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# Accurate Semiexperimental Structure of 1,3,4-Oxadiazole by the Mixed Estimation Method

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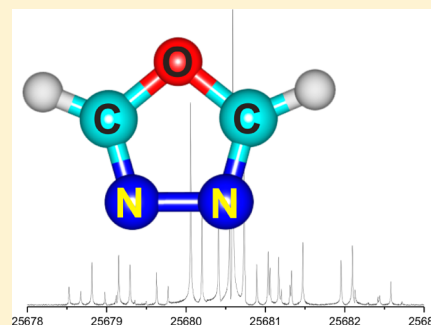
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## S Supporting Information

**ABSTRACT:** In order to determine an accurate equilibrium structure for 1,3,4-oxadiazole, microwave transitions and ground-state rotational constants are reported for the parent species and for the <sup>18</sup>O isotopologue measured in natural abundance. These rotational constants along with those of the <sup>13</sup>C, <sup>15</sup>N, and D<sub>1</sub> species were used together with vibration–rotation constants calculated from a cubic force field calculated at the B3LYP/6-311+G(3df,2pd) level of theory to derive a semiexperimental equilibrium structure. However, the results of this fit were not satisfactory; therefore, the structure was later significantly improved by the mixed estimation method. In this method, internal coordinates from good-quality quantum chemical calculations (with appropriate uncertainties) are fitted simultaneously with moments of inertia of the full set of isotopologues. The accuracy of this structure has been confirmed by using an extrapolation technique. All elements of the <sup>14</sup>N nuclear quadrupole coupling tensor have been determined.



## 1. INTRODUCTION

1,3,4-Oxadiazole (C<sub>2</sub>H<sub>2</sub>N<sub>2</sub>O, Figure 1) is a five-membered heterocyclic molecule known since around 1930<sup>1</sup> and that appears as a building block in a variety of pharmaceutical drugs like the HIV-integrase inhibitor raltegravir used to treat acquired immunodeficiency syndrome (AIDS), antibacterial furazolidone, or antihypertensive nesapidil.<sup>2</sup> The substitution of two =CH– groups in furan by two nitrogens reduces the ring

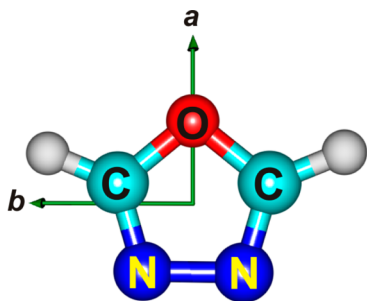


Figure 1. 1,3,4-Oxadiazole showing the principal inertial axes.

aromaticity; therefore, oxadiazole interestingly shows some character of a conjugated diene. The microwave spectrum of oxadiazole was first measured in 1966 at the University of Copenhagen<sup>3</sup> using Stark modulation spectroscopy. The rotational constants of the parent species and three isotopologues (<sup>13</sup>C, <sup>15</sup>N, and D) were later determined by Nygaard et al., and an approximate substitution (*r<sub>s</sub>*) structure was derived.<sup>4</sup> However, 1,3,4-oxadiazole contains two equivalent <sup>14</sup>N quadrupolar nuclei, which give rise to a very complex hyperfine structure that was only partially resolved with the available static gas frequency scanning techniques. Moreover, Stark modulation spectroscopy was not sensitive enough to detect the <sup>18</sup>O isotopologue in natural abundance. Recently, the high-resolution infrared spectrum was analyzed.<sup>5</sup>

A recent attempt to determine a semiexperimental equilibrium structure,<sup>6</sup> where the equilibrium rotational constants are derived from the experimental effective ground-state rotational constants and rovibrational corrections (based

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principally on an ab initio cubic force field) failed for two reasons; (i) the rotational constants of the  $^{18}\text{O}$  isotopologue were not available and (ii) the isotopic substitutions  $^{12}\text{C} \rightarrow ^{13}\text{C}$ ,  $^{14}\text{N} \rightarrow ^{15}\text{N}$ , and  $\text{H} \rightarrow \text{D}$  induced a very large rotation of the principal axis system (PAS), a behavior typical of oblate molecules (asymmetry parameter,  $\kappa = +0.952$ ). In those cases, the rovibrational corrections change significantly upon isotopic substitution, causing large errors in the structure because of ill-conditioned normal equations, as occurs for 1,3,4-oxadiazole. However, an accurate ab initio equilibrium structure ( $r_e^{\text{BO}}$ ) was computed at the CCSD(T) level of the coupled cluster (CC) techniques using a basis set of quadruple- $\zeta$  quality.<sup>6</sup>

The much higher resolution of modern rotational spectroscopy in supersonic jets<sup>7</sup> and the progress in computational chemistry permit successful determination also of the semi-experimental structure of ring molecules. For this reason, we decided to revisit the spectrum of the title compound. The goals of this paper are three-fold, (i) to measure the rotational spectrum of the parent species under sub-Doppler resolution and to determine accurate molecular parameters including the two nitrogen quadrupole coupling hyperfine tensors, (ii) to determine the previously unavailable rotational constants of the  $^{18}\text{O}$  isotopologue, and (iii) to derive a semiexperimental structure and to compare different approaches permitting improvement of the accuracy of this method.

