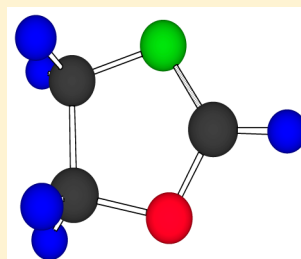


## Ring Planarity Problem of 2-Oxazoline Revisited Using Microwave Spectroscopy and Quantum Chemical Calculations

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## Supporting Information

**ABSTRACT:** In a previous infrared, Raman, and microwave spectroscopic work,<sup>1</sup> it was claimed that 2-oxazoline has a *planar* ring equilibrium conformation, and the ring-puckering potential function  $V(z) = 22.2(z^4 + 1.31z^2) \text{ cm}^{-1}$ , where  $z$  is a dimensionless reduced coordinate, was derived. This function poorly reproduces the rotational constants of the lowest and most important puckering states. The microwave spectrum has been reinvestigated and largely extended to include more than 4600 transitions of the ground state and six excited states of the ring-puckering vibration allowing accurate centrifugal distortion constants to be obtained for the first time. A new potential function  $V(z) = 38.8(z^4 - 0.65z^2) \text{ cm}^{-1}$  has been determined. This function yields much better agreement between calculated and observed rotational constants, especially for the lowest puckering states, than the previous function and predicts a *nonplanar* ring equilibrium conformation. The barrier to ring planarity is determined to be 49(8) J/mol. The ground-state energy level is 35  $\text{cm}^{-1}$  above the barrier maximum. Theory predicts that three of the five Watson centrifugal distortion constants,  $\Delta_{JK}$ ,  $\Delta_K$ , and  $\delta_K$ , should vary with the puckering state, whereas  $\Delta_J$  and  $\delta_J$  should be unaffected. It was found that  $\Delta_{JK}$  and  $\Delta_K$  indeed behave in the expected manner, while deviations were seen for the three other centrifugal distortion constants. The ab initio methods HF, MP2, CCSD, CCSD(T), and CCSD(T)-F12 with large basis sets as well as several DFT methods were used in an attempt to reproduce the low experimental barrier to the planar ring. Only the MP2 method yielded a satisfactory prediction of the barrier. The CCSD and the CCSD(T) calculations predict a planar ring, whereas the energy differences between a planar and a nonplanar ring obtained in the CCSD(T)-F12 computations are so small that a definite conclusion cannot be drawn.



## INTRODUCTION

The equilibrium conformations of four- and five-membered cyclic molecules have been studied extensively in the past by microwave (MW), infrared, and Raman spectroscopy.<sup>2,3</sup> Five-membered ring compounds with one double bond have been found either to be puckered or to have a planar ring equilibrium conformation.<sup>2,3</sup> 2-Oxazoline, shown in Figure 1 with atom

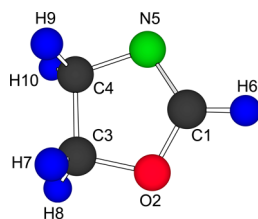


Figure 1. Model of 2-oxazoline with atom numbering.

numbering, is a five-membered ring compound with a C1N5 double bond. This molecule has been studied by Durig et al.<sup>1</sup> who used microwave, Raman, and infrared spectroscopy to determine its equilibrium conformation. These workers observed a series of Q-branches in the C–H stretching region in the infrared spectrum of gaseous 2-oxazoline and assigned

this series as a combination of ring-puckering and C–H stretching vibrations. The puckering frequencies obtained from this series were fitted to a potential function of the form  $V(z) = A(z^4 + Bz^2)$ , where  $A$  and  $B$  are constants and  $z$  is the dimensionless reduced ring-puckering coordinate.<sup>2,3</sup>  $A$  is often given in  $\text{cm}^{-1}$ , and  $B$  is dimensionless. Potentials of this form are normally found to be sufficient to describe puckering motions quite well.<sup>2,3</sup> A positive value of the  $B$  constant is taken as evidence that a molecule has a planar ring equilibrium conformation, whereas a negative value of  $B$  shows that there is a barrier to planar ring and that the *equilibrium* conformation is puckered.<sup>2,3</sup>

The function determined by Durig et al.<sup>1</sup> for 2-oxazoline using *only* data from the infrared spectrum was  $V(z) = 22.2(z^4 + 1.31z^2) \text{ cm}^{-1}$ . The fact that  $B$  is positive (+1.31) led to the conclusion that 2-oxazoline has a planar ring equilibrium conformation.<sup>1</sup> They also determined the dipole moment for the ground vibrational state, which was found to have a zero component along the  $c$ -principal inertial axis,<sup>1</sup> which is evidence pointing in the same direction. Microwave transitions very

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sensitive to the out-of-plane dipole moment component,  $\mu_{\text{O}}$  were selected for this purpose.

