values is concerned, to the best of our knowledge, this is restricted to F₂NO; therefore, we refer interested readers to ref 10. We briefly recall that the investigation by the present authors is the only systematic study at high level of theory reported in the literature. With respect to experiment, as far as we know, there are no data for comparison.

Finally, it has to be noted that, although the B3LYP/EPRIII geometries (Table 4) are not quantitatively accurate, they are sufficiently good to estimate anharmonic corrections to vibrational frequencies as well as vibrational effects on hyperfine couplings.

B. Spectroscopy. Isotropic hyperfine coupling constants of all X₂NO species, as obtained at the CCSD(T) level of theory by different basis sets, are summarized in Tables 5 and 6. In particular, in Table 5, we focus our attention on nitrogen and oxygen, while in Table 6, we report the results

for halogens. In this way, from Table 5, we can point out how *hcc*'s vary for N and O, whereas from Table 6, we can address the evolution of such constants along the halogen series. Concerning the latter, *hcc*'s are given only for F, Cl, and Br, that is, only for those halogens for which all-electron basis sets can be used. For bromine, it has to be noted that results are affected by the missing account for relativistic effects which are expected to be important for a nucleus as heavy as Br and that the effect of correlating inner core electrons of Br actually does not justify the additional computational effort (with respect to keeping 1s2s2p electrons of Br frozen). Test computations on other Br-containing radicals showed that this effect is at the most 5%. It should be recalled that some results for F₂NO were previously reported and discussed in ref 10.

Both Tables 5 and 6 allow us to investigate the basis-set effects on isotropic hyperfine coupling constants. First of all, in all cases the absolute values increase by enlarging the basis set. Concerning the convergence to the CBS limit, it is evident that the values are nearly converged at the CCSD(T)/CVQZ level; in fact, the differences between this level and the CBS2 limit are generally of the order of 1–3%. We only note a larger discrepancy for chlorine (about 7%), but this finding was actually expected as the convergence for energy and properties is known to be slower for second-row elements and for heavy atoms in general. From the comparison between frozen core and all electron calculations, the effect resulting from core correlation can be pointed out. We note that a general conclusion cannot be drawn as CV corrections are small for N, that is, lower than 1%, while they are relevant for O (~10%), F (<3%) and Cl (>10%). Furthermore, in all cases but Cl, CV corrections enlarge the absolute value of the *hcc*. With respect to the effect of diffuse functions (from the comparison between aCVTZ and CVTZ results), it can be noticed that this is not negligible, being in most cases on the order of 2–4%. Furthermore, it is surely worth noting the changes along the X₂NO series. First, it is evident from Table 5 that the *hcc* of N largely decreases when going from F₂NO to I₂NO; in fact, for instance at the CCSD(T)/aCVTZ level *hcc* varies from 89.1 G for F₂NO to 78.9 G for Cl₂NO, 70.0 G for Br₂NO, and 59.3 G for I₂NO. A similar trend is observed for oxygen; in fact, the *hcc* is negative for F₂NO, less negative for Cl₂NO, and positive for Br₂NO, and even more positive for I₂NO. For both constants these changes are related to the structural modifications observed along the series of radicals investigated (direct effect), as well as to the increased polarization of halogen atoms involved (indirect effect).

To further investigate structural effects on *hcc*'s, they have also been computed at the planar structures given in Table 2, and collected in Table 7. To gain proper hints, in Table 7 they are compared to *hcc*'s obtained at the same level of theory (CCSD(T)/CVTZ, all electrons correlated) but calculated at the CCSD(T)/aVTZ minimum structures. Let us now concentrate our attention on nitrogen hyperfine couplings, which represent one of the most widely used experimental probes for stereoelectronic and environmental effects.⁵ The nitrogen isotropic hyperfine couplings computed for planar structures allow to compare different radicals in

Table 5. Isotropic Hyperfine Coupling Constants (Gauss) of X₂NO: Nitrogen and Oxygen Atoms

