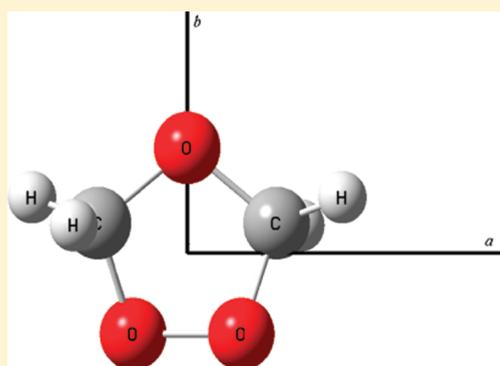


# Equilibrium Structures of Heterocyclic Molecules with Large Principal Axis Rotations upon Isotopic Substitution

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**ABSTRACT:** Equilibrium structures,  $r_e$ , of the heterocyclic molecules oxirane, furazan, furan, ethylene ozonide, and 1,3,4-oxadiazole have been determined using three different, somewhat complementary techniques: a completely experimental technique ( $r_m$ ), a semiexperimental technique ( $r_e^{SE}$ , whereby equilibrium rotational constants are derived from experimental effective ground-state rotational constants and corrections based principally on an ab initio cubic force field), and an ab initio technique ( $r_e^{BO}$ , whereby geometry optimizations are usually performed at the coupled cluster level of theory including single and double excitations augmented by a perturbational estimate of the effects of connected triple excitations [CCSD(T)] using quadruple- $\zeta$  Gaussian basis sets). All these molecules are asymmetric tops with the moment of inertia  $I_c$  much larger than the other two moments of inertia,  $I_a$  and  $I_b$ . Molecules of this shape experience a large rotation of the principal axis system upon certain isotopic substitutions. For such isotopologues it is difficult to obtain a good structural fit to the semiexperimental moments of inertia  $I_a$  and  $I_b$ , which may significantly reduce the accuracy of the  $r_e^{SE}$  structural parameters. The origin of this difficulty is explained. For the heavy-atom skeleton of these molecules it was possible to determine a rather accurate empirical mass-dependent structure without a priori knowledge of the equilibrium structure.



## 1. INTRODUCTION

The semiexperimental (SE) approach, which uses equilibrium rotational constants obtained from experimental ground-state rotational constants and computed rovibrational corrections, is believed to be the most accurate technique to determine equilibrium structures of free molecules.<sup>1–8</sup> Thanks to this method, the number of equilibrium structures that are accurately known, with uncertainty estimates on the order of 0.001–0.002 Å for bond lengths and 0.1–0.2° for angles, has grown exponentially during the last 20 years.<sup>8</sup> The success of this method is partially due to the fact that it has become straightforward to compute anharmonic force fields,<sup>9,10</sup> up to quartic terms, for molecular systems containing many atoms, see, for example, refs 11–13, even at high levels of wave function theory and employing basis sets of at least triple- $\zeta$  quality. The SE approach has several advantages over other methods of structure determination. For instance, it is faster, simpler, and often more accurate than purely experimental methods.<sup>14</sup> It also alleviates the computational demand required to obtain accurate ab initio equilibrium structures,  $r_e^{BO}$ .<sup>15</sup>

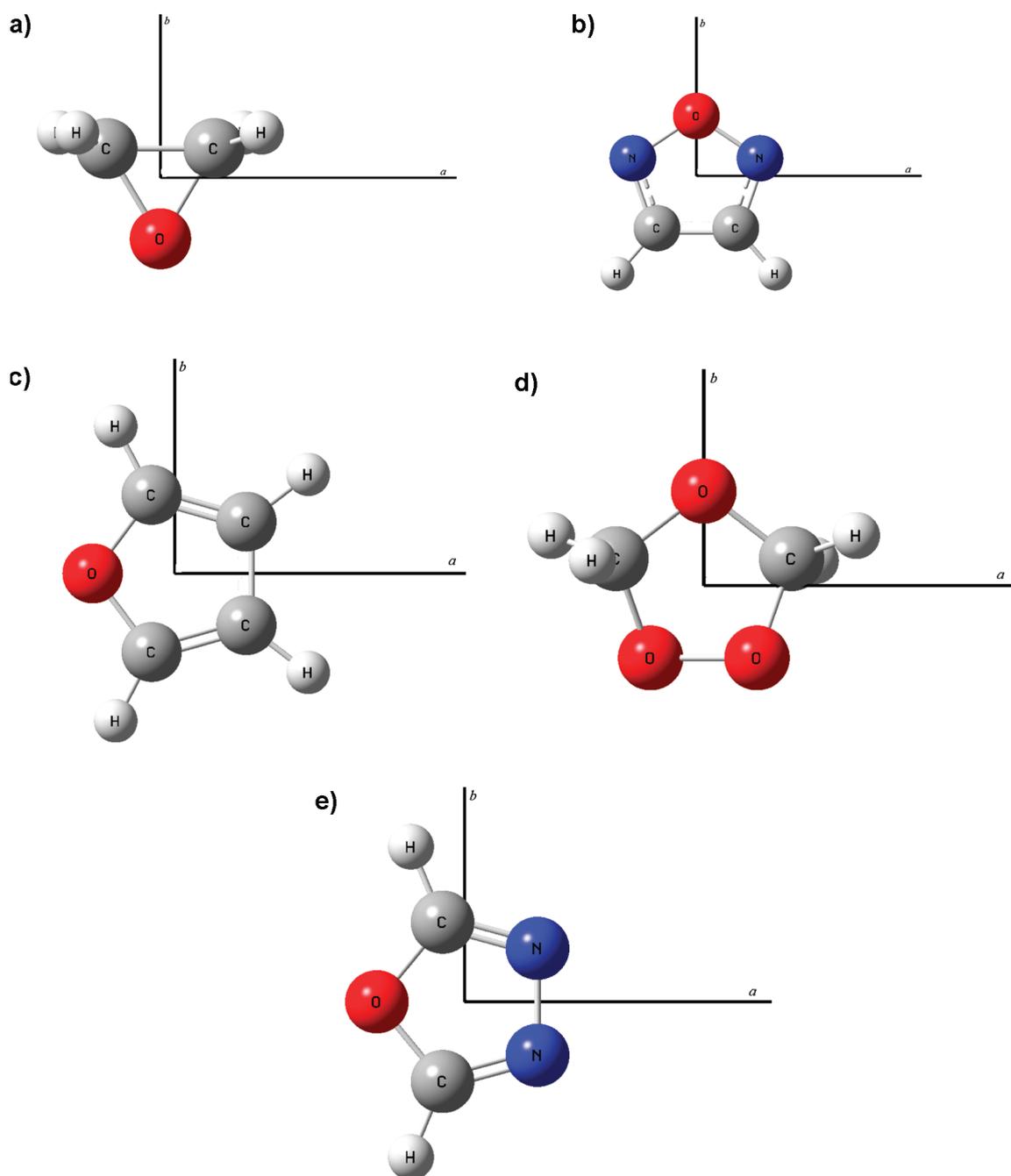
The SE approach has, however, certain limitations. (1) The experimental ground-state rotational constants for one or more isotopologues may be inaccurate.<sup>12</sup> This is, fortunately, rarely a problem as sophisticated techniques are now available to determine accurate rotational constants even from a limited amount of

experimental information.<sup>16</sup> (2) The perturbational approach to estimate the rovibrational corrections to the equilibrium rotational constants may be inadequate. This would be the case, in particular, for floppy molecules characterized by large-amplitude motions. It is straightforward to anticipate this difficulty, and it is possible to resort in such cases to a variational<sup>17</sup> or some other alternative treatment. (3) The computed rovibrational corrections to the rotational constants may be inaccurate due to the use of an inadequate level of electronic structure theory. This problem is again simple to identify, e.g., by comparing experimental and computed spectroscopic constants (band centers, centrifugal distortion constants, etc.). Though the lowest order rovibrational corrections to the rotational constants computed from a cubic force field may not be highly accurate, their magnitude is only about 0.5% of the rotational constants and their error, about 2% in the best cases, is mainly systematic. It is quite reasonable to accept that uncertainties of the rovibrational corrections have only a small effect on the resulting structures.<sup>18,19</sup> (4) The system of normal equations is ill conditioned in the least-squares refinement.<sup>20</sup> In such cases the ill-conditioning amplifies the errors introduced by (1)–(3). When the

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**Figure 1.** Molecular structures of (a) oxirane, (b) furazan, (c) furan, (d) ethylene ozonide, and (e) 1,3,4-oxadiazole in the principal axis system.

rovibrational corrections are similar for all isotopologues, the ill conditioning is often harmless. However, when there is a large rotation of the principal axis system (PAS) upon isotopic substitution, some of the rovibrational corrections change significantly. This effect appears to be especially significant for oblate molecules (with a Ray asymmetry parameter  $\kappa = (2B - A - C)/(A - C) > 0$ ). This effect has been studied by Kuczkowski et al.,<sup>21,22</sup> for example, in the case of the substitution structure ( $r_s$ ) of ethylene ozonide,  $c\text{-C}_2\text{H}_4\text{O}_3$  (1,2,4-trioxolane). They analyzed the rotational spectra of 20 isotopologues of  $c\text{-C}_2\text{H}_4\text{O}_3$  and were able to determine the  $\text{O}_p\text{-O}_p$  (peroxy linkage) bond distance six different ways. This distance was found to vary over  $0.05 \text{ \AA}$ , which is at least 1 order of magnitude larger than the expected uncertainty. Difficulties related to PAS

rotations were noticed for the semiexperimental equilibrium structure,  $r_e^{\text{SE}}$ , of other simple oblate molecules. In the case of difluorohydroxyborane,  $\text{BF}_2\text{OH}$  ( $\kappa = +0.915$ ), although the force field was computed at the gold standard CCSD(T)<sup>23,24</sup> level of electronic structure theory, it was not possible to obtain a good fit from the semiexperimental equilibrium rotational constants but the derived parameters were found to be inaccurate.<sup>25</sup> Likewise, in the case of nitric acid,  $\text{HNO}_3$  ( $\kappa = +0.730$ ), large residuals of similar magnitude but of opposite sign were observed for the rotational constants  $A$  and  $B$  of isotopologues subject to a large axis rotation.<sup>26</sup> For both  $\text{BF}_2\text{OH}$  and  $\text{HNO}_3$  nondynamical electron correlation is not negligible. Furthermore, the double potential governing the torsional motion of the OH group is highly anharmonic with a non-

negligible quartic term. These factors affect the accuracy of the computed cubic force field. Although the large PAS rotation must certainly play a role, the structural uncertainties for  $\text{BF}_2\text{OH}$  and  $\text{HNO}_3$  probably result from almost all of the above-listed sources of uncertainties.