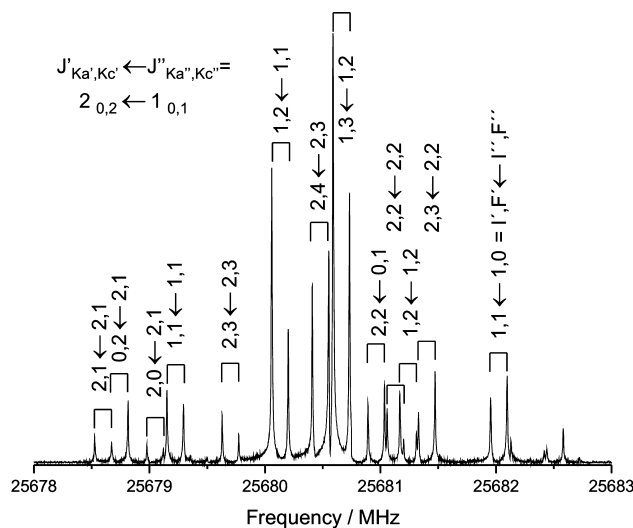
## 2. EXPERIMENTAL DETAILS

1,3,4-Oxadiazole was synthesized as previously reported by Ainsworth.<sup>8</sup>  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  8.53.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  153.2 ( $^1J_{\text{CH}} = 234.0$  Hz,  $^2J_{\text{CH}} = 5.9$  Hz).

The rotational spectrum was measured with two supersonic jet Balle-Flygare-type<sup>7,9</sup> Fourier transform microwave spectrometers in Hannover (2–26 GHz) and Bilbao (4–18 GHz). Both instruments have been described extensively;<sup>10,11</sup> therefore, only brief experimental details are given here. The liquid sample was inserted inside of a reservoir located at the nozzle exit and mildly heated below 50 °C. Neon at 2–4 bar was used as the carrier gas, creating a supersonic jet that was expanded along the axis of the evacuated Fabry–Perot resonators. Typically, microwave pulses of 1  $\mu\text{s}$  length were used to polarize the sample. The resulting free-induction decay (FID) was digitized in the time domain and Fourier transformed to the frequency domain, where the molecular signal was represented as its amplitude spectrum. The resonance frequencies appear as a Doppler doublet because of the coaxial orientation of the jet and the resonator axes. The accuracy of the frequency measurements is better than 3 kHz. The spectrum of  $^{18}\text{O}$ -oxadiazole was detected in natural abundance (0.2%).

While the focus of the present work was the spectrum of the  $^{18}\text{O}$  species of 1,3,4-oxadiazole, measurements of the rotational spectrum of the parent species were first accomplished to accurately determine the nuclear quadrupole coupling parameters of the two  $^{14}\text{N}$  nuclei (spin  $I = 1$ ) in the molecule. Oxadiazole is an oblate asymmetric rotor of  $C_{2v}$  symmetry; therefore, the observable transitions were limited to  $\mu_a$  selection rules. The measurements in Hannover and Bilbao (4–26 GHz) started from the previous assignment<sup>3,4</sup> and compose a set of seven  $^3\text{Q}$ -branch ( $J \leftarrow J$ ) and two  $^3\text{R}$ -branch ( $J + 1 \leftarrow J$ ) transitions, with low angular momentum quantum numbers in the range of  $J'' = 0$ –4. All transitions are split in complicated hyperfine patterns, initially analyzed with the aid of the previous

assignment and the ab initio calculations. The hyperfine patterns typically span a few MHz and include 10–20 intense components, as exemplified in Figure 2. A total of 112



**Figure 2.** The  $2_{0,2} \leftarrow 1_{0,1}$  rotational transition of 1,3,4-oxadiazole, illustrating the nuclear quadrupole coupling hyperfine splittings in this molecule.