		B3LYP/EPRIII	CCSD(T)/aCVTZ	CCSD(T)/(fc)CVTZ	CCSD(T)/CVTZ	CCSD(T)/CVQZ	CCSD(T)/CBS2	exptl ^a
F ₂ NO	N							
	vacuum	95.40	89.13 ^b	88.62	88.93	90.69 ^b	91.72	
	Δ_{vib}^c	0.35	0.35	0.35	0.35	0.35	0.35	
	Δ_{matrix}^d	0.79	0.79	0.79	0.79	0.79	0.79	
	total	96.54	90.27	89.76	90.07	91.83	92.86	93
								93.635(3)
	O							
	vacuum	-10.77	-14.03 ^b	-12.87	-13.98	-14.60	-14.95 ^b	
	Δ_{vib}^c	0.44	0.44	0.44	0.44	0.44	0.44	
	Δ_{matrix}^d	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	
	total	-10.34	-13.60	-12.44	-13.55	-14.17	-14.52	
Cl ₂ NO	N							
	vacuum	72.41	78.90	79.52	79.72	81.01	81.76	
	Δ_{vib}^c	-2.64	-2.64	-2.64	-2.64	-2.64	-2.64	
	Δ_{matrix}^d	0.68	0.68	0.68	0.68	0.68	0.68	
	total	74.37	76.94	77.56	77.76	79.05	79.80	
	O							
	vacuum	-0.67	-5.48	-4.80	-5.35	-5.69	-5.89	
	Δ_{vib}^c	0.42	0.42	0.42	0.42	0.42	0.42	
	Δ_{matrix}^d	0.06	0.06	0.06	0.06	0.06	0.06	
	total	-0.19	-5.00	-4.32	-4.87	-5.21	-5.41	
Br ₂ NO	N							
	vacuum	60.67	69.99	71.23	71.55	71.69 ^e	71.77	
	Δ_{vib}^c	-1.53	-1.53	-1.53	-1.53	-1.53	-1.53	
	Δ_{matrix}^d	0.38	0.38	0.38	0.38	0.38	0.38	
	total	59.52	68.84	70.08	70.40	70.54	70.62	
	O							
	vacuum	0.56	1.33	1.38	1.41	1.50 ^e	1.56	
	Δ_{vib}^c	0.46	0.46	0.46	0.46	0.46	0.46	
	Δ_{matrix}^d	0.04	0.04	0.04	0.04	0.04	0.04	
	total	1.06	1.83	1.88	1.91	2.00	2.06	
I ₂ NO	N							
	vacuum	44.89	59.32	53.45	53.45	60.57	70.53	
	Δ_{vib}^c	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50	
	Δ_{matrix}^d	0.15	0.15	0.15	0.15	0.15	0.15	
	total	44.54	58.97	53.10	53.10	60.22	70.18	
	O							
	vacuum	2.90	7.75	7.47	8.11	8.55	8.80	
	Δ_{vib}^b	0.85	0.85	0.85	0.85	0.85	0.85	
	Δ_{matrix}^c	0.05	0.05	0.05	0.05	0.05	0.05	
	total	3.80	8.65	8.37	9.01	9.45	9.70	

^a Ar-matrix: ref 8, upper line. SF6-matrix: ref 7, lower line. ^b Ref 10. ^c Vibrational corrections computed at the B3LYP/EPRIII level of theory. See text. ^d Environmental corrections computed at the B3LYP/EPRIII level of theory. See text. ^e Pseudopotential basis (cc-pVQZ-PP) has been used for Br.