Out of the difficulties summarized in the previous paragraph, the least thoroughly investigated and thus the most important to study in detail is the effect of large PAS rotations on semiexperimental structures of molecules. Therefore, this is the main theme of the present work. We determine  $r_e^{\text{SE}}$  structures of several “semirigid” (i.e., without large amplitude motion) oblate ring molecules. To help estimate the accuracy of the  $r_e^{\text{SE}}$  structures we compute definitive ab initio Born–Oppenheimer equilibrium structures,  $r_e^{\text{BO}}$ , at high levels of electronic structure theory and deduce fully empirical mass-dependent  $r_m$ -type structures as well. Good agreement between these structures is a strong indicator that the derived equilibrium structures are accurate. This assessment can be strengthened by a careful analysis of the residuals of the least-squares fits.<sup>2,20</sup> The first molecule studied is oxirane,  $c\text{-C}_2\text{H}_4\text{O}$  (ethylene oxide). Although it is an oblate molecule, there is no large rotation of the PAS upon substitution. Furthermore, accurate rotational constants for the parent and 10 isotopologues are available. Thus, the derived  $r_e^{\text{SE}}$  structure is expected to be accurate. Then, the  $r_e^{\text{SE}}$  structures of several molecules with large PAS rotations upon isotopic substitution are studied: furazan,  $c\text{-C}_2\text{H}_2\text{N}_2\text{O}$ , furan,  $c\text{-C}_4\text{H}_4\text{O}$ , ethylene ozonide,  $c\text{-C}_2\text{H}_4\text{O}_3$ , and 1,3,4-oxadiazole,  $c\text{-C}_2\text{H}_2\text{N}_2\text{O}$ . For drawings of the molecules studied see Figure 1.

## 2. THEORETICAL CONSIDERATIONS

It is simpler to discuss the effect of the rotation of the PAS upon isotopic substitution in the particular case of molecules with a plane of symmetry, although the conclusions drawn will be general and apply to less symmetric molecules as well.

The diagonal ground-state moment of inertia tensor for any isotopologue may be written as

$$\mathbf{I}^0 = \tilde{\mathbf{R}}_0(\mathbf{I}_e + \boldsymbol{\varepsilon})\mathbf{R}_0 \quad (1)$$

where  $\mathbf{I}_e$  is the equilibrium moment of inertia tensor,  $\boldsymbol{\varepsilon}$  is the rovibrational correction tensor, and both tensors are expressed in an arbitrary coordinate system and thus are nondiagonal.  $\mathbf{R}_0$  is the eigenvector matrix of  $(\mathbf{I}_e + \boldsymbol{\varepsilon})$ , which diagonalizes this tensor with axes  $a$ ,  $b$ , and  $c$ .

When the coordinate system takes into account an  $(a, b)$  plane of symmetry present in the parent as well as in the substituted species of the molecule, both  $\mathbf{I}_e$  and  $\boldsymbol{\varepsilon}$  become block-diagonal

$$\mathbf{I}_e + \boldsymbol{\varepsilon} = \begin{bmatrix} I_{aa}^e & I_{ab}^e & 0 \\ I_{ab}^e & I_{bb}^e & 0 \\ 0 & 0 & I_{cc}^e \end{bmatrix} + \begin{bmatrix} \varepsilon_{aa} & \varepsilon_{ab} & 0 \\ \varepsilon_{ab} & \varepsilon_{bb} & 0 \\ 0 & 0 & \varepsilon_{cc} \end{bmatrix} \quad (2)$$

The PAS of the parent species is usually chosen as the coordinate system. In this case,  $\mathbf{R}_0$  may be written as

$$\mathbf{R}_0 = \begin{bmatrix} \cos \theta_0 & -\sin \theta_0 & 0 \\ \sin \theta_0 & \cos \theta_0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (3)$$

with

$$I_g^0 = \frac{I_{aa}^e + I_{bb}^e + \varepsilon_{aa} + \varepsilon_{bb}}{2} \pm \frac{I_{aa}^e - I_{bb}^e + \varepsilon_{aa} - \varepsilon_{bb}}{2} \sqrt{(1 + \tan^2 2\theta_0)} \quad (4)$$

the plus sign for  $g = a$  and the minus sign for  $g = b$  and

$$\tan 2\theta_0 = \frac{2(I_{ab}^e + \varepsilon_{ab})}{I_{aa}^e + \varepsilon_{aa} - I_{bb}^e - \varepsilon_{bb}} \quad (5)$$

In order to determine an equilibrium structure we need the elements of the equilibrium moment of inertia tensor of the current isotopologue in its own principal axis system. This can be obtained from those given in the PAS of the parent in eq 2 by

$$I_g^e = \frac{I_{aa}^e + I_{bb}^e}{2} \pm \frac{I_{aa}^e - I_{bb}^e}{2} \sqrt{(1 + \tan^2 2\theta_e)} \quad (6)$$

(plus and minus as above) with

$$\tan 2\theta_e = \frac{2I_{ab}^e}{I_{aa}^e - I_{bb}^e} \quad (7)$$

For instance, in the typical case of furan,  $\theta_0 = 39.745^\circ$  and  $\theta_e = 39.753^\circ$ . In other words, the difference is quite small and may be usually neglected. With  $(1 + \tan^2 2\theta)^{1/2} = (\cos 2\theta)^{-1}$ , it follows from eq 6 that

$$I_{aa}^e - I_{bb}^e = (I_a^e - I_b^e) \cos 2\theta_e \quad (8)$$

From eqs 7 and 8 we obtain for the nondiagonal element

$$I_{ab}^e = \frac{1}{2} (I_a^e - I_b^e) \sin 2\theta_e \quad (9)$$

It can be deduced from eq 8 that for increasing angle  $\theta_e$  a sign change occurs at  $\theta_e = 45^\circ$ , corresponding to an  $(a, b)$ -axis switch of the isotopologue with reference to the parent isotopologue due to the isotopic substitution. We conclude further from eq 9 that the nondiagonal element  $I_{ab}$  is smaller than the difference  $I_a - I_b$ .

On the grounds that the rovibrational correction amounts to no more than approximately 1% of the respective moment of inertia, we may assume that the difference  $\theta_0 - \theta_e$  is practically always small, even for large angles  $\theta$  (for an exception see below). On this basis we obtain, from eqs 4 and 6 (where we no longer distinguish  $\theta_0$  from  $\theta_e$ ), that

$$\varepsilon_g = I_g^0 - I_g^e = \frac{\varepsilon_{aa} + \varepsilon_{bb}}{2} \pm \frac{\varepsilon_{aa} - \varepsilon_{bb}}{2} \sqrt{(1 + \tan^2 2\theta)} \quad g = a, b \quad (10)$$

with the plus sign for  $g = a$  and the minus sign for  $g = b$ .

When the rovibrational corrections,  $\varepsilon_g$  (with  $g = a, b$ ), are calculated with an inaccurate angle  $\theta$  it is possible to estimate its effect on  $\varepsilon_g$  by differentiating eq 10 with respect to  $\theta$  yielding

$$\delta\varepsilon_g = \pm(\varepsilon_{aa} - \varepsilon_{bb}) \frac{\tan 2\theta}{\cos 2\theta} \delta\theta \quad (11)$$

(plus and minus as above). This error can be huge, for instance, in the case of furan- $^{13}\text{C}$  the coefficient multiplying  $\delta\theta$  is as large as  $0.2 \text{ u}\text{\AA}^2 \text{ rad}^{-1}$ .

Equation 11 shows that for small angles  $\theta$  an error on  $\varepsilon_g$  is not important but becomes significant when the angle increases and approaches the axis switching limit. Furthermore, it is interesting

to note that the errors on  $\varepsilon_a$  and  $\varepsilon_b$  have the same value but are of opposite sign. Let us take a look at the limiting cases.

For a prolate molecule ( $I_{aa} \ll I_{bb}$ ), when the PAS of the parent is used as the axis system, the angles  $\theta_0$  and  $\theta_e$  themselves are small, not only their difference. Then,  $\mathbf{R}_0$  of eq 2 would hardly differ from a transformation  $\mathbf{R}_e$  which diagonalizes the tensor  $\mathbf{I}_e$  alone. For  $\theta_0 - \theta_e$  less than a few degrees (that is in most cases), eq 10 tends to

$$\varepsilon_g = I_g^0 - I_g^e \rightarrow \varepsilon_{gg}, \quad g = a, b \quad (12)$$

However, when the molecule is oblate,  $I_a^e \approx I_b^e$ . It then follows from eq 9 that  $I_{ab}^e$  is small. In this case, the situation may change significantly when the nondiagonal rovibrational tensor is added and  $\varepsilon_{ab}$  is large enough. Equation 5 could then even reveal an ( $a, b$ )-axis switch with reference to eq 7 depending on the magnitude and signs of  $\varepsilon_{aa}$  and  $\varepsilon_{bb}$  (this time the axis switch is due to the rovibrational contributions, not to the isotopic substitution as discussed above). More importantly, the reference structure used to calculate the force field is usually not identical to the true equilibrium structure, and therefore, the angle of rotation of the PAS upon isotopic substitution may be significantly different for the equilibrium structure and the reference structure. For instance, in the typical case of furan- $^{13}\text{C}$ , as discussed in section 6,  $\theta_e = 39.8^\circ$  whereas the reference structure used to calculate the force field gives  $\theta = 21.2^\circ$ . It follows that  $\varepsilon_g$  calculated from the force field may be extremely different from the true values, as predicted by eq 11, as they are calculated in an axis system which is different from the PAS.

In summary, for an oblate molecule (a)  $\varepsilon$  is no longer calculated in an axis system near the PAS of  $\mathbf{I}_e$  (as is the case for a prolate molecule), hence  $\varepsilon_g \neq \varepsilon_{gg}$  (in contrast to eq 12), (b) we do not know the value of  $\varepsilon_{ab}$ , which affects the value of  $\theta_0$ , and (c)  $\theta$ [reference structure] and  $\theta_e$  may be quite different, which may significantly affect the accuracy of the  $r_e^{\text{SE}}$  structure.

### 3. METHODS OF STRUCTURE DETERMINATION

**3.1. Ab Initio Born–Oppenheimer Equilibrium Structures,  $r_e^{\text{BO}}$ .**<sup>15</sup> 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),<sup>27</sup> and coupled cluster theory including single and double excitations<sup>23</sup> augmented with a perturbational estimate of the effects of connected triple excitations, CCSD(T).<sup>24</sup> The Kohn–Sham density functional theory (DFT)<sup>28</sup> using Becke’s three-parameter hybrid exchange functional<sup>29</sup> and the Lee–Yang–Parr correlation functional,<sup>30</sup> together denoted as B3LYP, was also employed. The ab initio and DFT geometry optimizations performed at the levels described yield estimates of the Born–Oppenheimer equilibrium structure,  $r_e^{\text{BO}}$ . The  $r_e^{\text{BO}}$  structures of all molecules of this study were computed in the present work in order to be able to make meaningful comparisons.

The correlation-consistent polarized  $n$ -tuple-zeta basis sets cc-pVnZ<sup>31</sup> with  $n \in \{\text{D, T, Q, 5}\}$  were employed for the CCSD(T) and B3LYP electronic structure computations. Throughout this paper these basis sets are abbreviated as VnZ. Versions of VnZ sets augmented with diffuse functions (aug-cc-pVnZ, AVnZ in short)<sup>32</sup> were also employed. Combination of an AVnZ basis on all non-hydrogen atoms and VnZ on H is denoted hereafter as A’VnZ. B3LYP computations were also performed with the split-valence basis set 6-311G including appropriate polarization

functions, as implemented in Gaussian03.<sup>33</sup> In order to improve computed properties, especially equilibrium structural parameters, by inclusion of core correlation effects,<sup>34</sup> the correlation-consistent polarized weighted core–valence  $n$ -tuple zeta (abbreviated here as wCVnZ)<sup>35,36</sup> basis sets were used. 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,<sup>37,38</sup> at least for first-row atoms.