hyperfine components and 115 previous rotational transitions<sup>3,4</sup> were analyzed using a Watson's  $S$ -reduced semirigid rotor Hamiltonian in the  $\text{III}^l$  representation.<sup>12</sup> This choice is justified by the very small value of the reduction parameter,  $s_{111}(\text{III-S}) = 4.9 \times 10^{-9}$  compared to  $s_{111}(\text{I-S}) = 1.6 \times 10^{-7}$ ,  $s_{111}(\text{I-A}) = 1.3 \times 10^{-7}$ , and  $s_{111}(\text{III-A}) = 2.3 \times 10^{-6}$ . This parameter, which should be as small as possible, indicates the rate of convergence of the Hamiltonian, and its definition is given in ref 12. To this Hamiltonian, the nuclear quadrupole part was added by using irreducible tensor methods and the  $I = I_{N(1)} + I_{N(2)}$ ,  $F = I + J$  coupling scheme of nuclear and rotational angular momenta.<sup>13</sup> According to the symmetry of the molecule, the quadrupole parameters of the two  $^{14}\text{N}$  nuclei were constrained to identical values except for the nondiagonal element  $\chi_{ab}$ , which differs in sign because the two nuclei are connected by an antisymmetric rotation in  $C_{2v}$ . All other off-diagonal elements of the quadrupole tensor are zero because the two  $^{14}\text{N}$  nuclei are contained in the  $ab$  inertial plane. The fit proceeded by direct diagonalization using Pickett's CALPGM suite of programs. The determined spectroscopic parameters in Table 1 thus include the rotational and quartic centrifugal distortion constants, all diagonal elements  $\chi_{aa}$  ( $\alpha = a, b, c$ ), and  $\chi_{ab}$ . Table 1 additionally offers the nuclear quadrupole coupling elements in their internal principal axes ( $\chi_{xx}, \chi_{yy}, \chi_{zz}$ ), obtained by tensor diagonalization. Because of the symmetry of the molecule, the transformation between the inertial and principal axes is equivalent to a rotation around the  $c$  inertial axis; therefore, it gives the orientation of the main axis of the electric field gradient ( $\alpha_{za} = 20.1(7)^\circ$ ). A meaningful comparison of the nuclear quadrupole coupling tensor is difficult because there are not many similar molecules for which the whole tensor has been determined.<sup>14</sup> However, we observed parallelisms with the cases of pyrimidine<sup>15</sup> and pyridazine.<sup>16</sup> In pyrimidine, with the nitrogen atom attached to two carbon atoms, the main axis of the electric field gradient is on the bisector of the CNC angle. Conversely, in oxadiazole and in pyridazine, where a nitrogen

Table 1. Experimental Spectroscopic Constants for the Ground States of 1,3,4-Oxadiazole and Its  $^{18}\text{O}$  Isotopologue

| constant                       | unit  | parent                     |                 |                       | $^{18}\text{O}^c$ |
|--------------------------------|-------|----------------------------|-----------------|-----------------------|-------------------|
|                                |       | previous work <sup>a</sup> | this work       | computed <sup>b</sup> |                   |
| $A$                            | (MHz) | 10315.038(15)              | 10315.0457(13)  |                       | 10315.8333(22)    |
| $B$                            | (MHz) | 10189.780(11)              | 10189.7875(10)  |                       | 9687.59929(46)    |
| $C$                            | (MHz) | 5122.607(11)               | 5122.62434(163) |                       | 4992.64086(37)    |
| $D_J$                          | (kHz) |                            | 4.05(14)        | 4.255                 |                   |
| $D_{JK}$                       | (kHz) |                            | −6.723(58)      | −6.599                |                   |
| $D_K$                          | (kHz) |                            | 3.02(18)        | 2.822                 |                   |
| $d_1$                          | (kHz) |                            | 0.0978(27)      | 0.0905                |                   |
| $d_2$                          | (kHz) |                            | 0.0307(28)      | 0.0299                |                   |
| $(3/2)\chi_{cc}$               | (MHz) | 2.67(3)                    | 2.6101(13)      | 3.378                 |                   |
| $(1/4)(\chi_{bb} - \chi_{aa})$ | (MHz) | 1.455(5)                   | 1.44419(41)     | 1.513                 |                   |
| $\chi_{ab}$                    | (MHz) | −2.65(5)                   | −2.43(12)       | −2.89                 |                   |
| $\chi_{aa}^d$                  | (MHz) | −3.80(1)                   | −3.7584(13)     | −4.0199               |                   |
| $\chi_{bb}^d$                  | (MHz) | 2.02(2)                    | 2.01835(93)     | 2.0329                |                   |
| $\chi_{cc}^d$                  | (MHz) | 1.78(2)                    | 1.74007(87)     | 1.9870                |                   |
| $\chi_{xx}$                    | (MHz) |                            | −4.649(83)      | −5.310                |                   |
| $\chi_{yy}$                    | (MHz) |                            | 2.909(83)       | 3.058                 |                   |
| $\chi_{zz}$                    | (MHz) |                            | 1.74007(89)     | 2.252                 |                   |
| $\alpha_{za}$                  | (deg) |                            | 20.08(74)       |                       |                   |
| $\alpha_{zb}$                  | (deg) |                            | 110.08(74)      |                       |                   |
| $N^e$                          |       |                            | 220             |                       | 41                |

