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The Case of the Weak N−X Bond: Ab Initio, Semi-Experimental, and Experimental Equilibrium Structures of XNO (X = H, F, Cl, OH) and FNO_2

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The equilibrium structures of FNO, ClNO, HONO, and FNO_2 have been determined using three different, somewhat complementary methods: a completely experimental, a semi-experimental (where the equilibrium rotational constants are derived from the experimental effective ground-state rotational constants and an ab initio cubic force field), and an ab initio, where geometry optimizations are usually performed at the coupled cluster level of nonrelativistic electronic structure theory using small to very large Gaussian basis sets. For the sake of comparison, the equilibrium structures of HNO and N_2O have also been redetermined, confirming and extending earlier results. The semi-experimental method gives structural parameters in good agreement with the reliable experimental results for each compound investigated. Because of inadequate treatment of electron correlation, the single-reference CCSD(T) method gives N−X (X═F, Cl, OH) bonds that are too strong and associate bond lengths that are significantly too short. The discrepancy increases with increase in the size of the basis set. A much more elaborate treatment of electron correlation at the CCSDTQ level solves this problem and results in increased bond lengths, correctly representing the weakness of the N−X bond in these XNO and XNO_2 species. The equilibrium structures determined are accurate to better than 0.001 Å and 0.1°.

1. Introduction

The XNO and XNO_2 (X═F, Cl, HO, ...) molecules play an important role in the chemistry of the earth's atmosphere.[1,2] Some of them are atmospheric degradation products of hydrofluorocarbons and hydrochlorofluorocarbons. Because the N−X bond is known to be weak, these species are easily photolyzed, yielding the radicals X (F, Cl, HO) that are important contributors to the depletion of the ozone layer.[1] HONO plays an important role in chemical dynamics and reaction kinetics studies.[3] HNO has been indicated[4] to have biological activity, joining NO and its oxidized congeners as small "inorganic" molecules vital for life.

Consequently, the XNO and XNO_2 molecules have been studied by different experimental techniques, including microwave (MW) and infrared (IR) spectroscopies. Several attempts have been made, for example, to determine equilibrium and vibrationally averaged structures of several of these molecules.[5−11] The equilibrium structures have also been the subject of several computational studies[12−14] and it has been found that lower levels of ab initio electronic structure theory do not perform well for these molecules. This is not completely surprising because these molecules contain several atoms with large electronegativities and HONO, for example, is isoelectronic with O_3, a notoriously difficult molecule to describe at low levels of electronic structure theory. Nevertheless, it has been argued[15] that the coupled-cluster (CC) method with single and double excitations (CCSD)[16] augmented by a perturbational estimate of the effects of connected triple excitations [CCSD(T)][17] gives accurate results for these molecules. However, when the ab initio structures are compared to dependable experimental ones, as done in this study, a rather poor agreement is found for the length of the N−X bond though not for the other structural parameters. In all cases studied, the ab initio N−X bond length is significantly too short, corresponding to a bond that is too strong.

The principal aim of this paper is to accurately redetermine the equilibrium structures of representatives of the XNO and XNO_2 molecules. To achieve this, three different, somewhat complementary techniques are employed: ab initio geometry optimization, a semi-experimental treatment, and an experimental structural determination including least-squares refinements. A subsequent aim is to analyze and explain the occasional discrepancies in the structural parameters derived using the different techniques.

The paper is organized as follows. Section 2 describes the techniques used for the determination of equilibrium structures. Section 3 is dedicated to the equilibrium structure of *trans*-HONO. This section is more detailed than the others because it explains and compares the methodologies used. The next sections are devoted to the equilibrium structures of FNO, ClNO, and FNO_2, in order. The structures of N_2O and HNO are discussed in Sections 7 and 8, respectively. The N_2O molecule does not have a weak N−X bond but its T_1 diagnostic value,[18] used to estimate the suitability of the single-reference CCSD(T) method for properly describing electron correlation effects

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for all molecules, is comparable to the other molecules treated. The paper ends with conclusions (Section 9).

2. Methods of Structure Determination

2.1. Ab Initio Born−Oppenheimer Equilibrium Structures, r_e^{BO}. Most correlated-level ab initio computations of this study have been carried out at two levels of electronic structure theory, second-order Møller−Plesset perturbation theory (MP2)[19] and CCSD(T).[17] The Kohn−Sham density functional theory[20] using Becke's three-parameter hybrid exchange functional[21] and the Lee−Yang−Parr correlation functional,[22] together denoted as B3LYP, was also employed. The ab initio geometry optimizations performed at the levels described yield estimates of the Born−Oppenheimer equilibrium structure, r_e^{BO}. No corrections to nonrelativistic electronic structure theory have been considered, though they have small but nonnegligible effects, as shown for water.[23]

Dunning's correlation-consistent polarized *n*-tuple zeta basis sets cc-pV*n*Z[24] with $n \in \{D, T, Q, 5\}$ were employed extensively. Throughout this paper, these basis sets are abbreviated as V*n*Z. Versions of V*n*Z sets augmented with diffuse functions (aug-cc-pV*n*Z, AV*n*Z in short)[25] were also employed. The combination of an AV*n*Z basis on all non-hydrogen atoms and V*n*Z on H is denoted hereafter as A'V*n*Z. A few calculations were performed with the basis set TZ2Pf, a valence triple-ζ plus double polarization plus *f* function basis set.[26,27] The correlation-consistent polarized weighted core-valence *n*-tuple zeta (wCV*n*Z)[29,30] and the original CV*n*Z basis sets were used in order to improve the computed properties, especially equilibrium structural parameters, through the inclusion of core correlation effects.[28] As to the effect of inclusion of diffuse functions in the basis on equilibrium structural parameters, it is usually sufficient to use the MP2 method,[31] at least for first-row atoms.

The CCSD(T) computations were performed with the MOLPRO[32−34] and ACESII[35] electronic structure program packages, while the lower-level B3LYP and MP2 computations utilized the GAUSSIAN03 program.[36] Higher-order coupled cluster (CCSDT for full inclusion of triples, and CCSDTQ, for full inclusion of triples and quadruples) computations have been carried out using the string-driven program MRCC developed by Kállay.[37−39]

The frozen-core approximation (hereafter denoted as FC), that is, keeping the 1s orbitals of the first-row atoms and the 1s, 2s, and 2p orbitals of Cl doubly occupied during correlated-level calculations, was used extensively. Partly because of technical limitations, geometry optimizations at the CCSD(T) level have also been carried out by correlating all electrons (hereafter denoted as AE).

2.2. Semi-experimental Structures, r_e^{SE}. Semi-experimental equilibrium rotational constants, that can be used to determine semi-experimental equilibrium structures, r_e^{SE}, are determined in this study by correcting the experimental ground-state rotational constants with vibration−rotation interaction constants (α)[40] computed ab initio. Before this correction, it is advantageous to adjust the rotational constants fitted to the observed spectrum for a small centrifugal distortion and a magnetic effect.[41,23] When the *g* constants needed to calculate the magnetic effect are not known, they have been calculated, with the help of the Gaussian03[36] program package, at the AVTZ B3LYP level of theory.