The CCSD(T) computations, including geometry optimizations employing analytic first derivatives,<sup>39</sup> were performed with the CFOUR<sup>40</sup> electronic structure program package, while the lower level B3LYP and MP2 computations utilized the Gaussian03 program suite.<sup>33</sup>

The frozen-core approximation (hereafter denoted as FC), i.e., keeping the 1s orbitals of first-row atoms doubly occupied during correlated-level calculations, was used at the MP2 and CCSD(T) levels, and all-electron (AE) wCVTZ MP2 and CCSD(T) and wCVQZ MP2 computations were also performed to gauge the effect of core correlation on the structural parameters.

**3.2. Semiexperimental Structures,  $r_e^{\text{SE}}$ .** Semiexperimental equilibrium rotational constants that can be used to determine semiexperimental equilibrium structures,  $r_e^{\text{SE}}$ , are determined by correcting the experimental ground-state rotational constants with lowest order vibration–rotation interaction constants ( $\alpha$ )<sup>2,41</sup> theoretically determined. The vibration–rotation interaction constants can be estimated if the cubic force field of the molecule, expanded about a reference (usually the equilibrium) structure, is known. We chose the MP2 level of electronic structure theory to determine the anharmonic force fields. In several cases the force fields have also been computed at the B3LYP level. The quadratic force fields were evaluated analytically<sup>42</sup> in Cartesian coordinates at the optimized molecular structure in order to avoid the nonzero force dilemma.<sup>43</sup> The cubic ( $\phi_{ijk}$ ) and semidiagonal quartic ( $\phi_{ijkk}$ ) normal coordinate force constants were then determined at the same reference structure with the use of finite difference procedures.<sup>2,44,45</sup> Evaluation of anharmonic spectroscopic constants was based on second-order vibrational perturbation theory.<sup>41,46,47</sup> The anharmonic force fields in normal coordinates were determined for all the isotopologues whose ground-state rotational constants are known.

In order to deduce equilibrium rotational constants from measured ones, besides the (first-order) rovibrational corrections, the modifications due to the small electronic effect<sup>48</sup> should also be considered. When the  $g$  constants required to determine the electronic effect are not known, they have been computed, using Gaussian03,<sup>33</sup> at the B3LYP level with the AVTZ or 6-311+G(3df,2pd) basis sets. In cases where comparison can be made between computed and experimental  $g$  constants, they show good agreement. The corrected values of the rotational constants are given by the relation

$$B_\xi^{\text{corr}} = \frac{B_\xi^{\text{exp}}}{1 + \frac{M_p}{M_\xi} g_{\xi\xi\xi}} \quad (13)$$

where  $g_{\xi\xi\xi}$  is expressed in units of the nuclear magneton,  $m$  is the electron mass,  $M_p$  the proton mass, and  $\xi = a, b, c$ . This correction is found to be rather small for the molecules investigated in this study and does not significantly affect the molecular structures determined.

The  $r_e^{\text{SE}}$  structures were obtained via a weighted least-squares fit to the semiexperimental moments of inertia. It is difficult to

estimate the precision of the moments of inertia; thus, the iterative reweighted least-squares method (IRLS) was used.<sup>20,49</sup> Huber's weighting, whereby the residuals  $e_i$  are gradually weighted down when they are larger than approximately  $2 \times \text{MAD}$ , was employed. The MAD (mean absolute deviation) is the median  $|e_i - \text{median}(e_i)|$ .

**3.3. Mass-Dependent Experimental Structures,  $r_m$ .** Many approximate methods have been developed to determine an empirical structure using only ground-state rotational constants. Of the methods proposed the perhaps most useful one is due to Watson et al.<sup>50</sup> This so-called mass-dependent ( $r_m$ ) structure technique takes into account the variation of the rovibrational correction upon isotopic substitution approximately and allows determination of structures close to the assumed equilibrium structure. Since the  $r_m$  method has been extensively used in this work, a short description follows.

In the principal axis system (PAS)  $\xi = a, b, c$  of the parent isotopologue ( $i = 1$ ) the three components of the ground-state moment of inertia of the parent are written as

$$I_{\xi}^0(1) = I_{\xi}^m(1) + c_{\xi} \sqrt{I_{\xi}^m(1)} + d_{\xi} \hat{M}(1) \quad (14)$$

with the approximation  $I_{\xi}^m = I_{\xi}^{\text{rigid}}$  (eq 31 of ref 50) for the  $r_m$  model. The last two terms of eq 14 provide the rovibrational contribution.  $\hat{M}(1)$  is a known, coordinate-independent function of the atomic masses of a particular isotopologue, here of the parent ( $i = 1$ ). In a center-of-mass coordinate system parallel to that of the parent the elements of the  $3 \times 3$  ground-state moment of inertia tensor of an isotopologue  $i$  must then be written as

$$I_{\xi\eta}^0(i) = I_{\xi\eta}^m(i) + c_{\xi\eta} \sqrt{I_{\xi\eta}^m(i)} + \delta_{\xi\eta} d_{\xi} \cdot \hat{M}(i) \quad (15)$$

with rovibrational parameters  $c_{\xi\eta}$  and  $d_{\xi}$ . Equation 15 defines elements of a nondiagonal tensor which, however, has not been expressed in its own PAS( $i$ )  $\xi' = a', b', c'$ . Depending on the shape of the molecule, the isotopic substitution will cause a (possibly large) rotation between the systems  $\xi, \eta = a, b, c$  and  $\xi', \eta' = a', b', c'$  (cf. section 2). It is a principal point of the theory (see eq 37 of ref 50) that the rovibrational contributions are added while the outline or shape of isotopologue  $i$  is in a position parallel to that of the parent even though the principal axis systems of isotopologue and parent will then usually differ in direction. When the tensor on the left side of eq 15 is diagonalized, we obtain the three moments of inertia  $I_{\xi'}^0(i), \xi' = a', b', c'$ , of the particular isotopologue  $i$ . Since the rovibrational contributions, the second plus third terms of eq 15, usually amount to no more than 1% of the first term,  $I_{\xi\eta}^m(i)$ , the eigenvalues of the latter and of the tensor  $I_{\xi\eta}^0$  of eq 15 will generally not differ considerably.

The  $I_{\xi}^0(1)$  of the parent and  $I_{\xi'}^0(i), i = 2, \dots$ , of the isotopologues must be expressed as functions of the (isotopologue-independent) internal coordinates of the molecule and the rovibrational parameters  $c_{\xi\eta}$  and  $d_{\xi}$ , which are finally obtained by least-squares fitting of the functions  $I_{\xi}^0(1)$  and  $I_{\xi'}^0(i), i = 2, \dots$ , to the experimental ground-state moments of inertia of the parent and the isotopologues.<sup>14</sup>

The model described above is named  $r_m^{(2r)}$ . Ignoring the PAS rotation of the isotopologues and directly using the moments of inertia of the isotopologues, all in their own PAS as in eq 14 for the parent, we obtain the  $r_m^{(2)}$  model "mixed" parameters  $c_{\xi\eta}$  with  $\xi \neq \eta$  are then no longer present. Setting in eqs 14 and 15  $d_{\xi} = 0$ , the models  $r_m^{(2r)}$  and  $r_m^{(2)}$  reduce to models  $r_m^{(1r)}$  and  $r_m^{(1)}$ , respectively. The accuracy is supposed to increase with the level of

refinement of the model ( $r_m^{(1)} \rightarrow r_m^{(2r)}$ ). However, as the number of parameters to be fitted increases, the least-squares regression tends to become ill conditioned and the accuracy may actually get worse.

For the C–H and C–D bonds of the molecules studied it is necessary to take into account the variation of the effective bond length upon deuteration (note that at equilibrium the difference between X–H and X–D bond lengths is minuscule as shown for O–H in ref 51). Watson et al.<sup>50</sup> have for this purpose proposed a two-parameter formulation which, however, often fails in practical problems due to an extremely high correlation of these (and other) parameters. In conclusion, the C–H bond lengths obtained by the  $r_m$  methods may not be reliable.

If a least-squares process with weights derived from evaluation of the experimental spectra has produced residuals of the ground-state moments of inertia to be fitted which are significantly larger than the experimental errors, an equally weighted ("unity-weighted") least-squares method should be preferred, or the more involved IRLS process could be used, whereby variable weights are automatically adjusted for the best fit. The case described here occurs when several or all of the experimental ground-state moments of inertia fitted are of higher accuracy than can at best be made use of by the inherently limited  $r_m$  model applied (in this work this happened for oxirane, furazan, and furan).

The choice of the most accurate mass-dependent structure is often not straightforward. The different structures are calculated in the order  $r_m^{(1)} \rightarrow r_m^{(1r)} \rightarrow r_m^{(2)} \rightarrow r_m^{(2r)}$ . One structure is better than the previous one if the standard deviation of the fit decreases significantly without an overly large increase of the condition number. Furthermore, the parameters, particularly the free rovibrational parameters  $c_{\xi\eta}$  and  $d_{\xi}$ , should be well determined.

#### 4. STRUCTURE OF OXIRANE

Oxirane (ethylene oxide) is an oblate ( $\kappa = +0.409$ ) molecule of  $C_{2v}$  point-group symmetry. Its structure is completely defined by five independent geometric parameters and has been determined several times. In 1974, Hirose<sup>52</sup> determined an effective  $r_0$  and a substitution  $r_s$  structure. In 1975, Haloui and Canet<sup>53</sup> obtained an approximate structure via nuclear magnetic resonance spectroscopy by measuring the direct spin–spin couplings of the molecule dissolved in a nematic phase. In 1989, Berry and Harmony<sup>54</sup> calculated a  $r_m^0$  structure (this is a mass-dependent structure quite similar to the  $r_m^{(1)}$  structure, but the rovibrational contribution  $\varepsilon$  is assumed to be proportional to the corresponding moment of inertia, instead of its square root). Although this last structure is purely empirical, it is believed to be a good approximation of the equilibrium structure of the molecule. The  $r_e^{\text{BO}}$  structure has been computed previously ab initio at the CCSD(T) level, with basis sets up to quadruple- $\zeta$  quality and extrapolated to the complete basis set limit with inclusion of core correlation effects, and it was shown that all previous structures are rather inaccurate.<sup>55</sup> It has been recomputed for this work in two different ways. First, it was computed at the VQZ CCSD(T)(FC) level of theory, and the core correlation was estimated at the MP2 level with the wCVQZ basis set. The wCVQZ MP2 level is indeed accurate enough for bond lengths involving first-row atoms.<sup>37,38</sup> In other words, the  $r_e^{\text{BO}}$  is obtained using the following equation

$$r_e^{\text{BO}}(1) = \text{VQZ CCSD(T)(FC)} + \text{wCVQZ MP2(AE)} - \text{wCVQZ MP2(FC)} \quad (16)$$