<sup>a</sup>Reference 4 <sup>b</sup>B3LYP/6-311+G(3df,2pd). <sup>c</sup>Centrifugal distortion and nuclear quadrupole coupling tensor for  $^{18}\text{O}$  fixed at the value of the parent species. <sup>d</sup>Derived parameter. <sup>e</sup>Number of measured transitions.

atom is bonded to a carbon and a nitrogen atom, the electric field gradient is not coincident with the NNC bisector ( $\sim 52.8^\circ$ ), instead approaching the NN bond. Differences in magnitude for the available nuclear quadrupole coupling constants should be attributed to the different electronic environment around the nitrogen atoms. For the  $^{18}\text{O}$  isotopologue, a total of 41 hyperfine components from three  $^a\text{R}$ - and two  $^a\text{Q}$ -branch transitions of were analyzed similarly as those for the parent species, but only the three rotational constants were fitted, all other parameters being fixed at the values of the parent species (results also in Table 1). The experimental frequencies of both species are listed in Table S1 of the Supporting Information.

### 3. DETERMINATION OF THE SEMIEXPERIMENTAL EQUILIBRIUM CONSTANTS, $B_e^{\text{SE}}$

To obtain the semiexperimental equilibrium rotational constants, the experimental ground-state rotational constants are corrected using the vibration–rotation interaction constants ( $\alpha$ -constants).<sup>17</sup> These  $\alpha$ -constants can be estimated by second-order perturbation theory from the cubic force field.<sup>18</sup> The force field up to semidiagonal quartic terms and the  $\alpha$ -constants were directly calculated using Gaussian 03 (g03).<sup>19</sup> This calculation was already made using two different levels of theory,<sup>6</sup> second-order Møller–Plesset perturbation theory (MP2)<sup>20</sup> and Kohn–Sham density functional theory (DFT)<sup>21</sup> using Becke’s three-parameter hybrid exchange functional<sup>22</sup> and the Lee–Yang–Parr correlation functional (B3LYP).<sup>23</sup> In both cases, the correlation-consistent polarized triple- $\zeta$  basis sets cc-pVTZ<sup>24</sup> was employed. Comparison of the computed molecular parameters with their experimental counterparts shows that the B3LYP/cc-pVTZ force field is more accurate for the prediction of the vibrational band centers, the infrared intensities, and the  $\alpha$ -constants.<sup>25</sup> Furthermore, it was found that using the larger cc-pVQZ basis set does not significantly improve the quality of the MP2 force field.<sup>6</sup> This was confirmed

by comparing the inertial defects, whose value should be zero at equilibrium. The computed values are (in  $\text{au } \text{\AA}^2$ ) MP2/cc-pVTZ: 0.0026; MP2/cc-pVQZ: 0.0019; and B3LYP/cc-pVTZ: −0.0008. For these reasons, we used the B3LYP method to calculate the  $\alpha$ -constants of the different isotopologues, but instead of the cc-pVTZ basis set, we employed the 6-311+G(3df,2pd) basis set (as implemented in g03) because it is known to give relatively more accurate results with the B3LYP DFT technique.<sup>26,27</sup>

After the first-order rovibrational corrections, it is useful to adjust the rotational constants for the small electronic effect<sup>28</sup> which can be estimated from the  $g$ -constants. As the  $g$ -constants needed to determine the electronic effect are not known, they have been computed, with the help of g03 at the B3LYP level with the aug-cc-pVTZ basis set.<sup>29</sup> The computed values are  $g_{aa} = -0.1197$ ,  $g_{bb} = -0.1629$ , and  $g_{cc} = 0.0297$ .

The corrected values of the rotational constants are given by the relation

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

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 generally rather small but was found to be significant in the present case. For instance, when neglected, the B3LYP/6-311+G(3df,2pd) inertial defect becomes −0.0099 instead of −0.0008. The experimental ground-state rotational constants and the derived semiexperimental equilibrium rotation constants are given in Table 2.

It is useful to try to understand the origin of the relatively poor behavior of the MP2 method. It may be seen in Table 3 that the MP2 structures are rather far from the equilibrium structure, whereas the B3LYP prediction is much closer.