The MW spectrum of the ground and five excited states of the puckering motion were assigned in the same work.<sup>1</sup> The rotational constants, especially of the lower puckering states, display an irregular variation,<sup>1</sup> which is strong evidence for a low barrier to planar ring conformation since in the absence of a barrier the variation is expected to be smooth.<sup>4</sup> The rotational constants were fitted<sup>1</sup> using  $B = 1.31$ . However, a fit with unusually large residuals for the rotational constants, particularly for the first excited puckering state, was thereby obtained. The rotational constants of the lowest vibrationally excited states are most sensitive to the existence of a barrier to planar ring, and the large residuals indicate that the reported potential function<sup>1</sup>  $V(z) = 22.2(z^4 + 1.31z^2) \text{ cm}^{-1}$  might be improved. Instead of using the reported puckering frequencies to derive a value for the pivotal  $B$  constant, we have instead utilized the rotational constants for this purpose, because they are very sensitive to a small barrier to planar ring.

Quartic centrifugal distortion constants are also sensitive to the puckering vibration and may vary considerably depending on the puckering state under consideration. Centrifugal distortion constants were not determined previously.<sup>1</sup> We have measured a total of about 4600 transitions to determine accurate centrifugal distortion constants for the ground vibrational state as well as for six excited puckering states and used this information to investigate the ring planarity problem using a theory by Creswell and Mills.<sup>5</sup> The spectroscopic work has been augmented with a series of ab initio and density functional theory (DFT) calculations to see if they are capable of predicting the very low barrier to planar ring in 2-oxazoline, which is determined in this work.

## EXPERIMENTAL SECTION

**Synthesis and Microwave Experiment.** A sample of 2-oxazoline (4,5-dihydro-1,3-oxazole) was synthesized and purified as previously reported.<sup>6</sup> The MW spectrum was studied using the Stark-modulated microwave spectrometer of the University of Oslo, whose detailed construction and operation of this device have been given elsewhere.<sup>7</sup> Salient features of this device are its resolution of about 0.5 MHz and spectral accuracy  $\approx 0.10$  MHz for strong, isolated transitions. The spectrum was recorded at room temperature in the 12.1–80.7 GHz spectral interval at a pressure of 5–10 Pa. Selected measurements were also performed in other frequency regions.

## THEORY OF PUCKERING VIBRATIONS

A simple one-dimensional wave equation

$$-(\hbar^2/2\mu)(d^2\psi/dx^2) + (V - E)\psi = 0 \quad (1)$$

where  $V = ax^4 + bx^2$  has been used to study the puckering problem of 2-oxazoline. This equation can conveniently be transformed into the dimensionless wave function (eq 2) in the manner described by, e.g., Laane.<sup>8</sup>

$$(d^2\psi/dz^2) + (\lambda - z^4 - Bz^2)\psi = 0 \quad (2)$$

The associated reduced potential function is  $V(z) = A(z^4 + Bz^2)$ . Definitions of  $A$ ,  $B$ ,  $z$ , and  $\lambda$  are given by Laane.<sup>8</sup> The eigenvalues of eq 2 can be calculated for various values of  $B$ . The constant  $A$  is adjusted to reproduce the puckering fundamental vibrational frequency once  $B$  has been determined.