The vibration−rotation interaction constants can be computed if the cubic force field of the molecule, expanded about the equilibrium structure, is known. Because the proper description of electron correlation is important for the molecules of this study containing highly electronegative atoms, we chose the CCSD(T) method to determine the anharmonic force fields. In several cases, the force fields have also been computed at the much less expensive though possibly less accurate B3LYP level. The quadratic force fields were evaluated analytically[42] in Cartesian coordinates at the optimized molecular structure, in order to avoid the nonzero force dilemma.[43] The cubic (ϕ_{ijk}) and semi-diagonal quartic (ϕ_{ijkk}) normal coordinate force constants were then determined at the same reference structure with the use of a finite difference procedure involving displacements along reduced normal coordinates (with step size $\Delta q = 0.03$) and the calculation of analytic Cartesian second derivatives at these displaced geometries.[44,45] The evaluation of anharmonic spectroscopic constants was based on second-order rovibrational perturbation theory.[40] The anharmonic normal coordinate force fields were determined for all of the isotopologues whose ground-state rotational constants are known.

2.3. Mass-Dependent Experimental Structures, $r_m^{(1)}$ and $r_m^{(2)}$. Determination of equilibrium structures from spectroscopic measurements alone is far from being a simple task. It is limited to relatively small molecules because it requires the determination of a whole set of accurate experimental vibration−rotation interaction constants, still very challenging when the number of atoms of the molecule increases above three. Many approximate methods have been developed to determine an empirical structure using only ground-state spectroscopic data, most importantly ground-state rotational constants.

Among the methods proposed, the perhaps most useful one was developed by Watson et al.[46] This so-called mass-dependent (r_m) structure technique takes into account the variation of the rovibrational correction upon isotopic substitution approximately and allows the determination of structures close to the assumed equilibrium structure. In this approach, the relation between the ground-state moments of inertia and the equilibrium ones is written as

$$I_g^0 = I_g^e + \epsilon_g, \quad g = a, b, c \tag{1}$$

where ϵ_g is the vibrational correction. Watson et al.[46] have shown that it is possible to express ϵ_g approximately as a function of the moments of inertia

$$\epsilon_g = c_g\sqrt{I_g^e}, \quad g = a, b, c \tag{2}$$

This gives the $r_m^{(1)}$ structure. When there are small coordinates, it may be better to refine this expression as

$$\epsilon_g = c_g\sqrt{I_g^e} + d_g\left[\frac{\prod_i m_i}{M}\right]^{1/(2N-2)} \qquad g = a, b, c \tag{3}$$

where N is the number of atoms in the molecule, m_i is the mass of atom i, M is the total mass of the molecule, and c_g and d_g are altogether six empirical parameters to be determined together with the structural parameters during the least-squares fit. This procedure defines the $r_m^{(2)}$ method.

For the O−H and O−D bonds of the molecules studied, it is necessary to take into account the variation of the effective bond length upon deuteration (at equilibrium the deviation in the two bond lengths is minuscule[23]). Watson et al.[46] assumed that the apparent shortening of O−D as compared to O−H is proportional to the respective reciprocal square root of the reduced mass (m_{red}) of the vibrator. The additional part of the bond length is hence different for the O−H and O−D bonds in the following way

$$r_H = r_m + \delta_H \mu_H \quad (4)$$

and

$$r_D = r_m + \delta_H \mu_{D,} \quad (5)$$

where δ_H is a common proportionality factor, determined in the least-squares fit, and $\mu = (m_{red})^{-1/2}$ is different for the H- and D-containing species.

3. Equilibrium Structures of *trans*-HONO

Nitrous acid, HONO, plays an important role in atmospheric chemistry.[2] HONO is also an interesting and simple model for experimental and first-principles chemical dynamics studies[3] and therefore several electronic structure and full six-dimensional nuclear motion investigations related to it have been published.[13,14]

As for the structure of HONO, Cox et al.[5] determined an effective (r_0) and a substitution (r_s) structure using the ground-state moments of inertia of several isotopologues. They also determined a zero-point average structure (r_z)[6] that was later refined by them.[7] They also attempted to determine r_e^{BO} of HONO using a rather crude model cubic force field.[6] As it turns out, this last structure is rather inaccurate. Furthermore, the r_z(OH) bond length at 0.947 Å seems to be too short, as shown below and in Table 1. Analysis of all of the fundamental vibrational bands of HONO by Guilmot et al.[47−50] provided the vibration−rotation interaction constants (α's) for the *trans* conformer and, thus, allowed determination of equilibrium rotational constants. Unfortunately, neglect of certain vibrational interactions resulted in α constants that led to an inertial defect that is much too large, $\Delta_e = 0.013$ uÅ.[2]

As a first application of their newly developed analytic first geometric derivatives CCSD(T) code, Lee and Rendell[12] have determined the equilibrium structures of the cis and trans conformers of nitrous acid at the TZ2P CCSD(T) level. Recently, Richter et al.[14] generated a full six-dimensional PES of HONO using the CCSD(T) method and correlating all electrons. As usual, the PES was determined through least-squares fitting to energy points. The minimum of the PES gave a structure significantly different from those of the previous determinations.[12,13]

3.1. Ab Initio Equilibrium Structure, r_e^{BO}. The results of geometry optimizations of this study performed at the CCSD(T) level with the basis sets V*n*Z, where *n* = T, Q, 5, are reported in Table 1. In favorable cases, CCSD(T) is able to yield results close to the exact *n*-particle solution within the given basis set.[51,52] Nevertheless, in the present case the coupled-cluster T_1 diagnostic value is 0.021 at the VQZ CCSD(T) level, slightly larger than the usual cutoff value, 0.020, indicating dominant single-reference character.[18] This suggests that nondynamical electron correlation has increased relevance for computations on HONO and that the CCSD(T) results are not fully reliable (see below). This deficiency for HONO was already pointed out by Lee and Rendell.[12] Note that T_1 is only 0.018 at the all-electron wCVQZ CCSD(T) level.

Improvement of the basis set from VTZ to VQZ shows that convergence at the VTZ level is not achieved, especially for the O═N and N−O bond lengths. Therefore, the structural effects of further basis set improvement (VQZ → V5Z) were also investigated at the MP2 level. Going from VQZ to V5Z, all bond distances remain almost unaffected (O═N and N−O decrease by 0.0007 and 0.0005 Å, respectively, while O−H increases by 0.0003 Å); the angle ∠(ONO) decreases by 0.018°, while the ∠(HON) angle increases by 0.18°. Assuming that basis-set effects are similar at the superior CCSD(T) level, we can conclude that convergence of the geometrical parameters of HONO within the V*n*Z series is almost achieved with the VQZ basis set.

TABLE 1: Molecular Structure of *trans*-HONO, with Distances (*r*) in Å and Angles (∠) in Degrees

method[a]	basis set	*r*(O═N)	*r*(N−O)	*r*(O−H)	∠(ONO)	∠(HON)
MP2 (fc)	VTZ	1.1777	1.4224	0.9677	110.78	101.20
MP2 (fc)	VQZ	1.1747	1.4175	0.9665	110.80	101.62
MP2 (fc)	V5Z	1.1740	1.4171	0.9669	110.78	101.80
MP2 (fc)	A'V5Z	1.1741	1.4172	0.9674	110.80	101.88
MP2 (fc)	wCVQZ	1.1745	1.4167	0.9667	110.80	101.65
MP2 (ae)	wCVQZ	1.1727	1.4128	0.9658	110.86	101.76
CCSD(T) (fc)	VTZ	1.1743	1.4280	0.9664	110.65	101.53
CCSD(T) (fc)	VQZ	1.1711	1.4218	0.9651	110.69	102.00
CCSD(T) (ae)	VQZ	1.1690	1.4178	0.9634	110.76	102.08
CCSD(T) (ae)	AVDZ	1.1831	1.4486	0.9734	110.32	101.82
CCSD(T) (ae)	AVTZ	1.1697	1.4227	0.9662	110.72	102.13
CCSD(T) (ae)	AVQZ	1.1691	1.4180	0.9647	110.78	102.33
CCSD(T) (ae)	wCVQZ	1.1693	1.4175	0.9644	110.75	102.12
r_e^{BO} [b]		1.1689	1.4180	0.9651	110.75	102.35
r_e^{SE} [c]		1.1686(1)	1.4258(1)	0.9651(3)	110.654(4)	102.035(22)
r_e^{SE} [d]		1.1689(3)	1.4250(3)	0.9647(6)	110.691(8)	102.086(45)
r_e(from r_z) [e]		1.171(2)	1.425(2)	0.950(3)	110.6(2)	101.7(3)
$r_m^{(1)}$		1.1726	1.4354	0.9646 (fix)	110.730	102.020
r_e [f]		1.1730	1.5430	0.9660	110.500	101.400
r_e [g]		1.1660	1.4330	0.9690	111.200	102.900
r_e [h]		1.1711	1.4272	0.9647	110.700	101.900
r_e [i]		1.163(5)	1.433(5)	0.954(5)	110.7(1)	102.1(3)