**Table 2. Rotational Constants (MHz), Inertial Defects  $\Delta$  (au  $\text{\AA}^2$ ), and Angle of Rotation  $\theta$  of the Principal Axis System upon Isotopic Substitution (degree) for the Isotopologues of 1,3,4-Oxadiazole**

| species         |          | $B_0^a$   | $B_e^{SEb}$ | $e - c^c$ | $e - c^d$ | $\theta$ |
|-----------------|----------|-----------|-------------|-----------|-----------|----------|
| parent          | A        | 10315.043 | 10408.73    | -0.18     | -0.06     | -        |
|                 | B        | 10189.783 | 10263.18    | -0.03     | -0.18     |          |
|                 | C        | 5122.626  | 5167.76     | -0.01     | -0.02     |          |
|                 | $\Delta$ | 0.0656    | -0.0008     |           |           |          |
| $^{15}\text{N}$ | A        | 10281.679 | 10369.13    | -1.70     | -1.79     | 24.67    |
|                 | B        | 9945.292  | 10021.58    | 1.84      | 1.69      |          |
|                 | C        | 5052.02   | 5096.23     | 0.10      | 0.04      |          |
|                 | $\Delta$ | 0.0658    | -0.0006     |           |           |          |
| $^{13}\text{C}$ | A        | 10206.119 | 10280.76    | -2.65     | -2.99     | 57.48    |
|                 | B        | 10058.143 | 10147.32    | 2.09      | 2.76      |          |
|                 | C        | 5062.451  | 5106.83     | -0.10     | -0.01     |          |
|                 | $\Delta$ | 0.0659    | -0.0006     |           |           |          |
| D               | A        | 10205.015 | 10280.23    | -1.09     | -0.25     | 67.89    |
|                 | B        | 9411.969  | 9492.02     | 0.44      | 0.05      |          |
|                 | C        | 4893.188  | 4935.25     | -0.09     | -0.01     |          |
|                 | $\Delta$ | 0.0642    | -0.0008     |           |           |          |
| $^{18}\text{O}$ | A        | 10315.833 | 10408.68    | -0.23     | -0.11     | 0        |
|                 | B        | 9687.599  | 9757.00     | 0.59      | 0.07      |          |
|                 | C        | 4992.641  | 5036.21     | 0.16      | 0.05      |          |
|                 | $\Delta$ | 0.0665    | -0.0011     |           |           |          |

<sup>a</sup>Ground state constants from ref 4 and this work for the  $^{18}\text{O}$  species.<sup>b</sup>Rovibrational correction calculated with the B3LYP/6-311+G-(3df,2pd) force field. <sup>c</sup>Residuals of a nonweighted fit to the semiexperimental rotational constants. <sup>d</sup>Residuals of a IRLS fit to the semiexperimental rotational constants; see the text.**Table 3. Different Ab Initio Structures for 1,3,4-Oxadiazole<sup>a</sup>**

| method basis set       | $r_e^{\text{BOB}}$ | MP2 cc-pVTZ | MP2 cc-pVQZ | B3LYP 6-311+G(3df,2pd) |
|------------------------|--------------------|-------------|-------------|------------------------|
| $r(\text{O}-\text{C})$ | 1.3540             | 1.3544      | 1.3514      | 1.3559                 |
| $r(\text{C}-\text{N})$ | 1.2854             | 1.2967      | 1.2940      | 1.2831                 |
| $r(\text{C}-\text{H})$ | 1.0737             | 1.0739      | 1.0733      | 1.0752                 |
| $r(\text{N}-\text{N})$ | 1.4064             | 1.3980      | 1.3938      | 1.4013                 |
| $\angle(\text{COC})$   | 101.36             | 101.38      | 101.56      | 101.76                 |
| $\angle(\text{NCO})$   | 113.78             | 113.70      | 113.52      | 113.24                 |
| $\angle(\text{CNN})$   | 105.54             | 105.61      | 105.69      | 105.89                 |
| $\angle(\text{OCH})$   | 118.08             | 118.02      | 118.12      | 118.17                 |
| $\angle(\text{NCH})$   | 128.14             | 128.28      | 128.35      | 128.59                 |

<sup>a</sup>Distances are in  $\text{\AA}$ , and angles are in degrees. <sup>b</sup>CCSD(T)/cc-pwCVTZ(AE) + MP2/cc-pwCVQZ(AE) - MP2/cc-pwCVTZ(AE); see ref 6.