Table 1. Structure of Oxirane (Ethylene Oxide) (Bond Lengths in Ångstroms, Angles in Degrees)

| method                                  | $r(\text{C}-\text{C})$ | $r(\text{C}-\text{O})$ | $r(\text{C}-\text{H})$ | $\angle(\text{HCH})$ | $\angle(\theta)^a$ |
|---|------------------------|------------------------|------------------------|----------------------|--------------------|
| $r_m^{o,b}$                             | 1.4594(4)              | 1.4252(3)              | 1.0840(4)              | 116.75(7)            | 157.95(17)         |
| $r_m^{(1\pm)}$                          | 1.4601(14)             | 1.4275(8)              | 1.0840(2)              | 116.48(5)            | 158.04(4)          |
| VTZ MP2(FC) <sup>c</sup>                | 1.4622                 | 1.4317                 | 1.0816                 | 116.24               | 157.51             |
| VQZ MP2(FC)                             | 1.4588                 | 1.4303                 | 1.0805                 | 116.256              | 157.743            |
| V(Q,S)Z MP2(FC)                         | 1.4584                 | 1.4303                 | 1.0808                 | 116.366              | 158.025            |
| A'VQZ MP2(FC)                           | 1.4594                 | 1.4319                 | 1.0808                 | 116.383              | 158.093            |
| wCVTZ MP2(AE)                           | 1.4577                 | 1.4273                 | 1.0799                 | 116.179              | 157.500            |
| wCVQZ MP2(AE)                           | 1.4553                 | 1.4262                 | 1.0789                 | 116.273              | 157.749            |
| wCVQZ MP2(FC)                           | 1.4585                 | 1.4294                 | 1.0804                 | 116.301              | 157.830            |
| VQZ CCSD(T)(FC)                         | 1.4653                 | 1.4299                 | 1.0834                 | 116.124              | 157.805            |
| wCVTZ CCSD(T)(AE)                       | 1.4639                 | 1.4279                 | 1.0828                 | 115.980              | 157.508            |
| $r_e^{\text{BO}}(\text{I})^d$           | 1.4621                 | 1.4267                 | 1.0819                 | 116.12               | 157.80             |
| $r_e^{\text{BO}}(\text{II})^e$          | 1.4615                 | 1.4268                 | 1.0818                 | 116.07               | 157.76             |
| $r_e^{\text{BO}}(\text{III})^f$         | 1.4623                 | 1.4283                 | 1.0819                 | 116.12               | 157.80             |
| $r_e^{\text{SE}}$ , this work, see text | 1.46082(2)             | 1.42726(2)             | 1.08209(2)             | 116.189(3)           | 157.951(8)         |

<sup>a</sup> Angle  $\angle(\text{CCy})$  where y is the middle of the distance HH. <sup>b</sup> Reference 54. <sup>c</sup> Structure used to calculate the force field. <sup>d</sup>  $r_e^{\text{BO}}(\text{I}) = \text{VQZ CCSD(T)}(\text{FC}) + \text{wCVQZ MP2(AE)} - \text{wCVQZ MP2(FC)}$ . <sup>e</sup>  $r_e^{\text{BO}}(\text{II}) = \text{wCVTZ CCSD(T)}(\text{AE}) + \text{wCVQZ MP2(AE)} - \text{wCVTZ MP2(AE)}$ . <sup>f</sup>  $r_e^{\text{BO}}(\text{III}) = r_e^{\text{BO}}(\text{I}) + \text{A'VQZ MP2(FC)} + \text{V(Q,S)Z MP2(FC)} - 2[\text{VQZ MP2(FC)}]$  for the C–C and C–O bonds.

Then it was computed at the wCVTZ CCSD(T)(AE) level of theory, and the effect of further basis set enlargement, wCVTZ → wCVQZ, was determined at the MP2 level. This gives the  $r_e^{\text{BO}}(\text{II})$  structure calculated with the following equation

$$r_e^{\text{BO}}(\text{II}) = \text{wCVTZ CCSD(T)}(\text{AE}) + \text{wCVQZ MP2(AE)} - \text{wCVTZ MP2(AE)} \quad (17)$$

It is worth noting that the two approximations yield almost identical results, as indicated in Table 1. Finally, it is not obvious that basis set convergence of the structural parameters is achieved at the quadruple- $\zeta$  level. To check this the structure was optimized at the MP2 level with a mixed basis set: VSZ on C and O and VQZ on H, in short V(Q,S)Z. Going from VQZ MP2(FC) to V(Q,S)Z MP2(FC), the C–C bond length is shortened by 0.0004 Å, the other parameters are almost unaffected. Because the O atom is highly electronegative, the effect of adding diffuse functions to the basis set must also be investigated. To estimate this correction, the MP2 method was used together with the A'VQZ basis set. The results are reported in Table 1. The only significant change is for the C–O bond, which is lengthened by 0.0016 Å. For the C–C and C–O bond lengths, the best  $r_e^{\text{BO}}$  structure is obtained using the following equation

$$r_e^{\text{BO}}(\text{III}) = r_e^{\text{BO}}(\text{I}) + \text{A'VQZ MP2(FC)} + \text{V(Q,S)Z MP2(FC)} - 2[\text{VQZ MP2(FC)}] \quad (18)$$

The only significant difference between  $r_e^{\text{BO}}(\text{I})$  and  $r_e^{\text{BO}}(\text{III})$  is that the C–O bond length is longer by 0.0016 Å in the latter case. This  $r_e^{\text{BO}}$  structure is given in Table 1 and will be used as a reference structure.

The anharmonic force fields of 11 isotopologues of oxirane have been computed at the VTZ MP2(FC) level of electronic structure theory. The theoretical lowest order vibration–rotation interaction constants deduced from the ab initio cubic force fields were combined with the known experimental ground-state rotational constants<sup>52,56</sup> to yield the semiexperimental rotational constants, which were then also corrected for the small electronic contribution using experimental  $g$  constants.<sup>56</sup> The  $r_e^{\text{SE}}$  structure

was determined using the least-squares method. The largest rotation of the PAS is 11.8° for the  $d_1$  isotopologue. The system of normal equations is extremely well conditioned, the condition number being as small as 16.7. The results are not sensitive to the weighting and are given in Table 1, where it appears that the  $r_e^{\text{SE}}$  and  $r_e^{\text{BO}}$  structural parameters are in excellent agreement. The residuals of the fit are given in Table S1 of the Supporting Information, and their inspection does not indicate any problems. There is another way to check the accuracy of the structure by using the pseudo inertial defect which allows us to determine the distance  $\text{H} \cdots \text{H}$  for the isotopologues which keep the  $C_{2v}$  symmetry. The results are 1.8374 (parent species), 1.8373 (<sup>18</sup>O species), 1.8374 (<sup>13</sup>C species), and 1.8371 ( $d_4$  species) Å to be compared with the  $r_e^{\text{SE}}$  value of 1.8372 Å.

The experimental ground-state moments of inertia, without any corrections, were subjected to a unity-weighted least-squares fit. The model  $r_m^{(1r)}$  leads to a much smaller standard deviation than  $r_m^{(1)}$ . On the other hand, there is no significant decrease of the standard deviation when the models  $r_m^{(2)}$  or  $r_m^{(2r)}$  are used. In this particular case the choice of the best structure is easy. It is the  $r_m^{(1r)}$  structure, given in Table 1. The deviations from the  $r_e^{\text{BO}}$  structure are less than 0.002 Å and 0.03°. The different  $r_m$  structures are given in Table S2 of the Supporting Information. Although the PAS rotation angles of the isotopologues are rather small, the difference between the structures  $r_m^{(1r)}$  and  $r_m^{(1)}$  are larger than their errors. An attempt to include the Laurie correction as formulated by eq 33 of ref 50 failed. It yielded the expected extremely high correlation of  $-0.999$  between  $r_m(\text{XH}) = 1.0787(29)$  Å and  $\delta_{\text{H}} = 0.0178(9)$  u<sup>1/2</sup> Å and also generally higher standard errors.

## 5. STRUCTURE OF FURAZAN

Furazan,  $c\text{-C}_2\text{H}_2\text{N}_2\text{O}$  (1,2,5-oxadiazole), is a planar molecule of  $C_{2v}$  point-group symmetry with an asymmetry parameter of  $\kappa = +0.715$ . Its microwave spectrum has been extensively studied by Stiefvater,<sup>57</sup> accurate rotational constants are available for nine isotopologues, and the structure is defined by six independent parameters. Empirical  $r_0$ ,  $r_s$ ,  $r_m^o$ , and mass-dependent  $r_m^{(1)}$  and  $r_m^{(2)}$

Table 2. Structure of Furazan (Bond Lengths in Ångstroms, Angles in Degrees)

| method<br>basis set | $r_m^{(1)}$ | MP2(FC) <sup>b</sup><br>VTZ | CCSD(T)(AE)<br>wCVTZ | MP2(AE)<br>wCVTZ | MP2(AE)<br>wCVQZ | $r_e^{BO(I)^c}$ | $r_e^{BO(II)^d}$ | $r_e^{SE}$ |
|---------------------|-------------|-----------------------------|----------------------|------------------|------------------|-----------------|------------------|------------|
| $r(O-N)$            | 1.3703(8)   | 1.3609                      | 1.3702               | 1.3576           | 1.3541           | 1.3665          | 1.3661           | 1.3665(5)  |
| $r(N-C)$            | 1.3029(14)  | 1.3244                      | 1.3048               | 1.3197           | 1.3176           | 1.3027          | 1.3035           | 1.3020(6)  |
| $r(C-C)^a$          | 1.4188(15)  | 1.4001                      | 1.4190               | 1.3962           | 1.3949           | 1.4178          | 1.4167           | 1.419(2)   |
| $r(C-H)$            | 1.0738(5)   | 1.0746                      | 1.0752               | 1.0732           | 1.0725           | 1.0745          | 1.0749           | 1.0742(5)  |
| $\angle(NON')$      | 111.27(5)   | 112.25                      | 111.343              | 112.147          | 112.136          | 111.33          | 111.30           | 111.28(5)  |
| $\angle(ONC)$       | 105.48(5)   | 104.93                      | 105.463              | 104.983          | 105.068          | 105.55          | 105.58           | 105.61(6)  |
| $\angle(NCC')^a$    | 108.88(4)   | 108.94                      | 108.865              | 108.943          | 108.864          | 108.79          | 108.77           | 108.75(5)  |
| $\angle(NCH)$       | 120.91(6)   | 120.27                      | 120.946              | 120.294          | 120.286          | 120.94          | 120.86           | 121.02(8)  |
| $\angle(CCH)^a$     | 130.20(3)   | 130.79                      | 130.189              | 130.763          | 130.850          | 130.28          | 130.37           | 130.23(4)  |

<sup>a</sup> Dependent structural parameter. <sup>b</sup> Structure used to calculate the force field. <sup>c</sup> This work, wCVTZ CCSD(T)(AE) + wCVQZ MP2(AE) – wCVTZ MP2(AE). <sup>d</sup> Reference 58. VQZ CCSD(T)(AE) + CVQZ MP2(AE) – VQZ MP2(AE) + AVQZ MP2(FC) – VQZ MP2(FC).

structural parameters have been determined for this molecule. An average  $r_z$  structure has also been calculated, and finally, the  $r_e^{BO}$  structure has been computed ab initio according to the following formula:<sup>58</sup>

$$r_e^{BO}() = \text{VQZ CCSD(T)(AE)} + \text{CVQZ MP2(AE)} \\ - \text{VQZ MP2(AE)} + \text{AVQZ MP2(FC)} \\ - \text{VQZ MP2(FC)} \quad (19)$$

The relevant structures are given in Table 2. The accuracy of the  $r_e^{BO}$  structure calculated with eq 19 was checked by computing the structure at the CCSD(T)(AE) level with the wCVTZ basis set and by correcting the effect of further basis set enlargement, wCVTZ  $\rightarrow$  wCVQZ, at the MP2 level, see eq 17. Both  $r_e^{BO}$  structures are given in Table 2, and it can be seen that the overall agreement is quite good, the largest difference being only 0.001 Å for the  $r(C-C)$  bond. The effect of diffuse functions has been investigated in ref 58. Their effect is smaller than in oxirane; they lengthen the N–O bond by 0.0008 Å and the N–C bond by 0.0004 Å.