In the present work, the  $B$  constant was determined using the rotational constants of the ground and excited states of the puckering vibration. The rotational constants,  $\beta_{\nu}$ , can be expanded in a power series as follows<sup>2,3</sup>

$$\beta_{\nu} = \beta_0 + \beta_2\langle z^2 \rangle_{\nu} + \beta_4\langle z^4 \rangle_{\nu} \quad (3)$$

where  $\beta_{\nu}$  represents the  $A_{\nu}$ ,  $B_{\nu}$ , or  $C_{\nu}$  rotational constants in the  $\nu$ th excited state of the puckering vibration.  $\langle z^2 \rangle_{\nu}$  and  $\langle z^4 \rangle_{\nu}$  are expectation values of  $z$ . The  $B$  constant of the reduced potential energy function (eq 2) is varied in a systematic manner, and the expectation values of  $z$  are calculated for each value of  $B$  and the empirical parameters  $\beta_0$ ,  $\beta_2$ , and  $\beta_4$  are least-squares adjusted to give the best fit to the experimental rotational constants,  $\beta_{\nu}$ . The value of  $B$  that results in the best fits of the rotational constants to the expression (eq 3) is assumed to be the optimal value of this constant.

The computer programs used to derive the puckering potential function for 2-oxazoline below have been described.<sup>9</sup> One of these programs has now been extended to calculate the dimensionless perturbation sum  $\Phi_{\nu}$  given by

$$\Phi_{\nu} = \sum \frac{\langle \nu | z | \nu' \rangle \langle \nu' | z | \nu \rangle}{(\lambda_{\nu} - \lambda_{\nu'})} \quad (4)$$

where  $z$  is the reduced puckering coordinate and  $\lambda_{\nu}$  are the eigenvalues of the dimensionless Schrödinger eq 2. This extension of the program was undertaken because  $\Phi_{\nu}$  is useful for the calculation of the variation of centrifugal distortion constants with the puckering mode, as discussed below.

Creswell and Mills<sup>5</sup> have developed a theory for the Watson quartic centrifugal distortion constants that takes the highly anharmonic nature of the double-minimum potential into account.

2-Oxazoline has  $C_s$  symmetry for a planar-ring conformation. The following expressions for Watson's  $A$ -reduction<sup>10</sup> centrifugal distortion are valid for molecules with the following symmetry<sup>11</sup>

$$\Delta_J = \Delta_J^*, \quad \delta_J = \delta_J^* \quad (5a,b)$$

$$\Delta_{JK} = \Delta_{JK}^* - 2K_{ac}\theta_{\nu} - 2K_{bc}\theta_{\nu} \quad (5c)$$

$$\Delta_K = \Delta_K^* + 2K_{ac}\theta_{\nu} + 2K_{bc}\theta_{\nu} \quad (5d)$$

$$\delta_K = \delta_K^* - \kappa K_{ac}\theta_{\nu} - K_{bc}\theta_{\nu} \quad (5e)$$

where

$$K_{ac} = [(\hbar^4/4h)/(I_a^2 I_b^2)](a_{24}^{(ac)})^2$$

$$K_{bc} = [(\hbar^4/4h)/(I_b^2 I_c^2)](a_{24}^{(bc)})^2$$

$$a_{24}^{(\alpha\beta)} = (\partial I_{(\alpha\beta)}/\partial Q_{24})$$

$\kappa$  is Ray's asymmetry parameter,<sup>12</sup>  $I_a$ ,  $I_b$ , and  $I_c$  are the principal moments of inertia, and  $Q_{24}$  is the ring puckering normal coordinate.  $\theta_{\nu}$  is given by

$$\theta_{\nu} = \sum \frac{\langle \nu | Q_{24} | \nu' \rangle \langle \nu' | Q_{24} | \nu \rangle}{(E_{\nu} - E_{\nu'})} \quad (6)$$

The starred terms in eqs 5a–5e represent the contribution from all other vibrations but puckering.

$\Delta_J$  and  $\delta_J$  are unaffected by the puckering vibration according to this theory (5a,b), while the remaining three quartic constants  $\Delta_{JK}$ ,  $\Delta_K$ , and  $\delta_K$  depend on the puckering state