#### 4. SEMIEXPERIMENTAL EQUILIBRIUM STRUCTURE, $r_e^{SE}$

A nonweighted least-squares fit of the semiexperimental equilibrium moments of inertia, excluding the  $^{18}\text{O}$  values, gives unacceptable results and a rather large condition number,  $\kappa = 756$ .<sup>6</sup> Inclusion of the  $^{18}\text{O}$  moments of inertia reduces the condition number by a factor of about two to  $\kappa = 345$ , but the derived parameters have large standard deviations and are still inaccurate; see column 4 of Table 4. Furthermore, large residuals of similar magnitude but opposite sign are observed for the isotopologues  $^{13}\text{C}$  and  $^{15}\text{N}$  (and to a lesser degree for the monodeuterated isotopologue), that is, for the isotopologues with a large rotation of the PAS upon isotopic substitution; see Table 2. Such a result is indeed expected in the case of a large PAS rotation.<sup>6</sup>

It is possible to significantly improve the situation by using the iterative reweighted least-squares method (IRLS).<sup>30,31</sup> Huber's weighting, whereby the residuals  $e_i$  are gradually weighted down when they are larger than approximately  $2 \times \text{MAD}$  (mean absolute deviation: median  $|e_i|$  - median( $e_i$ )), was also employed in some cases. The fit is indeed significantly improved (see column 5 of Table 4), but the main effect of the IRLS is to lower the weight of the moments of inertia  $I_a$  and  $I_b$  of the  $^{13}\text{C}$  and  $^{15}\text{N}$  isotopologues. Thus, the condition number increases to 363, and although the standard deviations are smaller, some parameters are still not well determined, in particular, the N=N bond length.

One way to improve the fit is to use the method of mixed regression (also called the method of predicate observations), in which the structure fitting uses simultaneously equilibrium moments of inertia and bond lengths and bond angles from high-level quantum chemical calculations.<sup>32-34</sup> Inspection of the IRLS fit shows that the least well determined parameter is the  $\angle(\text{OCH})$  angle. It is furthermore highly correlated with the  $r(\text{CO})$  and  $r(\text{CN})$  bond lengths. Using the  $r_e^{\text{BO}}$  value of this angle as the predicate,  $118.083^\circ$ , with a conservative uncertainty of  $0.3^\circ$  significantly improves the fit. However, the  $\angle(\text{OCN})$  and  $\angle(\text{CNN})$  angles are still not yet very precisely determined. By trial and error, it was found that the best result is obtained by using the  $r_e^{\text{BO}}$  value of the  $\angle(\text{OCN})$  angle,  $113.782^\circ$ , as the second predicate with the same conservative uncertainty of  $0.3^\circ$ . The results are given in the column 6 of Table 4.

Although it is much easier to compute accurate ab initio bond angles than bond lengths,<sup>35</sup> the obvious drawback of this method is that it requires relatively high level ab initio calculations. However, there is perhaps a simpler way to solve the problem. The A and B rotational constants of the  $^{13}\text{C}$  and  $^{15}\text{N}$  isotopologues have a small weight in the fit because they have large residuals of similar magnitude but opposite sign. The idea is that, instead of fitting  $I_a$  and  $I_b$  individually for these two isotopologues, it would be better to fit the sum of the rotational constants A and B such that the systematic error cancels. This approach seems promising, but it reduces the number of data, and in our particular case, it was necessary to introduce at least one predicate observation in order to get a good fit. Then, the results were almost identical to those of the fit with predicate observations; see column 6 of Table 4.

There is still another way to obtain an accurate structure by extrapolating the computed ab initio rotational constants to infinite basis set size.<sup>36,37</sup> The ab initio equilibrium values of the rotational constants of the parent species  $X_e$  ( $X = \text{A}, \text{B}, \text{C}$ ) are first calculated. For this goal, the ab initio structure is optimized with the CC method with single and double excitations<sup>38</sup> and a perturbative treatment of connected triples<sup>39</sup> [CCSD(T)] with the correlation-consistent polarized weighted core-covalence n-uple zeta (cc-pwCVnZ) basis set ( $n = \text{T}, \text{Q}$ ),<sup>40</sup> all electrons being correlated (AE). To these  $X_e(\text{T})$  and  $X_e(\text{Q})$  values, the rovibrational correction  $\Delta X_0 = X_0 - X_e$  is added, giving  $X_0(\text{T})$  and  $X_0(\text{Q})$  under the assumption that this rovibrational correction is almost constant, which is generally a good assumption<sup>41</sup> and which is furthermore verified in the present case. Then, the rotational constants  $X_0(\text{T})$  and  $X_0(\text{Q})$  are extrapolated as a function of the computed structural parameters  $r_e(\text{T})$  and  $r_e(\text{Q})$ . The intersection of the line with the experimental  $X_0$  of the parent species gives the extrapolated  $r_e$ . This procedure was first tried with the B3LYP/6-311+G(3df,2pd) force field and was repeated for each rotational constant  $X = \text{A}, \text{B}, \text{C}$ . The results given in Table 5