Table 6. Isotropic Hyperfine Coupling Constants (Gauss) of X₂NO at the CCSD(T) Level: Halogens

		aCVTZ	(fc)CVTZ	CVTZ	CVQZ	CBS2	exptl ^a
F ₂ NO	F						
	vacuum	139.27 ^b	126.61	129.81	137.72 ^b	142.33	
	Δ_{vib}^c	-3.84	-3.84	-3.84	-3.84	-3.84	
	Δ_{matrix}^d	2.04	2.04	2.04	2.04	2.04	
	total	137.47	124.81	128.01	135.92	140.53	143
Cl ₂ NO	Cl						143.235(5)
	vacuum	13.04	14.10	11.99	13.86	14.95	
	Δ_{vib}^c	-0.23	-0.23	-0.23	-0.23	-0.23	
	Δ_{matrix}^d	0.31	0.31	0.31	0.31	0.31	
	total	13.12	14.18	12.07	13.94	15.03	
Br ₂ NO	Br						
	vacuum	36.71	32.44	34.88	—	—	
	Δ_{vib}^c	-0.55	-0.55	-0.55	—	—	
	Δ_{matrix}^d	0.96	0.96	0.96	—	—	
	total	37.12	32.85	35.29	—	—	

^a Ar-matrix: ref 8, upper line. SF6-matrix: ref 7, lower line. ^b Ref 10. ^c Vibrational corrections computed at the B3LYP/EPRIII level of theory. See text. ^d Environmental corrections computed at the B3LYP/EPRIII level of theory. See text.

an unbiased way since only spin polarization contributions remain operative, which are roughly proportional to the π spin density on the nitrogen atom.⁵ Then, the nitrogen

hyperfine coupling parallels the contribution of nitrogen to the SOMO, which increases in going from fluorine to bromine and iodine. The anomalous behavior of chlorine is

Table 7. Isotropic Hyperfine Coupling Constants (Gauss) of X_2NO : Comparison of Planar and Equilibrium Structure Results

		CCSD(T)/VTZ	
		TS ^a	equilibrium ^a
F ₂ NO	N	20.24	89.93
	O	−19.74	−13.59
Cl ₂ NO	N	15.46	79.05
	O	−18.48	−2.83
Br ₂ NO	N	39.13	67.20
	O	2.66	0.75
I ₂ NO	N	54.73	55.18
	O	12.23	9.48

^a Optimized at the CCSD(T)/aVTZ level, where according to the text, aVTZ is the standard aug-cc-pVTZ basis set for first-row elements, the aug-cc-pV(T+d)Z basis for Cl, and the aug-cc-pVTZ-PP pseudopotential-based set for Br and I.

related to the “anomalous” behavior of the NO distance for planar structures, that is, it increases going from $X = F$ to $X = Cl$ and then decreases from $X = Cl$ to $X = I$. Going to pyramidal structures, the direct effect issuing from involvement of nitrogen s orbitals in the SOMO become operative: while this implies, of course, an increase of the hyperfine coupling constant, a direct comparison between different substituents is impaired by their different pyramidalization.

A rigorous comparison with or prediction of experiment needs to account for vibrational and environmental corrections. The former have been obtained as previously explained and have been found to be small but in general not entirely negligible, being of the order of 1–3%. Concerning the environmental effects, they are very small and thus mostly negligible for O, whereas they are larger, that is, on the order of 0.5–1%, for N. Furthermore, the latter show a monotonic trend along the series: they are always positive and decrease from F₂NO to I₂NO. Because the B3LYP/EPRIII level of theory has been employed for evaluating vibrational as well as environmental corrections, the corresponding results (given in Table 5), obtained at the corresponding optimized geometries, deserve to be mentioned. It is interesting to note that on average they are fairly good, that is, this level of theory is able to qualitatively well reproduce the hcc's.

As outlined above, some results for F₂NO were already published in ref 10. This point deserves to be briefly commented on. First, it has to be noted that some of the vibrational corrections reported in ref 10 were given with the wrong sign. In the second place, the matrix corrections of ref 10 differ from those here collected because in the present investigation the gas-phase equilibrium structure has been employed instead of that reoptimized in condensed phase. Finally, in ref 10, a little bit more accurate results were obtained from the extrapolation to the CBS limit of the aCVTZ and aCVQZ values. These are not here reported because we chose to deal only with those basis sets affordable for the other radicals considered.