[a] fc = frozen-core approximation, ae = all electrons correlated. [b] Assumed complete basis set (CBS) CCSD(T) structure, obtained using the additivity approximation all-electron wCVQZ CCSD(T) + frozen-core [A′V5Z − wCVQZ] MP2. [c] Using vibration−rotation interaction constants obtained from a TZ2Pf B3LYP cubic force field. [d] Using vibration−rotation interaction constants obtained from an all-electron VTZ CCSD(T) cubic force field. [e] See the text. [f] Reference 12. [g] Reference 13. [h] Reference 14. [i] Reference 6.

Because the O and N atoms are highly electronegative, the effect of adding diffuse functions to the basis must be investigated.[25] To estimate this correction, the MP2 method was used together with the A'V5Z basis set. The results are reported in Table 1. Going from V5Z to A'V5Z MP2, the change in the structural parameters is negligible.

The wCVQZ basis set was first employed at the MP2 level in order to estimate the core correlation effects on the computed molecular structure of HONO. The wCVQZ MP2 core correction leads to the expected shortening of the O−H and O═N bonds, by 0.0009 and 0.0018 Å, respectively, and a much larger shortening of the N−O bond (−0.0039 Å), whereas the angles are affected only slightly. To check the validity of the assumption that MP2 and CCSD(T) core corrections are highly similar, we calculated the core correction at the CCSD(T) level using a completely uncontracted VTZ basis supplemented by an appropriate (1p3d2f) set of primitive Gaussian-type orbitals for non-hydrogen atoms. The exponents of these additional functions were generated according to ref 53, except for not rounding them to the nearest integer or half-integer. These calculations, as well as those at the wCVQZ CCSD(T) level, indicate that the wCVQZ MP2 core correction is accurate. Adding the core corrections to the valence-only VQZ CCSD(T) structural parameters, we arrive at an improved theoretical estimate of the equilibrium structure of HONO. The resulting structural parameters are almost identical to the all-electron wCVQZ CCSD(T) ones. There is another way to calculate the r_e^{BO} equilibrium structure of HONO: the CCSD(T) method is used together with the VQZ basis set but with all electrons (AE) correlated. This method is known to give accurate structural results for molecules containing first-row atoms.[52] This holds in the present case, as well, the VQZ and wCVQZ basis sets give almost identical results at the all-electron CCSD(T) level (Table 1).

The equilibrium structure obtained in this study at the CCSD(T) level is in good agreement with the one obtained by Richter et al.,[14] except for the N−O bond length. As anticipated, the agreement of the structural parameters is worse with the B3LYP results of Luckhaus.[13] The agreement with the CCSD(T) structure of Lee and Rendell[12] is not pleasing either; it seems that the TZ2P basis set is too small. In comparison with the experimental and semi-experimental results (Section 3.2 and 3.3), it appears that the ab initio r_e^{BO}(N−O) bond length corresponding to the all-electron complete basis set (CBS) CCSD(T) level is too short by 0.01 Å. Because the largest basis sets used for the actual computations are obviously close to being complete, the problem must lie in the treatment of electron correlation, as also indicated by the T_1 diagnostic value mentioned before.

To correct for the deficiencies of the single-reference CCSD(T) technique, one must use the single-reference CCSDTQ technique, that is, including all excitations up to quadruples in the CC treatment. However, CCSDTQ calculations, although avoiding the usual problems associated with multireference electronic structure computations, are considerably more expensive than CCSD(T) because they scale with the tenth power of the number of basis functions. Therefore, complete geometry optimizations can be attempted only sparingly at this level of theory. Nevertheless, because only r_e^{BO}(N−O) appears to be problematic, constrained one-dimensional (1D) geometry optimizations have been performed for this parameter of HONO to check the frozen-core CCSDTQ − CCSD(T) difference. The basis set used is a relatively small DZ(P) basis, constructed from the pVDZ basis of Ahlrichs[54] on the middle atoms and the VDZ basis of Ahlrichs[54] on the terminal atoms. To understand the trends better, constrained optimizations have also been carried out with this basis set at the frozen-core CCSD, CCSD(T), and CCSDT levels. The results are detailed in Table 2. The five constrained structural parameters, optimized at the all-electron cc-pVQZ CCSD(T) level, are the same as those given in Table 1.

TABLE 2: Constrained Optimization of the *r*(N−O) Bond Length (in Å) in *trans*-HONO Using Various Levels of Theory

method[a]	*r*(N−O)[b]
CCSD	1.401
CCSD(T)	1.421
CCSDT	1.424
CCSDTQ	1.429

[a] The pVDZ basis of Ahlrichs[54] for the middle two atoms and the VDZ basis of Ahlrichs[54] for the two terminal atoms have been used. The frozen-core approximation is employed throughout. [b] The other structural parameters were fixed at r(O−H) = 0.9634 Å, r(N═O) = 1.1690 Å, ∠(ONO) = 110.7642°, and ∠(HNO) = 102.0827°.

It is clear from these constrained optimizations that the level of electron correlation chosen for the optimization has a huge effect on the N−O distance. The higher the level of electron correlation, the longer the computed N−O distance. In particular, the CCSDTQ − CCSD(T) difference is +0.008 Å. This correction is to be added to the large-basis CCSD(T) results in order to have an improved estimate of the N−O distance. The pleasing outcome is that now the computed and the empirical N−O distances are almost in full agreement.

3.2. Semi-experimental Structure, r_e^{SE}. The anharmonic force field of *trans*-HONO and its isotopologues has been computed at two levels of theory, all-electron VTZ CCSD(T) and TZ2Pf B3LYP.