Table 1. Spectroscopic Constants<sup>a</sup> of the Ground and Excited States of the Puckering Vibration

	vibrational state						
	ground state	first ex. state	second ex. state	third ex. state	fourth ex. state	fifth ex. state	sixth ex. state
$A_v$ (MHz)	8473.4432(37)	8476.6618(39)	8476.5598(50)	8475.8881(43)	8474.5008(54)	8472.586(11)	8470.211(16)
$B_v$ (MHz)	8122.1705(37)	8134.7886(39)	8139.5501(50)	8143.5004(42)	8146.1126(54)	8147.795(11)	8148.717(17)
$C_v$ (MHz)	4384.0958(37)	4406.4814(38)	4418.8083(48)	4430.6973(42)	4444.2285(52)	4450.891(11)	4459.860(14)
$\Delta_J$ (kHz)	2.664(45)	2.640(46)	2.543(62)	2.637(50)	2.684(64)	2.72(14)	2.67(22)
$\Delta_{JK}$ (kHz)	−1.9352(12)	−2.9304(14)	−2.7775(25)	−2.7914(22)	−2.7914(34)	−2.8143(81)	−2.823(15)
$\Delta_K$ (kHz)	−0.035(23)	1.060(24)	0.942(38)	0.887(33)	0.840(47)	1.005(84)	1.13(16)
$\delta_J$ (kHz)	0.019883(25)	0.016268(25)	0.02055(11)	0.021488(29)	0.022467(34)	0.023833(66)	0.02306(66)
$\delta_K$ (kHz)	10.9754(10)	10.9641(10)	11.3155(45)	11.4338(11)	11.5190(13)	11.5487(20)	11.533(22)
$\Phi_{JK}$ (Hz)	−0.04355(55)	−0.05931(35)	−0.0619(14)	−0.05712(98)	−0.0558(15)	−0.0645(38)	−0.060 <sup>c</sup>
$\Phi_K$ (Hz)	1.63(11)	2.01(12)	2.52(21)	1.86(16)	1.81(25)	2.72(42)	2.0 <sup>c</sup>
$P_c$ <sup>d</sup> (10 <sup>−20</sup> u m <sup>2</sup> )	3.294660(26)	3.527889(26)	3.670049(33)	3.810797(29)	3.940963(37)	4.084815(75)	4.18385(10)
rms <sup>e</sup>	1.181	1.150	1.163	1.156	1.160	1.273	1.009
$N^f$	1208	1134	654	794	525	237	57

<sup>a</sup>A-reduction III<sup>r</sup>-representation.<sup>10</sup> Uncertainties represent one standard deviation. <sup>b</sup>Further sextic constants preset at zero. <sup>c</sup>Fixed. <sup>d</sup>Planar moment defined by  $P_c = (I_a + I_b - I_c)/2$ , where  $I_a$ ,  $I_b$ , and  $I_c$  are the principal moments of inertia. Conversion factor: 505 379.05 × 10<sup>−20</sup> MHz u m<sup>2</sup>. <sup>e</sup>Root-mean-square deviation defined as  $\text{rms}^2 = \sum[(\nu_{\text{obs}} - \nu_{\text{calc}})/u]^2/(N - P)$ , where  $\nu_{\text{obs}}$  and  $\nu_{\text{calc}}$  are the observed and calculated frequencies,  $u$  is the uncertainty of the observed frequency,  $N$  is the number of transitions used in the least-squares fit, and  $P$  is the number of spectroscopic constants used in the fit. <sup>f</sup>Number of transitions used in the fit.

according to eqs 5c–5e.  $K_{ac}$ ,  $K_{bc}$ ,  $\kappa$ , and  $a_{24}^{(\alpha\beta)}$  are practically constant for all vibrational states, and the perturbation sum  $\theta_v$  is proportional to  $\Phi_v$ .<sup>5,11</sup> Equations 5c–5e can then to a good approximation conveniently be written as

$$\Delta_{JK} = \Delta_{JK}^* - c_1 \Phi_v \quad (7a)$$

$$\Delta_K = \Delta_K^* + c_1 \Phi_v \quad (7b)$$

$$\delta_K = \delta_K^* - c_2 \Phi_v \quad (7c)$$

where  $c_1$  and  $c_2$  are constants, which will be determined below.