Table 4. Equilibrium Structure of 1,3,4-Oxadiazole<sup>a</sup>

| type                   | $r_s^b$ | $r_e^{BOc}$ | semiexperimental, $r_e^{SE}$ |                   |                        |                        |
|------------------------|---------|-------------|------------------------------|-------------------|------------------------|------------------------|
|                        |         |             | unweighted                   | IRLS <sup>d</sup> | mixed fit <sup>e</sup> | extrapol. <sup>f</sup> |
| $r(\text{CO})$         | 1.348   | 1.3540      | 1.356(3)                     | 1.3537(15)        | 1.3548(16)             | 1.3537                 |
| $r(\text{CN})$         | 1.297   | 1.2854      | 1.282(4)                     | 1.2853(18)        | 1.2840(11)             | 1.2851                 |
| $r(\text{NN})$         | 1.399   | 1.4064      | 1.409(6)                     | 1.4056(30)        | 1.4058(13)             | 1.4057                 |
| $r(\text{CH})$         | 1.075   | 1.0737      | 1.075(3)                     | 1.0729(13)        | 1.0734(13)             | 1.0736                 |
| $\angle(\text{COC})$   | 102.0   | 101.36      | 101.2(2)                     | 101.38(11)        | 101.29(12)             | 101.39                 |
| $\angle(\text{OCN})$   | 113.4   | 113.78      | 113.9(3)                     | 113.76(14)        | 113.7820(20)           | 113.75                 |
| $\angle(\text{CNN})$   | 105.6   | 105.54      | 105.5(2)                     | 105.55(11)        | 105.572(60)            | 105.55                 |
| $\angle(\text{OCH})$   | 118.1   | 118.08      | 117.2(17)                    | 118.46(83)        | 118.0810(20)           | 118.10                 |
| $\angle(\text{NCH})$   | 128.5   | 128.14      | 128.9(17)                    | 127.78(83)        | 128.1370(29)           | 128.15                 |
| Predicate Observations |         |             |                              |                   |                        |                        |
| $\angle(\text{OCH})$   |         |             |                              |                   | 118.08(30)             |                        |
| $\angle(\text{OCN})$   |         |             |                              |                   | 113.78(30)             |                        |

<sup>a</sup>Distances are in Å, and angles are in degrees. <sup>b</sup>Empirical substitution structure of ref 4. <sup>c</sup>See footnote <sup>b</sup> of Table 3. <sup>d</sup>Iteratively reweighted fit with Huber weighting; see the text. <sup>e</sup>Mixed regression with two predicate observations; see the text. <sup>f</sup>Extrapolated structure; see the text and Table 5.

Table 5. Extrapolation of the Structure of Oxadiazole to Infinite Basis Set<sup>a</sup>

|                        | A         | B         | C        | $r_e(\text{OC})$ | $r_e(\text{CN})$ | $r_e(\text{CH})$ | $\angle_e(\text{OCH})$ | $\angle_e(\text{COC})$ | $\angle_e(\text{NCO})$ |
|------------------------|-----------|-----------|----------|------------------|------------------|------------------|------------------------|------------------------|------------------------|
| $X_0(\text{exp})$      | 10315.038 | 10189.78  | 5122.607 |                  |                  |                  |                        |                        |                        |
| $X_e - X_0$            | 93.70     | 73.40     | 45.36    |                  |                  |                  |                        |                        |                        |
| $X_e(\text{T})$        | 10379.940 | 10206.660 | 5146.290 | 1.35664          | 1.28688          | 1.07439          | 117.9705               | 101.1724               | 113.9686               |
| $X_e(\text{Q})$        | 10406.344 | 10254.770 | 5165.001 | 1.35408          | 1.28535          | 1.07369          | 118.0806               | 101.3599               | 113.7818               |
| $X_e(\text{extrapol})$ | 10410.661 | 10262.620 | 5168.055 |                  |                  |                  |                        |                        |                        |
| $X_0(\text{T})$        | 10286.240 | 10133.260 | 5100.930 |                  |                  |                  |                        |                        |                        |
| $X_0(\text{Q})$        | 10312.644 | 10181.370 | 5119.641 |                  |                  |                  |                        |                        |                        |
| $X_0(\text{extrapol})$ | 10316.961 | 10189.220 | 5122.695 |                  |                  |                  |                        |                        |                        |
| $r_e(\text{extrapol})$ |           |           |          |                  |                  |                  |                        |                        |                        |
| from $A_0$             |           |           |          | 1.3539           | 1.2852           | 1.0736           | 118.091                | 101.377                | 113.765                |
| from $B_0$             |           |           |          | 1.3536           | 1.2851           | 1.0736           | 118.100                | 101.393                | 113.749                |
| from $C_0$             |           |           |          | 1.3536           | 1.2851           | 1.0736           | 118.100                | 101.393                | 113.749                |
| mean                   |           |           |          | 1.3537           | 1.2851           | 1.0736           | 118.099                | 101.390                | 113.751                |