The theoretical vibration−rotation interaction constants deduced from the ab initio cubic force fields were combined with the known experimental ground-state rotational constants of $H^{16}O^{14}N^{16}O$, $H^{16}O^{15}N^{16}O$, $H^{18}O^{14}N^{16}O$, $H^{16}O^{14}N^{18}O$, and DONO to yield the appropriate semi-experimental equilibrium rotational constants. The experimental g constants were taken from ref 55. The equilibrium inertial defect, Δ_e, is more than 2 orders of magnitude smaller than the ground-state inertial defect ($\Delta_0 = 0.0824$ uÅ^2 vs $\Delta_e = 0.0006$ and 0.0024 uÅ^2 at the B3LYP and CCSD(T) levels, respectively), indicating that the equilibrium rotational constants are rather accurate. However, the equilibrium inertial defect is not exactly zero as it should be. This is probably due to the limited accuracy of the computed rotation-vibration interaction constants. The semi-experimental structure was determined using the iteratively reweighted least-squares method.[56] The objective of this method is to find suitable weights to compensate for the deficiencies of the model. A preliminary non-weighted regression gives residuals that are used to calculate a set of weights. A weighted least-squares fit allows us to obtain new residuals that are used to calculate new weights. This procedure is repeated until self-consistency is achieved. To determine the weights, we used Tukey's biweight estimator.[57] The residuals e_i are first scaled by the median of absolute values of nonzero residuals: $r_i = e_i/(1.4826 \times \text{median})$. If $r_i > 4.685$, then the corresponding datum is excluded from the fit. Otherwise, the estimator of the weight is calculated using the formula

$$w_i = [1 - (r_i/4.685)^2]^2 \qquad (6)$$

In our particular case, no data needed to be excluded from the fit. Furthermore, the final weights were quite similar for all moments of inertia and the condition number was only 92. This indicates that the results of the fit are likely to be reliable although the standard errors of the parameters are certainly much too small because they do not take into account the remaining systematic errors. The results are reported in Table 1. The agreement between the structural parameters r_e^{SE} and those of Richter et al.[14] is quite good. Likewise, the agreement between r_e^{BO} and r_e^{SE} is also quite good, except for the r(N−O) bond length when it is computed at the CCSD(T) level.

3.3. Experimental Structures. Before trying to determine an r_m structure, we determined an effective structure (r_0, which assumes $\epsilon_g = 0$) in order to check the conditioning of the system of normal equations. The condition number was found to be rather large, $\kappa = 415$. Furthermore, all of the structural parameters were found highly correlated (variance decomposition proportions larger than 0.93 and equal to 1.0 for the N−O and N═O bond lengths, respectively).

Determination of r_m structures involves at least three additional parameters (c_g of eq 2), resulting in an even larger condition number and higher correlation. This means that the derived parameters will be sensitive to small errors either in the input data or in the model. To keep the number of fitted parameters as small as possible, we have used the $r_m^{(1)}$ method (eq 2) and kept $r_m^{(1)}$ (O−H) fixed at the ab initio value (0.9646 Å, Table 1) because that is likely to be reliable.

Comparison of the $r_m^{(1)}$ structure (given in Table 1) with the ab initio r_e^{BO} structure shows fair agreement except for the N−O bond length whose $r_m^{(1)}$ value is much larger. However, it has to be noted that r_m(N−O) might not be very accurate because the a(N) Cartesian coordinate is small (0.15 Å). Furthermore, the b(O) Cartesian coordinate is not much larger either (−0.22 Å). In such a situation, utilization of the $r_m^{(2)}$ technique would be required. Unfortunately, it increases the number of parameters in such a way that the system becomes extremely ill-conditioned and, therefore, the derived parameters are inaccurate.

Overall, the $r_m^{(1)}$ structure also indicates that the directly computed CCSD(T) r(N−O) bond length is too short.

3.4. Estimation of r_e from r_z. The correction $r_z - r_e$ can be calculated exactly using an ab initio cubic force field,[58] computed at the TZ2Pf B3LYP level in the present case. A huge correction of $r_z - r_e = 0.0158$ Å results for the r(N═O) bond length (Table 1). Again, an extremely pleasing agreement is found with the structure of Richter,[14] except for the r(O−H) bond length, which seems to be too small by about 0.015 Å. It is interesting that the corrections $r_z - r_e$ used by Finnigan et al.[6] are different from the values deduced from the cubic force field. Finnigan et al.[6] assumed that a good portion of the cubic force constants comes from the nonlinear transformation of the quadratic constants. They found (in Å, exact values from the cubic force field are in parentheses) $r_z - r_e$[O−H] = 0.005 (−0.003), $r_z - r_e$[N−O] = 0.009 (0.016), and $r_z - r_e$[N═O] = 0.007 (0.002).

4. Equilibrium Structure of Nitrosyl Fluoride, FNO

The experimental equilibrium structure of FNO has been determined by Degli Esposti et al.[8] using the equilibrium rotational constants of $F^{14}N^{16}O$ and $F^{14}N^{18}O$. These authors also determined an experimental force field up to cubic terms. Estimates to r_e^{BO} have been given at relatively high levels of theory by Lee,[9] Dibble et al.,[10] and Martin et al.[11] The results have been collected and compared by Martin et al.,[11] who also computed the anharmonic force field at the VTZ CCSD(T) level of theory, adding diffuse Gaussian basis functions on F. However, as to the structure of FNO, the highest level of theory employed previously is AVTZ CCSD(T) on a molecule whose multireference character has been noted some time ago.[10]

TABLE 3: Vibration−Rotation Interaction Constants (in MHz) for FNO

	Degli Esposti et al.[8]	ref 59	AVTZ CCSD(T) [a]
α_1^A	393.2	394.096(33)	363.55
α_1^B	−14.42	−14.4237(33)	−19.86
α_1^C	−8.958	−8.9387(29)	−13.52
α_2^A	−327.8	−327.874(62)	−344.89
α_2^B	30.12	30.0956(55)	28.07
α_2^C	45.49	45.4860(58)	42.53
α_3^A	−620.0	−620.009(14)	−572.74
α_3^B	89.02	88.9824(14)	85.48
α_3^C	91.12	91.1555(14)	89.09
$A_e - A_0$	−277.3	−276.893(36)	−277.04
$B_e - B_0$	52.36	52.3272(33)	46.85
$C_e - C_0$	63.826	63.8514(33)	59.05
Δ_e [b]	−0.00074		0.00119

[a] This work, all-electron computation. [b] Equilibrium inertial defect.

TABLE 4: Molecular Structure of FNO, with Distances (r) in Å and Angles (∠) in Degrees

method	r(N−F)	r(N═O)	∠(FNO)
$r_e^{exp\ a}$	1.51658(25)	1.13155(23)	109.9220(72)
r_e^{SE}	1.51681(23)	1.13176(21)	109.9361(66)
r_e^{BO}[AVTZ CCSD(T)]	1.5145	1.1329	109.975
r_e^{BO}[ACVQZ CCSD(T)]	1.5120	1.1322	109.975

[a] Reference 8.

Because all fundamental bands of FNO have been reanalyzed recently,[59,60] testing the accuracy of the experimental structure of Degli Esposti et al.[8] is relatively straightforward. The reanalysis[59] proved to be particularly important for the ν_1 band that is perturbed by a Coriolis interaction. The vibration−rotation interaction constants used by Degli Esposti et al.[8] and those obtained in ref 59 are reported in Table 3. The agreement is almost perfect between the two sets of constants, indicating that the structure of Degli Esposti et al. is likely to be accurate. As part of the present work, anharmonic force fields have been computed at the all-electron AVTZ CCSD(T) level for the three isotopologues $F^{14}N^{16}O$, $F^{15}N^{16}O$, and $F^{15}N^{18}O$, whose ground state rotational constants are available.[8,59,61] The α constants of FNO derived from an ab initio force field are also given in Table 3. Their agreement with the experimental values is satisfactory.

The semi-experimental structure of FNO was calculated using the same method as for HONO. The semi-experimental rotational constants A_e, B_e, and C_e of $F^{14}N^{16}O$, and B_e and C_e of $F^{15}N^{16}O$ and $F^{15}N^{18}O$ have been utilized (no accurate A_0 constants have been determined for the latter two isotopologues). The experimental g constants were taken from ref 62. The results are given in Table 4 together with the experimental equilibrium structure of Degli Esposti et al.[8] As expected, the agreement is excellent, confirming the accuracy of the equilibrium structure.