The anharmonic force field of furazan and its eight isotopologues has been computed in this study at the VTZ MP2(FC) level. The theoretical vibration–rotation constants deduced from the ab initio cubic force field were combined with the known experimental ground-state rotational constants<sup>57</sup> to yield the semiexperimental rotational constants which were corrected for the small electronic contribution using  $g$  constants computed at the aug-cc-pVTZ B3LYP level. The semiexperimental structure was determined using the IRLS method with Huber weighting. The system of normal equations is moderately well conditioned with a condition number of 262. The  $r_e^{SE}$  parameters are in excellent agreement with the  $r_e^{BO}$  parameters (Table 2). However, it has to be noted that the  $r(C-C)$  bond length is less precisely determined although the Cartesian coordinates of the carbon atoms are not small,  $a = \pm 0.7095(7)$  Å and  $b = 0.9274(2)$  Å, Table 2.

For the isotopologues furazan- $d_1$  and furazan- $d_2$ -<sup>13</sup>C, there is a moderate rotation about the negative  $c$  axis, the angles being 30.66° and 20.06°, respectively. For the isotopologue 3,4- $d_2$ -<sup>18</sup>O, there is an ( $a$ ,  $b$ )-axis switch, i.e., a 180° rotation about an axis in the  $a$ ,  $b$  plane and bisecting the fourth quadrant. Inspection of the residuals does not indicate any significant problems with the fitting. Nevertheless, the residuals of the  $A$  and  $B$  rotational constants of the 3,4- $d_2$ -<sup>13</sup>C isotopologue are about 1 order of magnitude larger than for the other ones. Furthermore, it is interesting to note that

the residual is +2.7 MHz for  $A$ , whereas it is –2.2 MHz for  $B$ . This indicates that the rovibrational correction is too large for  $A$  and too small for  $B$ . Eliminating these two data slightly improves the fit without affecting significantly the values of the parameters with the exception of the  $r(C-C)$  bond length, which is, in this latter case,  $r(C-C) = 1.4179(9)$  Å.

It is straightforward to explain the large value of the residuals for the furazan- $d_2$ -<sup>13</sup>C isotopologue. Using the semiexperimental equilibrium structure to calculate the rotation of the PAS upon isotopic substitution, we get  $\theta_e = 20.06^\circ$ , whereas with the VTZ MP2(FC) structure used to calculate the cubic force field  $\theta = 31.11^\circ$ . Such a large difference affects both  $\varepsilon_a$  and  $\varepsilon_b$  but, in a planar molecule, not their sum, see eq 11. Comparing the VTZ MP2(FC) structure used to calculate the force field to the equilibrium structure, significant differences are observed for the  $r(ON)$ ,  $r(CC)$ , and  $r(NC)$  bond lengths as well as for the  $\angle(NON')$  bond angle. This explains the large variation of the rotation angle. On the other hand, the axis switching, i.e., a rotation of 180°, is without consequence.

The satisfactory accuracy of the  $r_e^{SE}$  structure is due to the fact that the number of available isotopologues is large, that the harmful effect of isotopologues with large PAS rotation is balanced by isotopologues with a smaller PAS rotation, and that the IRLS method downweights the isotopologues with a large PAS rotation. On the other hand, if we try to calculate the Cartesian coordinates of the atoms using the special Kraitchman equations for a planar asymmetric top,<sup>14,59</sup> we get unsatisfactory results. For instance, for the coordinates of the C atom, using furazan- $d_2$  as parent species and furazan- $d_2$ -<sup>13</sup>C as an isotopologue, we get  $a(C) = 0.721$  Å and  $b(C) = 0.869$  Å, whereas the correct values (from the  $r_e^{BO}$  structure) are 0.709 and 0.879 Å, respectively.

We used the experimental ground-state rotational constants, without corrections, for calculating the empirical structures  $r_m^{(1)}$ ,  $r_m^{(1r)}$ ,  $r_m^{(2)}$ , and  $r_m^{(2r)}$ . The results form an example of what these purely empirical models can accomplish and where they must fail due to the fact that the isotopologue-independent rovibrational parameters can, in principle, only insufficiently reproduce the often significant changes of the true rovibrational contributions from one isotopologue to the other. Nonetheless, the increase of adjustable parameters from the  $r_m^{(1)}$  to the  $r_m^{(2)}$  model as well as the effort to apply the rovibrational contributions to an isotopologue only after it has been rotated to the position the parent has in its own PAS as described above, i.e., the progress from  $r_m^{(2)}$  to  $r_m^{(2r)}$

Table 3. Ab Initio Structures of Furan (Bond Lengths in Ångstroms, Angles in Degrees)

| method<br>basis set                 | MP2(FC)          |        | CCSD(T)(FC) |        | CCSD(T) AE | MP2(AE) |        | $r_e^{\text{BO}}(\text{I})^a$ | $r_e^{\text{BO}}(\text{II})^b$ |
|-------------------------------------|------------------|--------|-------------|--------|------------|---------|--------|-------------------------------|--------------------------------|
|                                     | VTZ <sup>c</sup> | wCVQZ  | VTZ         | VQZ    | wCVTZ      | wCVTZ   | wCVQZ  |                               |                                |
| $r(\text{C}-\text{O})$              | 1.3587           | 1.3557 | 1.3650      | 1.3619 | 1.3615     | 1.3551  | 1.3529 | 1.3591                        | 1.3593                         |
| $r(\text{C}-\text{H}_\alpha)$       | 1.0742           | 1.0735 | 1.0759      | 1.0753 | 1.0745     | 1.0728  | 1.0721 | 1.0739                        | 1.0738                         |
| $r(\text{C}=\text{C})$              | 1.3644           | 1.3613 | 1.3611      | 1.3583 | 1.3568     | 1.3597  | 1.3581 | 1.3551                        | 1.3552                         |
| $r(\text{C}-\text{C})$              | 1.4255           | 1.4228 | 1.4395      | 1.4371 | 1.4354     | 1.4212  | 1.4196 | 1.4339                        | 1.4338                         |
| $r(\text{C}-\text{H}_\beta)$        | 1.0753           | 1.0746 | 1.0770      | 1.0765 | 1.0757     | 1.0739  | 1.0731 | 1.0750                        | 1.0749                         |
| $\angle(\text{COC})$                | 106.72           | 106.85 | 106.42      | 106.57 | 106.41     | 106.71  | 106.86 | 106.58                        | 106.56                         |
| $\angle(\text{OCH}_\alpha)$         | 115.87           | 115.90 | 115.81      | 115.84 | 115.86     | 115.93  | 115.97 | 115.91                        | 115.90                         |
| $\angle(\text{OC}=\text{C})$        | 110.58           | 110.48 | 110.87      | 110.77 | 110.85     | 110.56  | 110.47 | 110.75                        | 110.76                         |
| $\angle(\text{C}=\text{CH}_\alpha)$ | 133.55           | 133.62 | 133.32      | 133.39 | 133.28     | 133.51  | 133.56 | 133.34                        | 133.34                         |
| $\angle(\text{C}=\text{CC})$        | 106.06           | 106.09 | 105.92      | 105.95 | 105.94     | 106.08  | 106.11 | 105.96                        | 105.96                         |
| $\angle(\text{C}=\text{CH}_\beta)$  | 126.12           | 126.10 | 126.40      | 126.38 | 126.40     | 126.13  | 126.11 | 126.39                        | 126.38                         |
| $\angle(\text{CCH}_\beta)$          | 127.82           | 127.81 | 127.68      | 127.67 | 127.66     | 127.79  | 127.79 | 127.65                        | 127.66                         |

<sup>a</sup> VQZ CCSD(T)(FC) + wCVQZ MP2(AE) – wCVQZ MP2(FC). <sup>b</sup> wCVTZ CCSD(T)(AE) + wCVQZ MP2(AE) – wCVTZ MP2(AE). <sup>c</sup> Structure used to calculate the force field.

(likewise from  $r_m^{(1)}$  to  $r_m^{(1r)}$ ), will generally reduce the standard deviation of the least-squares fit and the standard errors of the structural parameters determined and let them look more precise than they are, see Table S3 of the Supporting Information. For furazan, all angles of the  $r_m^{(2r)}$  structure are very near to the  $r_e^{\text{BO}}$  values (deviations are less than  $0.07^\circ$ ); also,  $r(\text{NO})$  is best reproduced by the  $r_m^{(2r)}$  model (with a difference of  $0.003 \text{ \AA}$ ). However, the remaining bond lengths  $r(\text{NC})$ ,  $r(\text{CC})$ , and  $r(\text{CH})$  of this  $r_m^{(2r)}$  model approximate the  $r_e^{\text{BO}}$  values less well than  $r_m^{(2)}$  does. Nevertheless, as can be seen in Table S3 of the Supporting Information, going from  $r_m^{(1)}$  to a more sophisticated model does not decrease the standard deviation without a large increase of the condition number. It follows that the  $r_m^{(1)}$  structure should be the most accurate. This is indeed confirmed by comparing it to the  $r_e^{\text{SE}}$  and  $r_e^{\text{BO}}$  equilibrium structures, see Table 2.

## 6. STRUCTURE OF FURAN

Furan,  $c\text{-C}_4\text{H}_4\text{O}$ , is a planar heterocyclic molecule of  $C_{2v}$  point-group symmetry. Its asymmetry parameter is  $\kappa = +0.916$ , and its structure is completely defined by only eight parameters. This molecule has been the subject of many investigations in the centimeter-wave range, mainly by the Copenhagen group,<sup>60,61</sup> who determined the ground-state rotational constants of eight isotopologues allowing them to determine a complete  $r_s$  structure. More recently, the rotational constants of a ninth isotopologue, furan-3,4- $d_2$ , were obtained by Fourier transform microwave spectroscopy.<sup>62</sup>

The hyperfine structure (spin–spin and spin–rotation interactions of the four protons of the molecule) has been resolved with a maser beam spectrometer.<sup>63</sup> This allowed derivation of approximate values for the distances between the hydrogen atoms.