<sup>a</sup>Rotational constants are in MHz, distances are in Å, and angles are in degrees.

are highly consistent. The procedure was repeated with the different isotopologues, giving results in perfect agreement with those of the parent species; see Table S2 of the Supporting Information. Finally,  $\Delta X_0$  calculated with the MP2/cc-pVTZ force field was also used, giving again consistent results; see Table S2 of the Supporting Information. The big advantage of this method is that only one isotopologue is necessary. Its drawback is that it requires very high level ab initio calculations. We tried to use smaller basis sets, cc-pwCVDZ and cc-pwCVTZ instead of cc-pwCVTZ and cc-pwCVQZ. However, there was a huge loss of precision, the final results not being better than the CCSD(T)/cc-pwCVTZ(AE) structure; see Table S2 of the Supporting Information. It has to be noted that, in this last case, the extrapolation is significantly more accurate when one uses the experimental  $B_0$  value. Likewise, the cheaper MP2 method does not give satisfactory results.

## 5. DISCUSSION

As previously emphasized, the substitution ( $r_s$ ) structure is sometimes a poor approximation of the equilibrium ( $r_e$ ) structure.<sup>42</sup> The empirical  $r_s$  structure obtained from the ground-state rotational constants is given in Table 4 for the sake of comparison. In the original work,<sup>4</sup> the uncertainty of the structure parameters was estimated using Costain's rule,<sup>43</sup>  $\delta x = 0.0012/x$ . It was concluded that "the substitution structure should represent the equilibrium structure within 0.005 Å".

However, inspection of Table 4 shows that the  $r_s$  structure is less accurate than predicted. In particular, for the CN bond length, the  $r_s$  value is 0.012 Å longer than the  $r_e$  value. The basic assumption of the  $r_s$  method is that the rovibrational contribution remains constant upon isotopic substitution. This is not true in the present case because of the large rotation of axes.

It is worth noting that the IRLS fit gives a  $r_e^{SE}$  structure quite close to the results of the mixed fit. Furthermore, these two  $r_e^{SE}$  structures are also quite close to the extrapolated ab initio equilibrium structure, giving us confidence that these structures are accurate.

The comparison of the structure of 1,3,4-oxadiazole with that of furane<sup>6</sup> shows that the CO bond length is shorter in oxadiazole (1.354 compared to 1.359 Å), the COC bond angle is smaller in oxadiazole (101.3 compared to 106.6°), and the CH bond is less tilted toward oxygen ( $\angle(\text{OCH}) = 118.1$  compared to 115.9°). The N–N bond length at 1.406 Å seems to be long. Nevertheless, it is shorter than the value found in hydrazine,  $r(\text{N–N}) = 1.432$  Å,<sup>44</sup> which is the prototype of the N–N single bond.

## 6. CONCLUSION

The semiexperimental method is believed to be the most accurate method to determine the equilibrium structure of a molecule, provided accurate ground-state rotational constants

are available for a sufficiently large number of isotopologues (generally the parent species and all monosubstituted isotopologues). However, in a few cases, the semiexperimental method gives unsatisfactory results, a typical example being 1,3,4-oxadiazole. This issue is mainly due to the fact that oxadiazole is an oblate rotor. For such a molecule, there is a large rotation of the principal axis system upon isotopic substitution that may amplify the errors.<sup>6</sup> Three different remedies are proposed here to mitigate this difficulty. The first one is the method of mixed regression, where in the fit of the semiexperimental moments of inertia, the values of some ab initio structural parameters are used as additional data. This method generally gives good results provided reliable predicate observations are available. In other words, in most cases, high-level quantum chemical calculations are required. In the second method, instead of fitting  $I_a$  and  $I_b$  individually for the isotopologues with a large PAS rotation, the sum of the rotational constants  $A + B$  is fitted. The obvious inconvenience of this method is that it decreases the number of input data that may deteriorate the quality of the fit. A straightforward solution is to add the rotational constants of additional isotopologues, which is often not easy. The third method is to extrapolate the ground-state rotational constants computed at the CCSD(T)/cc-pwCVTZ(AE) and CCSD(T)/cc-pwCVQZ(AE) levels of theory toward the experimental value. It should give a structure of almost CCSD(T)/cc-pwCV5Z quality. The big advantage of this method is that one isotopologue is enough, but on the other hand, it is extremely computer-intensive.

The different methods discussed in this work, including the IRLS, are quite general and could be used whenever there are difficulties determining a sufficiently accurate standard semiexperimental structure.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Table S1 contains the experimental frequencies for the ground state of 1,3,4-oxadiazole (parent species and <sup>18</sup>O species). Table S2 gives the results of the extrapolation of the structure of 1,3,4-oxadiazole to infinite basis set. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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