Finally, the structure of FNO was calculated at the CCSD(T) level, all electrons being correlated using the AVTZ and ACVQZ basis sets (Table 4). As for the N−F bond length, the all-electron ACVQZ CCSD(T) value is too short by almost 0.005 Å as compared to either the experimental or semi-experimental structures. It might be argued that convergence is

TABLE 5: Molecular Structure of ClNO with Distances (r) in Å and Angles (∠) in Degrees

method	basis set	r(Cl−N)	r(N═O)	∠(ClNO)	comment
r_e		1.97263(7)	1.13571(7)	113.405(3)	ref 63
r_s		1.9721(4)	1.1364(2)	113.56(2)	ref 64
r_e^{SE}		1.97308(32)	1.13566(32)	113.380(16)	this work
$r_m^{(2)}$		1.97096(8)	1.13670(3)	113.51(2)	this work[a]
CCSD(T) (fc)	TZ2P	2.001	1.141	113.4	ref 66
CCSD(T) (ae)	CVQZ	1.9658	1.1358	113.339	ref 15
CCSD(T) (fc)	V(Q+d)Z	1.9714	1.1376	113.335	this work
CCSD(T) (fc)	V(5+d)Z	1.9662	1.1372	113.298	
CCSD(T) (ae)	AVTZ	1.9759	1.1382	113.410	
CCSD(T) (ae)	AV(Q+d)Z	1.9608	1.1362	113.420	
MP2 (fc)	wCVQZ	2.0151	1.1332	113.611	
MP2 (ae)	wCVQZ	2.0087	1.1313	113.635	
MP2 (fc)	V(Q+d)Z	2.0161	1.1334	113.629	
MP2 (fc)	AV(Q+d)Z	2.0136	1.1338	113.669	

[a] The claimed uncertainties correspond to standard deviations of the fit and do not correctly reflect inherent modeling errors, which are expected to be much larger.

not yet achieved at the quadruple-ζ level but, because a larger basis set is expected to give a still shorter bond, it should be concluded that this effect is a result of the multireference character of the ground electronic state of FNO.

5. Equilibrium Structure of Nitrosyl Chloride, ClNO

The experimental equilibrium rotational constants of $^{35}Cl^{14}N^{16}O$ and $^{35}Cl^{15}N^{16}O$ were derived, and the equilibrium structure of ClNO was determined from these constants by Cazzoli et al.[63] By combining ab initio and experimental results and utilizing a cubic force field, the authors were able to determine the semi-experimental equilibrium rotational constants of a larger set of isotopologues and obtain an estimate of the equilibrium structure of ClNO. More recently, the MW spectrum of ClNO was remeasured by MW Fourier-transform (MWFT) spectroscopy[64] and a substitution structure (r_s) was determined. It was found to be in good agreement with the equilibrium structure of Cazzoli et al.[63] (Table 5). Thus, the accuracy of this equilibrium structure seems to be well established. To provide further evidence, we determined new r_e^{BO} and $r_m^{(2)}$ structures for ClNO. ClNO is a case where the $r_m^{(2)}$ method should give dependable results. It is a small molecule without hydrogens and the ground-state rotational constants have been determined for several isotopologues.[64] The $r_m^{(2)}$ structure (Table 5) is indeed precise and it is in good agreement with the r_e structure, confirming the accuracy of the latter. It has to be noted that the r(N−Cl) bond length, 1.973 Å, is much longer than the normal single N−Cl bond length in NH_2Cl, where it is r_s(N−Cl) = 1.748(1) Å.[65] Although this latter value corresponds to a substitution structure and it is probably less accurate than stated, the large difference cannot be questioned.

The anharmonic force field of ClNO has also been calculated at the AVTZ CCSD(T) level for those six isotopologues ($^{35}Cl^{14}N^{16}O$, $^{37}Cl^{14}N^{16}O$, $^{35}Cl^{15}N^{16}O$, $^{37}Cl^{15}N^{16}O$, $^{35}Cl^{14}N^{18}O$, and $^{37}Cl^{14}N^{18}O$), whose ground-state rotational constants are available.[63,64] The semi-experimental r_e^{SE} structure of ClNO was calculated using the same method as for HONO and FNO. The derived structural parameters are also given in Table 5. The internal consistency of the r_e,[63] $r_m^{(2)}$, and r_e^{SE} structures is remarkable, the bond lengths and the ∠(ClNO) bond angle agree with each other to better than 0.002 Å and 0.13°, respectively. Especially pleasing is the agreement between r_e and r_e^{SE}.

Estimates of the r_e^{BO} structure of ClNO have already been computed ab initio several times. In particular, Lee[66] used the CCSD(T) level of theory but, as for HONO, with the TZ2P basis set, which is slightly too small. Quite recently, Coriani et al.[15] recalculated the structure of ClNO at the CVQZ CCSD(T) level, all electrons being correlated. They noticed a disagreement with the experimental structure for the r_e(N−Cl) bond length and suggested to revise the experimental determination. The accuracy of the experimental r_e structure of ClNO being confirmed above, we have recomputed the ab initio structure of this molecule at the MP2 and CCSD(T) levels using several basis sets. For the Cl atom, we used the cc-pV(n+d)Z basis sets, which are more appropriate for a second-row atom.[67,68] The results are reported in Table 5. The coupled-cluster T_1 diagnostic is 0.021 at the V(Q+d)Z CCSD(T) level, the same as for HONO. Although the ab initio r(N═O) and ∠(ClNO) parameters are in good agreement with the corresponding experimental values, the ab initio r(Cl−N) bond length seems to be much too short at the CVQZ CCSD(T) level. Furthermore, the convergence is not yet fully achieved at this level and, going from V(Q+d)Z to V(5+d)Z shortens the bond even further. Addition of diffuse functions also shortens the bond. Therefore, the single-reference CCSD(T) technique is not sufficient to obtain a reliable estimate of r_e^{BO} of ClNO.

6. Equilibrium Structure of Nitrylfluoride, FNO_2

The ab initio structure of FNO_2 has been computed before[69] at the CCSD(T) level but, as for HONO and ClNO, only with the somewhat too small TZ2P basis set. Alternatively, there are several structures available from experimental studies. Legon and Millen[70] determined the ground-state rotational constants of three different isotopologues by MW spectroscopy. They also obtained an effective (r_0) structure of FNO_2. Recently, the gas-phase infrared spectrum of FNO_2 was analyzed under high resolution, permitting the determination of reliable rotational constants for all fundamental states as well as improved ground-state constants.[71,72] Unfortunately, this work allows us to derive experimental equilibrium rotational constants only for the main isotopologue. This is not enough to determine a complete structure of FNO_2 because, with the molecule being planar, we have only two independent constants but three structural parameters. However, it should allow us to check the accuracy of the ab initio structure. Before this, one needs to check the accuracy of the experimental data.