To our knowledge, there is no high-level ab initio equilibrium structure available for this molecule. The BO equilibrium structure was computed in this work in two independent ways. The CCSD(T) level of electronic structure theory was used with the VTZ and VQZ basis sets in the frozen core approximation and with the wCVTZ basis set, all electrons being correlated with this last basis set. In the first case, the MP2 method with the wCVQZ basis set was used to estimate the core–core and core–valence correlation effects, see eq 16.<sup>34</sup> In the second case, the effect of

further basis set enlargement, wCVTZ  $\rightarrow$  wCVQZ, was determined at the MP2 level, see eq 17. It is worth noting that both methods give almost identical results, as indicated in Table 3. The effect of diffuse functions has been investigated at the AVQZ MP2-(FC) level of theory. Their effect is small, as in furazan, the most significant one being a lengthening of the C–O bond by  $0.001 \text{ \AA}$ .

The anharmonic force fields in normal coordinates of parent furan and its eight isotopologues have been computed at the VTZ MP2(FC) level. The theoretical vibration–rotation interaction constants deduced from the ab initio cubic force fields were combined with the known experimental ground-state rotational constants to yield the semiexperimental equilibrium rotational constants, which were further corrected for the small electronic contribution using experimental  $g$  constants.<sup>64,65</sup> The semiexperimental structure was determined using the IRLS method with Huber weighting. The system of normal equations is not well conditioned; the condition number is 503. The  $r_e^{\text{SE}}$  parameters are in excellent agreement with the  $r_e^{\text{BO}}$  parameters, see Table 4. However, it has to be noted that the  $r(\text{C}-\text{C})$  bond length is less precisely determined. This may be partly explained by the presence of a small coordinate:  $a(C_\alpha) = -0.3177(4) \text{ \AA}$ .

For the isotopologue furan-<sup>13</sup>C<sub>2</sub>, there is a rotation of  $39.8^\circ$  ( $r_e^{\text{BO}}$  structure) about the  $+c$  axis (calculated from the  $r_e^{\text{SE}}$  structure of Table 4), while the isotopologues <sup>13</sup>C<sub>3</sub> and  $d_3$  show rotations about the  $-c$  axis, the angles being  $20.09^\circ$  and  $30.94^\circ$ , respectively. For furan- $d_2$ , there is an  $(a, b)$ -axis switch plus a rotation in the  $(a, b)$  plane. Finally, for the isotopologues furan- $d_2d_5$  and perdeuterated furan there is a pure  $(a, b)$ -axis switch. Inspection of the residuals of the fit does not indicate any significant problem. Nevertheless, the residuals of the  $A$  and  $B$  rotational constants of the <sup>13</sup>C<sub>2</sub> isotopologue are about 1 order of magnitude larger than the other ones. Furthermore, the residual is  $+2.2 \text{ MHz}$  for  $A$ , whereas it is  $-2.0 \text{ MHz}$  for  $B$ . This indicates that the rovibrational correction is too large for  $A$  and too small for  $B$ . Eliminating these two data improves the fit slightly without affecting significantly the values of the parameters, and it decreases the uncertainty of the  $r(\text{C}-\text{C})$  bond length by a factor of 2.

For furan-<sup>13</sup>C<sub>2</sub>, using the semiexperimental equilibrium structure, the angle of rotation of the PAS upon isotopic substitution is  $\theta_e = 39.9^\circ$ , whereas with the VTZ MP2(FC) structure used to

Table 4. Structure of Furan (Bond Lengths in Ångstroms, Angles in Degrees)

|                                       | MP2(FC) VTZ | B3LYP 6-311G(3df,2pd) | $r_e^{\text{BO}}(\text{I})^a$ | $r_e^{\text{BO}}(\text{II})^b$ | $r_e^{\text{SE}}$ | $r_m^{(2r)}$ |
|---------------------------------------|-------------|-----------------------|-------------------------------|--------------------------------|-------------------|--------------|
| $r(\text{C}-\text{O})$                | 1.3587      | 1.3590                | 1.3591                        | 1.3593                         | 1.3594(7)         | 1.3603(6)    |
| $r(\text{C}-\text{H}_\alpha)$         | 1.0742      | 1.0746                | 1.0739                        | 1.0738                         | 1.0735(7)         | 1.0726(4)    |
| $r(\text{C}=\text{C})$                | 1.3644      | 1.3541                | 1.3551                        | 1.3552                         | 1.3552(8)         | 1.3579(9)    |
| $r(\text{C}-\text{C})^c$              | 1.4255      | 1.4315                | 1.4339                        | 1.4338                         | 1.432(2)          | 1.4303(2)    |
| $r(\text{C}-\text{H}_\beta)$          | 1.0753      | 1.0760                | 1.0750                        | 1.0749                         | 1.0753(6)         | 1.0744(4)    |
| $\angle(\text{COC})^c$                | 106.72      | 106.88                | 106.58                        | 106.56                         | 106.63(6)         | 106.57(4)    |
| $\angle(\text{OCH}_\alpha)$           | 115.87      | 115.99                | 115.91                        | 115.90                         | 115.88(6)         | 115.86(4)    |
| $\angle(\text{OC}=\text{C})$          | 110.58      | 110.44                | 110.75                        | 110.76                         | 110.66(9)         | 110.67(5)    |
| $\angle(\text{C}=\text{CH}_\alpha)^c$ | 133.55      | 133.57                | 133.34                        | 133.34                         | 133.46(9)         | 133.47(5)    |
| $\angle(\text{C}=\text{CC})^c$        | 106.06      | 106.12                | 105.96                        | 105.96                         | 106.03(7)         | 106.04(3)    |
| $\angle(\text{C}=\text{CH}_\beta)$    | 126.12      | 126.46                | 126.39                        | 126.38                         | 126.32(11)        | 126.30(6)    |
| $\angle(\text{CCH}_\beta)$            | 127.82      | 127.42                | 127.65                        | 127.66                         | 127.66(5)         | 127.66(3)    |

<sup>a</sup>VQZ CCSD(T)(FC) + wCVQZ MP2(AE) – wCVQZ MP2(FC). <sup>b</sup>wCVTZ CCSD(T)(AE) + wCVQZ MP2(AE) – wCVTZ MP2(AE).

<sup>c</sup>Dependent structural parameter.

calculate the cubic force field  $\theta_{\text{MP2}} = 21.2^\circ$ . As for furazan, such a large difference affects both  $\varepsilon_a$  and  $\varepsilon_b$  but not their sum, see eq 11. The origin of the discrepancy is mainly due to the inaccurate value of the C=C bond length at the VTZ MP2(FC) level of theory. As the difference between the equilibrium angle  $\theta_e$  and the VTZ MP2 angle  $\theta_{\text{MP2}}$  is particularly large, we use this chance to check whether the large residuals for the  $^{13}\text{C}_2$  isotopologue are only due to the geometrical effect of the rotation or whether the problem is more complex. It was possible to find a level of theory, 6-311G(3df,2pd) B3LYP, which gives a structure with a rotation angle in good agreement with  $\theta_e$ ,  $\theta_{\text{B3LYP}} = 40.9^\circ$ . The cubic force field was computed at this level of theory leading to a new semiexperimental structure. The derived structure is almost identical to that calculated with the VTZ MP2 force field, but residuals of the A and B rotational constants are almost as large, albeit with opposite signs:  $-1.81$  MHz for A and  $+1.56$  MHz for B. In summary, although the 6-311G(3df,2pd) B3LYP structure is closer to the equilibrium structure than the VTZ MP2(FC) structure (in particular, with respect to the PAS rotation upon isotopic substitution), the corresponding semiexperimental structure has not been improved. This shows that an accurate structure is not enough to calculate a force field which gives accurate rovibrational corrections.

To explain at least semiquantitatively this behavior we will assume that the error depends only on the rotation angle. If  $e_a^1$  and  $e_b^1$  are the errors on the moments of inertia  $I_a^1$  and  $I_b^1$  of the parent species and if  $e_a^2$  and  $e_b^2$  are the errors on the moments of inertia  $I_a^2$  and  $I_b^2$  of the substituted species, we have, following eq 4

$$e_{a,b}^2 = \frac{e_a^1 + e_b^1}{2} \pm \frac{e_a^1 - e_b^1}{2} \sqrt{1 + \tan^2 2\theta} \quad (20)$$

where  $\theta$  is the angle of rotation upon isotopic substitution. Knowing the value of this angle and the errors  $e_a^2$  and  $e_b^2$ , it is straightforward to calculate  $e_a^1$  and  $e_b^1$ . In the case of furan, for the  $^{13}\text{C}_2$  species we have  $r_a^2 = 2.21$  and  $r_b^2 = -2.02$  MHz, where  $r$  is the error on the corresponding rotational constants. Using  $\theta = 39.9^\circ$ , we get  $r_a^1 = 0.47$  MHz and  $r_b^1 = -0.28$  MHz, which are in satisfactory agreement with the experimental values. A slightly larger angle would give even better agreement.

As for furazan, section 5, the satisfactory accuracy of the  $r_e^{\text{SE}}$  structure is due to the fact that the number of available isotopologues is large, that the negative effect of isotopologues

with large PAS rotation is balanced by isotopologues with a smaller PAS rotation, and that the IRLS method downweights the isotopologues with large PAS rotation. On the other hand, if we calculate the coordinates of the  $\text{C}_2$  atom using the special Kraitchman equations for a planar asymmetric top,<sup>14,59</sup> we obtain  $a(\text{C}_2) = 0.329$  Å and  $b(\text{C}_2) = 1.087$  Å, whereas the correct values (from the  $r_e^{\text{BO}}$  structure) are 0.320 and 1.090 Å, respectively.

The empirical structures  $r_m^{(1)}$ ,  $r_m^{(1r)}$ ,  $r_m^{(2)}$ , and  $r_m^{(2r)}$  have been determined in the same way as for the previous molecules. The results are given in Table S4 of the Supporting Information. From the standard deviation of the fit and the condition number it appears that the  $r_m^{(2r)}$  structure should be the best one. It is indeed the closest one to the  $r_e^{\text{SE}}$  structure. Only the bond length  $r(\text{C}=\text{C})$  is slightly less accurate than with the  $r_m^{(2)}$  structure, but the difference is not substantial. This structure is given in Table 4.

## 7. STRUCTURE OF ETHYLENE OZONIDE

Ethylene ozonide, with an asymmetry parameter of  $\kappa = +0.918$ , is formed by ozonolysis of ethene according to a mechanistic scheme proposed by Criegee<sup>66</sup> and confirmed by analysis of the rotational spectra of its isotopologues. A substitution structure has been determined from the microwave spectra of many isotopologues. It was found that this five-membered ring has a  $\text{C}_2$  conformation and does not show any evidence of free or pseudorotation.<sup>66</sup> However, it was difficult to obtain a reliable structure because the  $r_s$  method assumes that the rovibrational corrections remain constant upon isotopic substitution, which is not true for this molecule, in particular because of several large rotations of the PAS upon isotopic substitution.