Since rather accurate experimental data are available for F₂NO, we can take the opportunity of their comparison to our theoretical results for estimating the accuracy reachable by CCSD(T) computations. On the basis of this comparison and of the extent of the effects previously

discussed (especially convergence to CBS and core correlation), we can claim that for first row elements our best estimated hcc's are accurate to a few percent, that is, 1–2%. For heavier atoms, we expect a lower accuracy because of the slower convergence to the CBS limit, as well as to the neglect of relativistic effects (mostly for bromine). On the whole, we may conclude that our results can provide useful predictions for future experimental investigations.

Moving to IR spectroscopy, computed frequencies at both the harmonic and anharmonic levels are reported in Table 8 for all X_2NO species. The comparison with previous theoretical calculations and the available experimental results is also reported.

On the basis of the results and discussions reported in refs 10, 41, and 42, we can point out that the typical accuracy of 15–20 cm^{−1} (refs 43 and 44) for vibrational frequencies of closed-shell molecules calculated at the CCSD(T) level in conjunction with triple- ζ quality basis sets also applies to open-shell species. Therefore, such a level of theory is able to either check reliability of experiment or provide reliable predictions for experimental determinations. In ref 10, we already showed that such a level of theory was able to cast doubts on the assignment of the experimental vibrational spectra of F₂NO recorded in argon matrix and allowed us to suggest some revisions.

For improving our predictive capabilities, we went beyond the harmonic approximation as explained in the computational section, that is, anharmonic frequencies have been estimated by adding the anharmonic corrections at the B3LYP/EPRIII level to the CCSD(T) harmonic frequencies; the resulting values are reported in Table 8. This mixed approach has been validated quite convincingly for closed-shell systems,³⁹ and very recently, it has been successfully used for a number of free radicals.^{10,41,42} On the basis of the results presented in refs 10, 41, and 42, our anharmonic vibrational frequencies are expected to have an accuracy better than 15 cm^{−1}.

The results collected in Table 8 allow us to discuss two interesting points: first, how the NO stretching (i.e., ν_1) changes along the series considered; second, how the frequency of the rocking mode (i.e., ν_4) involving halogens varies from F₂NO to I₂NO and how this change is related to the extent of pyramidalization and to the barrier to planarity. Concerning the former effect, we note that the frequency parallels the trend of the N–O distance from F₂NO to I₂NO. In fact, as we note that the N–O bond length decreases from $X = F$ to $X = Br$ (by about 0.03 Å) and slightly increases from $X = Br$ to $X = I$ (by about 0.001 Å), the frequency increases from F₂NO to Br₂NO (by ~200 cm^{−1}) and only slightly decreases from Br₂NO to I₂NO (by about 6 cm^{−1}). Therefore, we note that as the N–O distance is very similar in Br₂NO and I₂NO, in the same way ν_1 is very similar in the two species. With respect to the rocking mode, which correlates with the out-of-plane bending mode of planar structure, it is evident that reduction of the pyramidalization is paralleled by a lowering of the frequency value up to a nearly vanishing value from 413 cm^{−1} for F₂NO to 117 cm^{−1} for Cl₂NO,