The {ν_5, ν_3, ν_6, ν_2} Coriolis interacting tetrad of FNO_2 has been analyzed carefully taking into account all interactions.[71]

TABLE 6: Molecular Structures of FNO_2 with Distances (r) in Å and Angles (∠) in Degrees

		r(F−N)	r(N═O)	∠(FNO)	∠(ONO)
r_0 [a]		1.467(15)	1.180(5)	112.0	136.0(15)
CCSD(T) (fc)	TZ2P[b]	1.471	1.184	112.2	135.7
CCSD(T) (fc)	VTZ	1.4502	1.1836	112.27	135.45
CCSD(T) (fc)	VQZ	1.4512	1.1799	112.20	135.60
CCSD(T) (fc)	V5Z	1.4521	1.1791	112.16	135.69
CCSD(T) (fc)	AVDZ	1.4886	1.1923	111.93	136.14
CCSD(T) (fc)	AVTZ	1.4635	1.1829	112.03	135.94
CCSD(T) (fc)	AVQZ	1.4556	1.1799	112.12	135.76
CCSD(T) (fc)	uncTZ[c]	1.4500	1.1802	112.24	135.53
CCSD(T) (ae)	uncTZ[c]	1.4485	1.1783	112.24	135.53
CCSD(T) (ae)	CBS[d]	1.4506	1.1772	112.16	135.69
r_e^{SE}		1.4560(28)	1.1792(12)	112.26(15)	135.49(30)

[a] Reference 70. [b] Reference 69. [c] uncTZ = completely uncontracted VTZ basis, supplemented by an appropriate 1p3d2f set [see the text (Section 3.1)]. [d] Using the additivity assumption CCSD(T)(fc)/V5Z + [CCSD(T)(ae)/uncTZ − CCSD(T)(fc)/uncTZ].

TABLE 7: Molecular Structure of N_2O with Distances (r) in Å

method	basis	r(NN)	r(NO)
r_e [a]		1.1273	1.1851
MP2 (fc)	VQZ	1.1514	1.1777
MP2 (fc)	AVQZ	1.1516	1.1784
MP2 (fc)	V5Z	1.1508	1.1776
CCSD(T) (fc)	VDZ	1.1477	1.1955
CCSD(T) (fc)	VTZ	1.1329	1.1896
CCSD(T) (fc)	VQZ	1.1292	1.1869
CCSD(T) (fc)	AVDZ	1.1490	1.2021
CCSD(T) (fc)	AVTZ	1.1328	1.1910
CCSD(T) (fc)	wCVQZ	1.1288	1.1868
CCSD(T) (ae)	wCVQZ	1.1267	1.1848
CCSD(T)	CBS[b]	1.1267	1.1854

[a] Reference 74. [b] Obtained using the following additivity approximations: CCSD(T)(fc)/VQZ + [CCSD(T)(ae)/wCVQZ − CCSD(T)(fc)/wCVQZ] + [MP2/AVQZ − MP2/VQZ] + [MP2/V5Z − MP2/VQZ].

Thus, the derived constants are likely to be reliable. The $\upsilon_4 = 1$ level was found to be unperturbed.[72] Therefore, if there is a problem with the experimental spectroscopic constants, it can only come from the $\upsilon_1 = 1$ state, which is perturbed. A satisfactory fit was obtained for the corresponding fundamental band fitted using a triad model. Nevertheless, the derived centrifugal distortion constants are significantly different from those of the ground state, indicating that some perturbations are perhaps not taken into account correctly. To check whether this problem has a significant effect on the derived equilibrium rotational constants, we first calculated the equilibrium inertial defect, which was found to be quite small, $\Delta_e = -0.0022$ uÅ^2, unlike the ground-state inertial defect, $\Delta_0 = 0.157$ uÅ^2. Furthermore, we compared the experimental rovibrational corrections to those computed ab initio at the AVTZ B3LYP level of theory. The results are (in MHz, calculated values in parentheses) $A_e - A_0 = 78.8$ (62.3), $B_e - B_0 = 73.3$ (60.1), and $C_e - C_0 = 51.3$ (42.3). There is a small systematic deviation that probably indicates that the chosen level of theory is not good enough but, what is more important, these results show that the experimental values have the right order of magnitude.

We have computed the ab initio structure of this molecule at levels similar to the preceding molecules. The results are reported in Table 6. The coupled-cluster T_1 diagnostic is 0.019 at the VQZ CCSD(T) level, slightly smaller than the values found for HONO, FNO, and ClNO. It is interesting to note that the frozen-core V*n*Z and AV*n*Z CCSD(T) structural parameters converge toward the same limit for the N═O bond length and the bond angles though for the N−F bond length the convergence seems to be extremely slow. If we use the ab initio equilibrium values to calculate the moments of inertia, we find values that are extremely different from the corresponding experimental ones, the difference being as large as 0.34 uÅ^2 for I_b and I_c. Trial and error calculations indicate that the ab initio r(N═O) bond length and the ∠(FNO) bond angle are compatible with the experimental equilibrium moments of inertia but the ab initio r(N−F) bond length is much too short, similar to the r(N−X) bond lengths in the XNO (X═HO, F, Cl) molecules discussed previously. The correct equilibrium value should be close to 1.458 Å, that is, about 0.007 Å larger than the ab initio value. It has to be noted that this bond length is much longer than the normal single N−F equilibrium bond length, which is 1.422 Å in NH_2F.[73]

Finally, as a check, we also calculated the semi-experimental structure using the AVTZ B3LYP anharmonic force field and the experimental ground-state rotational constants ($F^{14}N^{16}O_2$, $F^{15}N^{16}O_2$, and $F^{14}N^{18}O_2$).[70,71] FNO_2 has small rotational constants, there is no isotopic substitution available for the fluorine atom, and the N atom is close to the center of mass (0.2 Å). For these reasons, the system of normal equations is not well conditioned and the derived semi-experimental structure given in Table 6 cannot be very precise. Nevertheless, in good agreement with the preceding discussion, we can conclude that the ab initio N−F bond length is too short.

At this stage, we can confirm that the coupled-cluster T_1 diagnostic seems to be an indicator of the importance of nondynamical electron correlation and, consequently, it is difficult to compute, using single-reference ab initio techniques, the r(N−X), X═F, Cl, OH bond length in the molecules studied.

To gain further insight into the reliability of the T_1 diagnostics, we have computed the ab initio structure of nitrous oxide, N_2O, for which the T_1 diagnostic has a value quite similar to that found for HONO, FNO, ClNO, and FNO_2, though the bond lengths are short in N_2O.

7. Equilibrium Structures of Nitrous Oxide, N_2O

The structure of the simple linear molecule N_2O has been studied thoroughly; in particular, a very accurate experimental equilibrium structure is available for it.[74] The ab initio structure and the anharmonic force field of N_2O has been calculated repeatedly.[75−78]

In this study, estimates of the r_e^{BO} structure of N_2O have been computed at the MP2 and CCSD(T) levels (Table 7). The coupled-cluster T_1 diagnostic is 0.0198 at the VQZ CCSD(T) level, slightly larger than for FNO_2, but slightly smaller than that for HONO and FNO. The best r_e^{BO} structure derived is in excellent agreement with the experimental equilibrium structure, the deviations being only 0.0006 and 0.0003 Å for r(NN) and r(NO), respectively.

8. Equilibrium Structures of Nitrosyl Hydride, HNO

HNO is somewhat different from the XNO and XNO_2 molecules of this study because H is not highly electronegative and, consequently, the T_1 diagnostic value characterizing HNO is small, 0.013 at the VQZ CCSD(T) level. Nevertheless, HNO has an important similarity to those molecules, namely, that its NH bond has the longest known length, 1.053 Å, the next longest NH bond length is 1.036 Å for the radical NH.[73] The ab initio structure of HNO has been calculated repeatedly.[73,79] The anharmonic force field of HNO has been computed at the frozen-core VTZ CCSD(T) level.[80] An experimental cubic force

TABLE 8: Molecular Structure of HNO with Distances (r) in Å and Angles (∠) in Degrees

method	basis	r(N−H)	r(N═O)	∠(HNO)
r_e (expt)[a]		1.063(3)	1.206(3)	109.1(2)
CCSD(T) (ae)	ACVQZ	1.0525	1.2087	108.18
CCSD(T) (ae)	VQZ	1.0510	1.2082	108.09
CCSD(T) (ae)	AVQZ	1.0515	1.2083	108.18
CCSD(T) (ae)	AV5Z	1.0507	1.2071	108.20
CCSD(T) (fc)[c]	AV6Z + CV[d]	1.0518	1.2076	108.10
CBS[b]		1.0518	1.2075	108.19
r_e^{SE}		1.0536	1.2087	108.12

[a] Reference 81. [b] Obtained using the following additivity approximation, all numbers taken at the all-electron CCSD(T) level: ACVQZ + [AV5Z − AVQZ]. [c] Reference 79. [d] Corrected for core correlation effect.

field is also available.[81] As part of this study, the cubic force field was computed at the all-electron VTZ CCSD(T) level.