The  $r_e^{\text{BO}}$  structure was calculated at the all-electron wCVTZ CCSD(T) level of electronic structure theory, and the effect of basis set improvement (wCVTZ  $\rightarrow$  wCVQZ) was computed at the MP2 level, just like for furan. To check the adequacy of using the single-reference CCSD(T) technique to determine the  $r_e^{\text{BO}}$  structure, the  $T_1$  diagnostic<sup>67</sup> was calculated. Its value,  $T_1 = 0.013$ , is well below the cutoff value of 0.02, indicating the suitability of the single-reference CCSD(T) method for properly describing electron correlation effects. The structure was also determined at the MP2 level with the aug-cc-pVQZ basis set for the heavy atoms and the VQZ set for the hydrogen atoms. The results are reported in Table S6 of the Supporting Information. They are close to the VQZ MP2(FC) results, the two CO bond lengths being 0.0013 Å longer when the

Table 5. Structure of Ethylene Ozonide (Bond Lengths in Ångstroms, Angles in Degrees)

|                               | B3LYP 6-311+G(3df,2pd) | CCSD(T)(AE) wCVTZ | MP2(AE)  |          | $r_e^{\text{BO}^a}$ | $r_e^{\text{SE}}$ | $r_m^{(1r)}$ |
|-------------------------------|------------------------|-------------------|----------|----------|---------------------|-------------------|--------------|
|                               |                        |                   | wCVTZ    | wCVQZ    |                     |                   |              |
| $r(\text{C}-\text{O}_e)$      | 1.4174                 | 1.4144            | 1.4123   | 1.4106   | 1.4127              | 1.4135(3)         | 1.4137(9)    |
| $\angle(\text{COC})$          | 105.09                 | 104.234           | 103.934  | 104.122  | 104.42              | 104.51(3)         | 104.63(5)    |
| $r(\text{C}-\text{H}_a)$      | 1.0935                 | 1.0917            | 1.0891   | 1.0882   | 1.0908              | 1.0907(5)         | 1.0947(8)    |
| $\angle(\text{H}_a\text{CO})$ | 109.82                 | 109.859           | 109.827  | 109.811  | 109.84              | 109.88(5)         | 109.82(8)    |
| $\tau(\text{H}_a\text{COC})$  | 104.21                 | 103.322           | 103.217  | 103.138  | 103.24              | 102.90(6)         | 102.98(9)    |
| $r(\text{C}-\text{H}_e)$      | 1.0897                 | 1.0881            | 1.0855   | 1.0847   | 1.0872              | 1.0859(5)         | 1.090(1)     |
| $\angle(\text{H}_e\text{CO})$ | 110.94                 | 110.866           | 110.844  | 110.865  | 110.89              | 110.90(4)         | 110.71(6)    |
| $\tau(\text{H}_e\text{COC})$  | -131.21                | -132.101          | -132.054 | -131.939 | -131.99             | -131.94(5)        | 131.5(1)     |
| $r(\text{C}-\text{O}_p)$      | 1.4110                 | 1.4083            | 1.4053   | 1.4039   | 1.4069              | 1.4080(3)         | 1.4083(9)    |
| $\angle(\text{OCO})$          | 105.47                 | 105.781           | 105.875  | 105.710  | 105.62              | 105.53(2)         | 105.63(5)    |
| $\tau(\text{O}_p\text{COC})$  | -15.70                 | -16.478           | -16.614  | -16.536  | -16.40              | -16.454(7)        | 16.25(6)     |
| $r(\text{O}_p-\text{O}_p)$    | 1.4555                 | 1.4601            | 1.4555   | 1.4520   | 1.4566              | 1.4577(3)         | 1.4591(9)    |

<sup>a</sup> CCSD(T)/wCVTZ(AE) + MP2/wCVQZ(AE) - MP2/wCVTZ(AE).

Table 6. Structure of 1,3,4-Oxadiazole (Bond Lengths in Ångstroms, Angles in Degrees)

| method             | B3LYP 6-311 |        |        |                |        |                                       |   |                      |                  |                  |
|--------------------|-------------|--------|--------|----------------|--------|---------------------------------------|---|----------------------|------------------|------------------|
|                    | basis       | $r_0$  | $r_s$  | MP2(FC)<br>VTZ | +      | $r_e^{\text{SE}}$<br>MP2 <sup>a</sup> | $r_e^{\text{SE}}$<br>B3LYP <sup>b</sup> | CCSD(T)(AE)<br>wCVTZ | MP2(AE)<br>wCVTZ | MP2(AE)<br>wCVQZ |
| $r(\text{CO})$     | 1.359(21)   | 1.3479 | 1.3544 | 1.3559         | 1.2560 | 1.4830                                | 1.3566                                  | 1.3509               | 1.3483           | 1.3540           |
| $r(\text{CN})$     | 1.290(15)   | 1.2973 | 1.2967 | 1.2831         | 1.3504 | 1.2103                                | 1.2869                                  | 1.2923               | 1.2908           | 1.2854           |
| $r(\text{CH})$     | 1.074(6)    | 1.0755 | 1.0739 | 1.0752         | 1.0691 | 1.0655                                | 1.0744                                  | 1.0725               | 1.0718           | 1.0737           |
| $r(\text{NN})$     | 1.416(23)   | 1.3987 | 1.3980 | 1.4013         | 1.3799 | 1.4812                                | 1.4108                                  | 1.3942               | 1.3898           | 1.4064           |
| $\angle\text{COC}$ | 101.5(15)   | 102.06 | 101.38 | 101.76         | 110.13 | 93.38                                 | 101.17                                  | 101.420              | 101.607          | 101.36           |
| $\angle\text{OCN}$ | 113.81(77)  | 113.38 | 113.70 | 113.24         | 110.37 | 117.07                                | 113.97                                  | 113.650              | 113.463          | 113.78           |
| $\angle\text{CNN}$ | 105.47(96)  | 105.59 | 105.61 | 105.89         | 104.57 | 106.24                                | 105.45                                  | 105.640              | 105.733          | 105.54           |
| $\angle\text{OCH}$ | 118.1(38)   | 118.13 | 118.02 | 118.17         | 125.27 | 117.86                                | 117.97                                  | 118.087              | 118.197          | 118.08           |
| $\angle\text{NCH}$ | 128.1(39)   | 128.49 | 128.28 | 128.59         | 124.36 | 125.07                                | 128.06                                  | 128.263              | 128.340          | 128.14           |

<sup>a</sup> Rovibrational correction from the VTZ MP2(FC) anharmonic force field. <sup>b</sup> Rovibrational correction from the 6-311+G(3df,2pd) B3LYP anharmonic force field. <sup>c</sup> CCSD(T)/wCVTZ(AE) + MP2/wCVQZ(AE) - MP2/wCVTZ(AE).

diffuse functions are taken into account. However, it is known that this small lengthening decreases when the correction VQZ → VSZ is added. The final structure is given in Table 5.

The anharmonic force fields in normal coordinates of the 20 isotopologues of ethylene ozonide for which measurements are available have been computed at the 6-311+G(3df,2pd) B3LYP level. The theoretical vibration–rotation interaction constants deduced from the ab initio cubic force field were combined with the known experimental ground-state rotational constants to yield the semiexperimental equilibrium rotational constants. The semiexperimental structure was determined using the IRLS method with Huber weighting. The system of normal equations is moderately well conditioned with a condition number of 340. The  $r_e^{\text{SE}}$  parameters are all rather accurate and in excellent agreement with the  $r_e^{\text{BO}}$  parameters, see Table 5. However, the residuals of the A and B rotational constants of the  $\text{H}_2\text{C}^{18}\text{OOCH}_2\text{O}$  isotopologue are about 1 order of magnitude larger than those of the other isotopologues; they are -1.3 MHz for A and +1.3 MHz for B. This is again due to the very large rotation of the PAS upon isotopic substitution,  $\theta_e = 42.4^\circ$ , whereas the 6-311+G(3df,2pd) B3LYP value is  $\theta = 37.9^\circ$ .

As for furazan and furan, the satisfactory accuracy of the  $r_e^{\text{SE}}$  structure is due to the fact that the number of available isotopologues is large, that the negative effect of isotopologues

with large PAS rotation is balanced by isotopologues with a smaller PAS rotation, and that the IRLS method downweights the isotopologues with large PAS rotation. On the other hand, if we calculate the  $r(\text{O}_p-\text{O}_p)$  bond length using the Kraitchman equations,<sup>14,59</sup> its range is still quite large, 0.043 Å, i.e., the same order of magnitude as for the empirical substitution structure.<sup>21</sup>

The empirical structures  $r_m^{(1)}$ ,  $r_m^{(1r)}$ ,  $r_m^{(2)}$ , and  $r_m^{(2r)}$  have been determined the same way as for the previous molecules. The results are given in Table S5 of the Supporting Information. Going from  $r_m^{(1)}$  to a more sophisticated model does not significantly decrease the standard deviation, and the condition number does not increase much, except for the  $r_m^{(2r)}$  model. Furthermore, it has to be noted that all models give similar structural parameters. Both structures,  $r_m^{(1)}$  as well as  $r_m^{(1r)}$ , are of similar quality, the  $r_m^{(1r)}$  one being perhaps slightly more accurate. It is this structure which is reported in Table 5.

## 8. STRUCTURE OF 1,3,4-OXADIAZOLE

From the results for the molecules presented above (sections 4–7) one may get the impression that it is not a problem to determine an accurate  $r_e^{\text{SE}}$  structure even when there is a large rotation of the PAS upon certain isotopic substitutions. The truth

**Table 7. Rovibrational Corrections (in MHz) for the Parent Species of 1,3,4-Oxadiazole**

|                        | $A_e - A_0$ | $B_e - B_0$ | $C_e - C_0$ |
|------------------------|-------------|-------------|-------------|
| VTZ MP2(FC)            | 94.10       | 78.58       | 46.87       |
| VQZ MP2(FC)            | 94.24       | 78.62       | 46.95       |
| 6-311+G(3df,2pd) B3LYP | 93.02       | 72.49       | 45.24       |

is that the four cases dealt with above are rather favorable ones. The satisfactory results are due to the fact that there is a large number of isotopologues for which accurate rotational constants are available and that, even more importantly, the information furnished by the isotopologues with a large PAS rotation is also obtained from isotopologues for which the PAS rotation is small.

In this section we are discussing a typical example where it is possible to determine a reasonable empirical effective structure but for which the derived semiexperimental structure becomes extremely inaccurate. 1,3,4-Oxadiazole,  $c$ -C<sub>2</sub>H<sub>2</sub>N<sub>2</sub>O, is an isomer of furazan, see Figure 1e. It is also a planar, oblate molecule ( $\kappa = +0.952$ ) of C<sub>2v</sub> point-group symmetry. Its microwave spectrum has been studied by Nygaard et al.;<sup>68</sup> they could determine a substitution structure using the special Kraitchman equations for a planar asymmetric top.<sup>14,59</sup> The accuracy of this structure was estimated to be 0.005 Å. Contrary to furazan, the number of available isotopologues is small, four instead of eight, and they are used to determine six independent structural parameters. To check this structure, the empirical effective  $r_0$  structure was calculated from the experimental ground-state rotational constants. The results are presented in Table 6. The condition number of the least-squares refinement is rather high,  $\kappa = 756$ , and the derived parameters are not accurate. Still, there is satisfactory agreement with the  $r_s$  structure for the parameters which are not highly correlated,  $r(\text{CH})$  and  $\angle(\text{HCO})$ . Furthermore, the agreement is good for all bond angles.