Table 8. Harmonic and Anharmonic Vibrational Frequencies (cm⁻¹) of X₂NO

	ν_1 (a') NO str	ν_2 (a') sym NX ₂ str	ν_3 (a') sym bend	ν_4 (a') rock	ν_5 (a'') asym NX ₂ str	ν_6 (a'') NX ₂ sciss
F₂NO^a						
harmonic						
B3LYP/EPRIII	1632.2	738.2	582.0	383.3	812.9	429.4
CCSD(T)/VTZ	1592.3	769.7	614.0	429.3	873.9	470.6
CCSD(T)/aVTZ	1594.8	751.4	595.1	413.1	846.1	458.1
anharmonic						
B3LYP/EPRIII ^b	1612.4 (-30)	717.0 (-21)	557.1 (-25)	360.0 (-23)	807.9 (-5)	412.2 (-17)
VTZ+ anarm contr (DFT)	1562	749	589	406	869	454
aVTZ+anarm contr (DFT)	1565	730	570	390	841	441
experiment	1572.7	761	552.7		813	
Cl₂NO						
harmonic						
B3LYP/EPRIII	1868.9	386.9	259.7	92.5	596.5	123.8
CCSD(T)/VTZ	1738.5	477.2	290.3	91.7	635.6	136.0
CCSD(T)/aVTZ	1675.4	492.2	301.3	117.0	648.8	195.5
anharmonic						
B3LYP/EPRIII ^b	1845.2 (-24)	325.1 (-62)	226.2 (-34)	71.9 (-21)	588.3 (-8)	69.5 (-54)
VTZ+ anarm contr (DFT)	1715	415	256	71	628	82
aVTZ+anarm contr (DFT)	1651	430	267	96	641	142
Br₂NO						
harmonic						
B3LYP/EPRIII	1882.6	292.3	214.9	58.1	557.9	117.2
CCSD(T)/VTZ	1821.6	282.0	235.6	37.7	551.5	120.4
CCSD(T)/aVTZ	1779.8	313.1	213.2	49.4	566.0	107.6
anharmonic						
B3LYP/EPRIII ^b	1860.8 (-22)	216.2 (-76)	179.9 (-35)	40.4 (-18)	540.4 (-18)	59.7 (-57)
VTZ+ anarm contr (DFT)	1800	206	201	20	534	63
aVTZ+anarm contr (DFT)	1758	237	178	31	548	51
I₂NO						
harmonic						
B3LYP/EPRIII	1838.4	228.7	180.8	44.3	514.0	117.6
CCSD(T)/aVTZ	1779.1	204.8	161.3	31.3	519.4	80.4
anharmonic						
B3LYP/EPRIII ^b	1811.5 (-27)	158.5 (-70)	163.5 (-17)	34.4 (-10)	496.3 (-18)	91.0 (-27)
aVTZ+anarm contr (DFT)	1752	135	144	21	511	53

^a Ref 10. ^b Anharmonic contributions reported in parentheses.

49 cm⁻¹ for Br₂NO, and 31 cm⁻¹ for I₂NO. As a matter of fact, the heavier species, I₂NO, is characterized by a nearly planar structure with very large amplitude out-of-plane bending.

IV. Conclusion

The present paper analyzes the structure, vibrational spectrum, and hyperfine couplings for the X₂NO series of free radicals, with X being an halogen atom. In most cases, CCSD(T) calculations have been carried out in conjunction with hierarchical series of bases and, when possible, accounting for extrapolation to the CBS limit and core correlation as well as relativistic effects. The estimated accuracy of our results is such that we are confident they may provide suitable benchmarks for the more approximate methods to be used for larger systems as well as reliable predictions for experiments, and allow the definition of more accurate magneto-structural relationships.

For spectroscopic properties an effective combination of coupled-cluster equilibrium values and harmonic frequencies,

together with vibrational corrections and anharmonic contributions obtained by hybrid density-functional methods, is reported.

Substitution of fluorine by larger halogen atoms leads to a progressive decreasing of the pyramidal character and, in parallel, to a progressive decreasing of the semirigidity of the radical. This is clearly reflected in the properties investigated. For instance, in addition to the lowering of the rocking mode frequencies discussed a few paragraphs above, we may recall that the nitrogen isotropic hyperfine coupling decreases along the series because of the reduction of the contribution of its 2s orbitals to the nominally single occupied orbital up to its complete vanishing for a planar structure.

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