We extended the ab initio determination of the structure of HNO up to the all-electron AV5Z CCSD(T) level (Table 8). For the NH bond length, there is almost no difference starting from the VQZ CCSD(T) level, indicating that convergence is achieved at the CCSD(T) level. As for the NO bond length, there is a decrease of 0.001 Å when going from VQZ to AV5Z, in agreement with the conclusions of Demaison et al.[73] There is excellent agreement between the frozen-core CCSD(T) structural parameters of Feller and Dixon[79] and those obtained here at the all-electron CCSD(T) level.

The anharmonic force field of HNO permitted evaluation of the semi-experimental equilibrium rotational constants of HNO and DNO, which were used to determine a semi-experimental structure. Only the B and C rotational constants have been used during the least-squares refinement because the vibrational correction for the A rotational constants is so large that the perturbational calculation is probably not valid. The derived semi-experimental structure, r_e^{SE}, is also given in Table 8. Because it has been determined from only four rotational constants, it is difficult to assess its accuracy. Nevertheless, if we assume that the uncertainty of the ab initio structure is as much as 0.002 Å for the bond lengths, the r_e^{BO} and r_e^{SE} structures are in good agreement.

9. Conclusions

It has been accepted, see, for example, ref 10, that it is not easy to calculate accurate ab initio structures for the XNO and XNO_2 molecules (where X═F, Cl, OH). Nevertheless, it has been often assumed, implicitly or explicitly, see, for example, ref 15, that the CCSD(T) method gives reliable structural results, provided that a large basis set with diffuse functions is used. We have shown here that this is not necessarily true and that the T_1 diagnostic indicates the lack of accuracy of the single-reference CCSD(T) method for these systems. Note that in the case of HONO T_1 is somewhat sensitive to the choice of the basis set. The T_1 value is 0.021 with the VQZ basis set in the frozen core approximation but only 0.018 with the wCVQZ basis set, all electrons being correlated, falling below the usually applied cutoff value of 0.02 indicating dominant single-reference character. Note also that CASSCF calculations indicated[14] that the wave function of the ground electronic state of HONO has only one leading configuration. It is noteworthy that only the unusually long N−X bond is calculated unreliably at the CCSD(T) level, the rest of the structural parameters are predicted with the expected precision.[12,15,52] It seems that the CCSDTQ method could give highly reliable results but, unfortunately, it is still too expensive for everyday use, even for these small systems.

The semi-experimental method, where the experimental ground-state rotational constants are corrected for vibrational effects using an ab initio cubic force field, seems to be much less sensitive to systematic errors. For this class of compounds, the semi-experimental techniques provide the most reliable equilibrium structures, because (a) for them accurate ground-state rotational constants of several isotopologues have been determined experimentally; and (b) the vibrational corrections are only a very small percentage of the rotational constants (less than 1%). Accuracy of the semi-experimental structures determined is better than 0.001 Å and 0.1°.

The mass-dependent method of Watson et al.[46] seems to be significantly less accurate than the semi-experimental technique because (a) more parameters need to be determined, for example, for HONO not only the five geometric parameters but seven additional ones would need to be determined during the least-squares refinement; and (b) the method does not work well for X−H (X═N, O) bond lengths.

As a result of the above conclusions, we tried to employ the semi-experimental methodology for the unstable $ClNO_2$ molecule, for which the T_1 diagnostic is 0.021 at the VTZ CCSD(T) level. Unfortunately, there is not enough experimental data available to determine a reliable equilibrium structure for this molecule.

In conclusion, this work provides further evidence that for small molecules the best approach to determine equilibrium structural parameters with an accuracy of about 0.001 Å and 0.1° is through the semi-experimental technique.

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References and Notes

(1) Solomon, S. *Rev. Geophys.* **1999**, *37*, 275.

(2) Dehayem-Kamadjeu, A.; Pirali, O.; Orphal, J.; Kleiner, I.; Flaud, P.-M. *J. Mol. Spectrosc.* **2005**, *234*, 182 and references cited therein.

(3) (a) Reiche, F.; Abel, B.; Beck, R. D.; Rizzo, T. R. *J. Chem. Phys.* **2002**, *116*, 10267. (b) McDonald, P. A.; Shirk, J. S. *J. Chem. Phys.* **1982**, *77*, 2355. (c) de Maré, G. R.; Moussaoui, Y. *Int. Rev. Phys. Chem.* **1999**, *18*, 91.

(4) Bartberger, M. D.; Fukuto, J. M.; Houk, K. N. *Proc. Natl. Acad. Sci.* **2001**, *98*, 2194.

(5) Cox, A. P.; Brittain, A. H.; Finnigan, D. J. *Trans. Faraday Soc.* **1971**, *67*, 2179.

(6) Finnigan, D. J.; Cox, A. P.; Brittain, A. H.; Smith, J. G. *J. Chem. Soc. Faraday Trans.* 2 **1972**, *68*, 548.

(7) Cox, A. P.; Ellis, M. C.; Attfield, C. J.; Ferris, A. C. *J. Mol. Struct.* **1994**, *320*, 91.

(8) Degli Esposti, C.; Cazzoli, G.; Favero, P. G. *J. Mol. Spectrosc.* **1985**, *109*, 229.

(9) Lee, T. J. *J. Chem. Phys.* **1993**, *99*, 9785.

(10) Dibble, T. S.; Francisco, J. S.; Deeth, R. J.; Hand, M. R.; Williams, I. H. *J. Chem. Phys.* **1994**, *100*, 459.

(11) Martin, J. M. L.; François, J.-P.; Gijbels, R. *J. Phys. Chem.* **1994**, *98*, 11394.

(12) Lee, T. J.; Rendell, A. P. *J. Chem. Phys.* **1991**, *94*, 6229.

(13) Luckhaus, D. *J. Chem. Phys.* **2003**, *118*, 8797.

(14) Richter, F.; Hochlaf, M.; Rosmus, P.; Gatti, F.; Meyer, H.-D. *J. Chem. Phys.* **2004**, *120*, 1306.

(15) Coriani, S.; Marchesan, D.; Gauss, J.; Hätting, C.; Helgaker, T.; Jørgensen, P. *J. Chem. Phys.* **2005**, *123*, 184107.

(16) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(17) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(18) Lee, T. J.; Taylor, P. R. *Int. J. Quantum Chem. Symp.* **1989**, *23*, 199.

(19) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*,618.

(20) Kohn, W.; Sham, L. J. *Phys. Rev.* A **1965**, *140*, 1133.

(21) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(22) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev.* B **1988**, *37*, 785.

(23) Császár, A. G.; Czakó, G.; Furtenbacher, T.; Tennyson, J.; Szalay, V.; Shirin, S. V.; Zobov, N. F.; Polyansky, O. L. *J. Chem. Phys.* **2005**, *122*, 214305.

(24) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(25) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(26) Dunning, T. H., Jr. *J. Chem. Phys.***1971**, *55*, 716.