The  $r_e^{\text{BO}}$  structure of 1,3,4-oxadiazole was computed at the CCSD(T) level of theory with the wCVTZ basis set. The small effect of basis set enlargement, from triple- $\zeta$  to quadruple- $\zeta$ , was

estimated at the MP2 level, see eq 17. This structure is also given in Table 6, and it is seen that the BO bond angles are in good agreement with the corresponding empirical values, either  $r_0$  or  $r_s$ .

For the parent species, the anharmonic force field has been determined at three levels of electronic structure theory: VTZ MP2(FC), VQZ MP2(FC), and 6-311+G(3df,2pd) B3LYP. The derived rovibrational corrections are similar for the three levels, indicating that the anharmonic force field is likely to be reliable, see Table 7. For the isotopologues, the anharmonic force field was calculated at two levels of theory: VTZ MP2(FC) and 6-311+G(3df,2pd) B3LYP. The theoretical vibration-rotation constants deduced from the ab initio cubic force field were combined with the known experimental ground-state rotational constants to yield the semiexperimental rotational constants which were corrected for the small electronic contribution using  $g$  constants computed at the aug-cc-pVTZ B3LYP level. The derived semiexperimental equilibrium rotational constants are given in Table 8 for both levels of theory. For both levels, the semiexperimental equilibrium inertial defect is much smaller than the ground state inertial defect,  $\Delta_0 = 0.066$  in u Å<sup>2</sup>, indicating that most of the rovibrational contribution is correctly taken into account, see Table 8. The two corresponding  $r_e^{\text{SE}}$  structures were determined using the special Kraitchman equations for a planar asymmetric top;<sup>14,59</sup> they are given in Table 6, while the Cartesian coordinates are given in Table 9. The two semiexperimental structures are obviously not compatible. Furthermore, they are extremely far from the BO structure. In conclusion, these two  $r_e^{\text{SE}}$  structures are extremely inaccurate.

The most significant difference between the  $r_s$  and the  $r_e^{\text{SE}}$  structures is an attempt in the latter case to correct for the rovibrational contributions. Although these contributions are calculated with an accuracy better than 10%, as shown in Table 7, the effect of the small errors is hugely amplified by the large PAS rotations: 24.7° for the <sup>15</sup>N isotopologue, 122.3° for the <sup>13</sup>C isotopologue, and 112.1° for the D isotopologue. To estimate the errors, it is possible to compare the semiexperimental rotational

**Table 8. Rotational Constants (MHz) and Inertial Defects  $\Delta$  (u Å<sup>2</sup>) for the Isotopologues of 1,3,4-Oxadiazole**

|                 |          | $B_0^a$    | $r_e^{\text{BO}b}$ | $B_e^{\text{SE}}[\text{MP2}]^c$ | $r_e^{\text{BO}} - B_e^{\text{SE}}[\text{MP2}]$ | $B_e^{\text{SE}}[\text{B3LYP}]^d$ | $r_e^{\text{BO}} - B_e^{\text{SE}}[\text{B3LYP}]$ |
|-----------------|----------|------------|--------------------|---------------------------------|---|-----------------------------------|---|
| N               | A        | 10 315.038 | 10 407.10          | 10 409.82                       | -2.72   | 10 408.73                         | -1.64   |
|                 | B        | 10 189.78  | 10 254.67          | 10 269.27                       | -14.59  | 10 263.18                         | -8.51   |
|                 | C        | 5122.607   | 5165.16            | 5169.40                         | -4.23   | 5167.76                           | -2.60   |
|                 | $\Delta$ | 0.0656     | 0                  | 0.0026                          |   | -0.0008                           |   |
| <sup>15</sup> N | A        | 10 281.679 | 10 367.95          | 10 374.29                       | -6.34   | 10 369.13                         | -1.18   |
|                 | B        | 9945.292   | 10 012.57          | 10 023.69                       | -11.12  | 10 021.58                         | -9.00   |
|                 | C        | 5052.02    | 5093.58            | 5097.90                         | -4.32   | 5096.23                           | -2.65   |
|                 | $\Delta$ | 0.0658     | 0                  | 0.0018                          |   | -0.0006                           |   |
| <sup>13</sup> C | A        | 10 206.119 | 10 276.96          | 10 295.69                       | -18.74  | 10 280.76                         | -3.80   |
|                 | B        | 10 058.143 | 10 141.04          | 10 139.39                       | 1.66  | 10 147.32                         | -6.27   |
|                 | C        | 5062.451   | 5104.27            | 5108.40                         | -4.13   | 5106.83                           | -2.56   |
|                 | $\Delta$ | 0.0659     | 0                  | 0.0014                          |   | -0.0006                           |   |
| D               | A        | 10 205.015 | 10 273.07          | 10 286.51                       | -13.44  | 10 280.23                         | -7.16   |
|                 | B        | 9411.969   | 9489.11            | 9492.19                         | -3.08   | 9492.02                           | -2.91   |
|                 | C        | 4893.188   | 4932.77            | 4936.64                         | -3.87   | 4935.25                           | -2.48   |
|                 | $\Delta$ | 0.0642     | 0                  | 0.0013                          |   | -0.0008                           |   |

<sup>a</sup> Experimental ground-state rotational constants from ref 68. <sup>b</sup> Equilibrium rotational constants calculated from the  $r_e^{\text{BO}}$  structure, last column of Table 6. <sup>c</sup> Semiexperimental equilibrium rotational constants calculated with the rovibrational correction from the MP2/VTZ(fc) anharmonic force field. <sup>d</sup> Semiexperimental equilibrium rotational constants calculated with the rovibrational correction from the B3LYP/6-311+G(3df,2pd) anharmonic force field.

**Table 9. Cartesian Coordinates of Atoms in 1,3,4-Oxadiazole (Angstroms)**

| atom | coord | $r_e^{\text{BO}}$ | $r_s$        | $r_e^{\text{SE}}[\text{MP2}]^b$ | $r_e^{\text{SE}}[\text{B3LYP}]^c$ |
|------|-------|-------------------|--------------|---------------------------------|-----------------------------------|
| O    | $a^a$ | -1.1455           | -1.1418      | -1.0673                         | -1.2397                           |
|      | $b$   | 0.0000            | 0.0000       | 0.0000                          | 0.0000                            |
| C    | $a$   | -0.2875           | -0.2941      | -0.3481                         | -0.2225                           |
|      | $b$   | $\pm 1.0475$      | $\pm 1.0480$ | $\pm 1.0296$                    | $\pm 1.0791$                      |
| H    | $a$   | -0.7001           | -0.7127      | -0.7101                         | -0.5665                           |
|      | $b$   | $\pm 2.0388$      | $\pm 2.0387$ | $\pm 2.0356$                    | $\pm 2.0876$                      |
| N    | $a$   | 0.9509            | 0.9555       | 0.9590                          | 0.9395                            |
|      | $b$   | $\pm 0.7032$      | $\pm 0.6993$ | $\pm 0.6899$                    | $\pm 0.7406$                      |

<sup>a</sup> From the center of mass condition,  $\sum m_i a_i = 0$ . <sup>b</sup> Rovibrational correction from the VTZ MP2(fc) anharmonic force field. <sup>c</sup> Rovibrational correction from the 6-311+G(3df,2pd) B3LYP anharmonic force field.

constants with the values calculated with the  $r_e^{\text{BO}}$  structure. Although the accuracy of the latter computed constants is limited to a few MHz,<sup>7,19</sup> this comparison is informative. If, for a given rotational constant, the errors were the same for all isotopologues they would not affect the structure which is derived from the differences of the moments of inertia. However, as can be seen in Table 8, the errors vary hugely from one isotopologue to the other, the variation being the largest for the largest rotations of the PAS. As for furan, it is possible to roughly estimate the errors for the isotopologues using eq 20 and, as input, the errors of the parent species and the rotation angle of the PAS. For instance, for the <sup>13</sup>C isotopologue, where the rotation is the largest, it gives  $e_a \approx -22.4$  MHz and  $e_b \approx +5.2$  MHz, to be compared with the experimental values  $e_a = -18.7$  MHz and  $e_b = +1.7$  MHz. This confirms that the origin of the problem determining the  $r_e^{\text{SE}}$  structure of 1,3,4-oxadiazole based on the available rotational constants information is the large rotation of the PAS for several isotopologues.

## 9. SUMMARY AND CONCLUSIONS

It is shown in this study that a large rotation of the PAS upon isotopic substitution and relative to the parent species may affect significantly the accuracy of semiexperimental equilibrium structures. Our analysis indicates that this is mainly due to inaccuracies in the reference structure used to compute the anharmonic force field, as it may fail to predict the correct value of the angle of rotation due to isotopic substitution. Numerical tests show that when the system of normal equations is well conditioned and the number of isotopologues for which accurate rotational constants are available is large (and the substitutions are sufficiently diverse), the failure to predict an accurate rotation angle affects only slightly the resulting  $r_e^{\text{SE}}$  structure. The best, though often inaccessible, way to avoid these difficulties is to use isotopologues which keep the symmetry of the parent species. For oxirane, furazan, furan, and ethylene ozonide it was possible to obtain an accurate  $r_e^{\text{SE}}$  structure because the structure could be determined using many isotopologues without large PAS rotation. It has to be noted that the IRLS methods permit one to downweight the influence of isotopologues with a large PAS rotation. The drawback of this method is that it requires rotational constants for many isotopologues. For instance, in the case of 1,3,4-oxadiazole, section 9, the number of available isotopologues is extremely limited and, furthermore, they are all subject to a large rotation of the PAS, leading to a considerable amplification of the errors, as

discussed in section 2. One may wonder whether improving the accuracy of the computed force field, for instance, using the more costly CCSD(T) method, would improve the situation. Unfortunately, in most cases, use of the CCSD(T) method instead of the MP2 one only leads to a slight improvement of the accuracy,<sup>19</sup> which is clearly not sufficient to render harmless the amplification of errors. The accuracy of the  $r_e^{\text{SE}}$  structures was checked by computing  $r_e^{\text{BO}}$  structures at the CCSD(T) level with extended Gaussian basis sets. The empirical  $r_m$  structures were also calculated, and for all molecules it was possible to find an accurate  $r_m$  structure.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Experimental rotational constants (MHz), residuals of the semiexperimental fit (MHz), and angle of rotation of the principal axis system upon isotopic substitution (degrees); mass-dependent structures of oxirane (ethylene epoxide), unity-weighted fits (bond lengths in Angstroms, angles in degrees); mass-dependent structures of furazan, unity-weighted fits (bond lengths in Angstroms, angles in degrees); mass-dependent structures of furan, unity-weighted fits (bond lengths in Angstroms, angles in degrees); mass-dependent structures of ethylene ozonide, unity-weighted fits (bond lengths in Angstroms, angles in degrees); computed structures of ethylene ozonide (bond lengths in Angstroms, angles in degrees). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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