(27) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(28) Császár, A. G.; Allen, W. D. *J. Chem. Phys.* **1996**, *104*, 2746.

(29) Peterson, K. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **2002**, *117*, 10548.

(30) Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 6/19/03, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76. RLO 1830. Contact David Feller or Karen Schuchardt for further information.

(31) Margulès, L.; Demaison, J.; Rudolph, H. D. *J. Mol. Struct.* **2001**, *599*, 23.

(32) MOLPRO 2000 is a package of ab initio programs written by Werner, H.-J. and Knowles, P. J. with contributions from Amos, R. D.; Bernhardsson, A.; Berning, A.; Celani, P.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Hampel, C.; Hetzer, G.; Korona, T.; Lindh, R.; Lloyd, A. W.; McNicholas, S. J.; Manby, F. R.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pitzer, R.; Rauhut, G.; Schütz, M.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.

(33) Hampel, C.; Peterson, K. A.; Werner, H.-J. *Chem. Phys. Lett*. **1992**, *190*, 1 and references therein.

(34) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, *227*, 321.

(35) Stanton, J. F.; Gauss, J.; Watts, J. D.; Szalay, P. G.; Bartlett, R. J. Mainz-Austin-Budapest version of ACESII, with contributions from Auer, A. A.; Bernholdt, D. B.; Christiansen, O.; Harding, M. E.; Heckert, M.; Heun, O.; Huber, C.; Jonsson, D.; Jusélius, J.; Lauderdale, W. J.; Metzroth, T.; Ruud, K. Integral packages included are MOLECULE (Almlöf, J.; Taylor, P. R.), PROPS (Taylor, P.), and ABACUS (Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.). For a current version see http://www.aces2.de.

(36) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.04; Gaussian, Inc.: Wallingford, CT, 2004.

(37) Kállay, M.; Surján, P. R. *J. Chem. Phys.* **2001**, *115*, 2945.

(38) Kállay, M.; Gauss, J.; Szalay, P. G. *J. Chem. Phys.* **2003**, *119*, 2991.

(39) For a current version, see http://mrcc.hu.

(40) Mills, I. M. In *Molecular Spectroscopy: Modern Research*; Mathews, C. W., Ed.; Academic Press: New York, 1972; Vol. 1, pp 115−140.

(41) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*; Wiley: New York, 1984. See Chapter VIII for the centrifugal distortion correction and Chapter XI for the magnetic correction.

(42) (a) Gauss, J.; Stanton, J. F. *Chem. Phys. Lett.* **1997**, *276*, 70. (b) Stratmann, R. E.; Burant, J. C.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **1997**, *106*, 10175. (c) Johnson, B. G.; Frisch, M. J. *J. Chem. Phys.* **1994**, *100*, 7429.

(43) Allen, W. D.; Császár, A. G. *J. Chem. Phys.* **1993**, *98*, 2983.

(44) Schneider, W.; Thiel, W. *Chem. Phys. Lett.* **1989**, *157*, 367.

(45) Stanton, J. F.; Lopreore, C.; Gauss, J. *J. Chem. Phys.* **1998**, *108*, 7190.

(46) Watson, J. K. G.; Roytburg, A.; Ulrich, W. *J. Mol. Spectrosc.* **1999**, *196*, 102.

(47) Guilmot, J.-M.; Carleer, M.; Godefroid, M.; Herman, M. *J. Mol. Spectrosc.* **1990**, *143*, 81.

(48) Kleiner, I.; Guilmot, J.-M.; Carleer, M.; Herman, M. *J. Mol. Spectrosc.* **1991**, *149*, 341.

(49) Guilmot, J.-M.; Godefroid, M.; Herman, M. *J. Mol. Spectrosc*. **1993**, *160*, 387.

(50) Guilmot, J.-M.; Mélen, F.; and Herman, M. *J. Mol. Spectrosc.* **1993**, *160*, 401.

(51) Lee, T. J.; Scuseria, G. E. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer: Dordrecht, 1995; pp 47−108.

(52) Helgaker, T.; Gauss, J.; Jørgensen, P.; Olsen, J. *J. Chem. Phys.* **1997**, *106*, 6430.

(53) Martin, J. M. L.; Taylor, P. R. *Chem. Phys. Lett.* **1994**, *225*, 473.

(54) Schafer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(55) Hübner, D.; Sutter, D. H. *Z. Naturforsch.* A **1989**, *39*, 55.

(56) Hamilton, L. C. *Regression with Graphics*; Duxbury Press: Belmont, CA, 1992.

(57) Mosteller, F.; Tukey, J. W. *Data Analysis and Regression*, Addison-Wesley: Reading, MA, 1977.

(58) Mills, I. M. *J. Phys. Chem.* **1976**, *80*, 1187.

(59) Evans, C. J.; McNaughton, D.; Dexter, P.; Lawrance, W. *J. Mol. Spectrosc.* **1998**, *187*, 75.

(60) Foster, S. C.; Johns, J. W. C. *J. Mol. Spectrosc.* **1984**, *103*, 176.

(61) Buckton, K. S.; Legon, A. C.; Millen, D. J. *Trans. Faraday Soc.* **1969**, *65*, 1975.

(62) Rohwer, F.; Garnieri, A. *Z. Naturforsch. A* **1980**, *35*, 336.

(63) Cazzoli, G.; Degli Esposti, C.; Palmieri, P.; Simeone, S. *J. Mol. Spectrosc.* **1983**, *97*, 165.

(64) Gatehouse, B.; Müller, H. S. P.; Heineking, N.; Gerry, M. C. L. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 3347.

(65) Cazzoli, G. Lister, D. G.; Favero, P. G. *J. Mol. Spectrosc.* **1972**, *42*, 286.

(66) Lee, T. J. *J. Chem. Phys.* **1993**, *99*, 9783.

(67) Dunning, T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244.

(68) Tarczay, G.; Császár, A. G.; Leininger, M. L.; Klopper, W. *Chem. Phys. Lett.* **2000**, *322*, 119.

(69) Lee, T. J.; Rice, J. E. *J. Chem. Phys.* **1992**, *97*, 4223.

(70) Legon, A. C.; Millen, D. J. *J. Chem. Soc. A* **1968**, 1736.

(71) Hegelund, F.; Bürger, H.; Pawelke, G. *J. Chem. Phys.* **1997**, *184*, 350.

(72) Kruse, H.; Hegelund, F.; Bürger, H.; Pawelke, G. *J. Mol. Spectrosc.* **2000,** *203*, 273.

(73) Demaison, J.; Margulès, L.; Boggs, J. E. *Chem. Phys.* **2000**, *260*, 65.

(74) Teffo, J.-L.; Chédin, A. *J. Mol. Spectrosc.* **1989**, *135*, 389.

(75) Allen, W. D.; Yamaguchi, Y.; Császár, A. G.; Clabo, A. D.; Remington, R. B.; Schaefer, H. F. *Chem. Phys.* **1990**, *145*, 427.

(76) Martin, J. M. L.; Taylor, P. R.; Lee, T. J. *Chem. Phys. Lett.* **1993**, *205*, 535.

(77) Martin, J. M. L. *Chem. Phys. Lett.* **1995**, *242*, 343.

(78) Császár, A. G. *J. Phys. Chem.* **1994**, *98*, 8823.

(79) Feller, D.; Dixon, D. A. *J. Phys. Chem. A* **2003**, *107*, 10419.

(80) Dateo, C. E.; Lee, T. J.; Schwenke, D. W. *J. Chem. Phys.* **1994**, *101*, 5853.

(81) Hirota, E. *Chem. Soc. Jpn.* **1986**, 1438.