## RESULTS

**Microwave Spectrum and Assignments.** 2-Oxazoline was seen to be formed readily from 2-isocyanoethanol (HOCH<sub>2</sub>CH<sub>2</sub>NC) in the MW cell in our study<sup>13</sup> of the alcohol. In fact, 2-oxazoline was formed so rapidly that it was the predominating gas-phase species. It was identified by its published microwave spectrum.<sup>1</sup> The majority of the present spectral measurements were performed with 2-oxazoline formed this way. Selected MW measurements were also undertaken employing 2-oxazoline that had been synthesized as described above.<sup>6</sup>

Durig et al.<sup>1</sup> assigned transitions up to  $J = 6$  in the 12.4–40 GHz spectral interval. The present measurements were made in the whole 12.1–80.7 GHz frequency region, as well as in other selected regions. 2-Oxazoline is an oblate rotor (Ray's asymmetry parameter<sup>12</sup>  $\kappa = 0.828$ ) and has a rich and comparatively strong  $a$ - and  $b$ -type spectrum dominated by Q-branch lines. The fact that transitions including high values of the quantum number  $J$  exist in the investigated spectral range made it possible to obtain accurate values for the majority of the Watson quartic centrifugal distortion constants,<sup>10</sup> none of which were reported in the previous work.<sup>1</sup>

The reported rotational constants<sup>1</sup> were used as the starting point in the assignment procedure, which was successively extended to include more than 4600 transitions belonging to the ground state and to six excited states of the puckering vibration. It was possible to assign <sup>b</sup>Q-branch lines with a maximum value of  $J = 59$  and  $K_{+1,\text{max}} = 12$  in the case of the

ground vibrational state. The microwave spectra are listed in the Supporting Information, Tables S1–S7, whereas the resulting spectroscopic constants (A-reduction III<sup>r</sup>-representation<sup>10</sup>) are collected in Table 1. Sørensen's program Rotfit<sup>14</sup> was used to least-squares fit the spectra. This table also contains the planar moment,  $P_c$  defined by  $P_c = (I_a + I_b - I_c)/2$ , where  $I_a$ ,  $I_b$ , and  $I_c$  are the principal moments of inertia derived from the rotational constants.

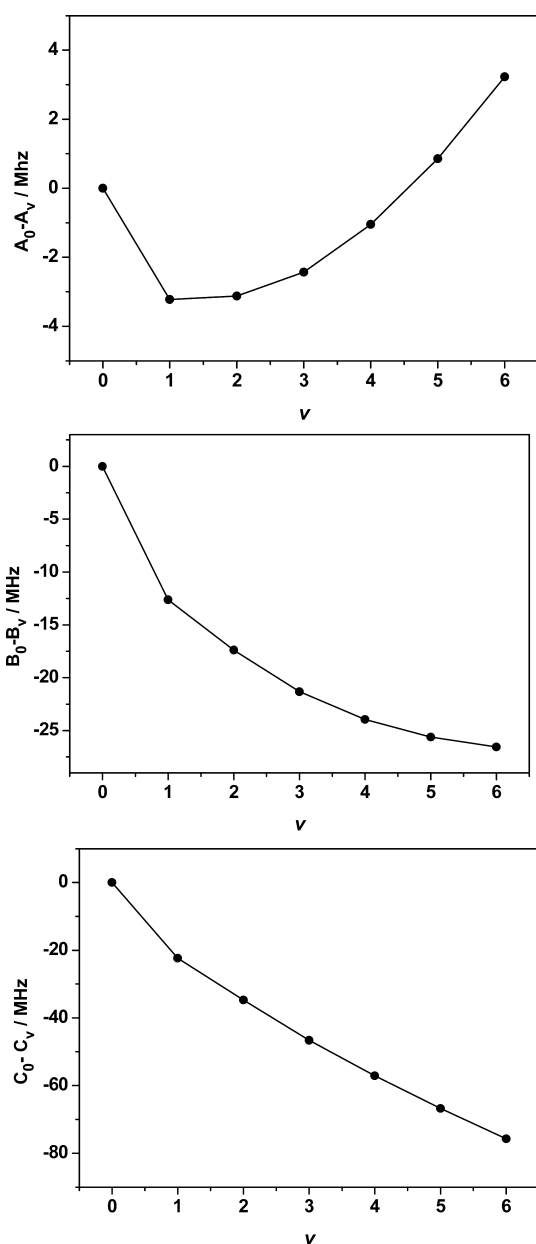
Accurate values were obtained for the rotational and the five quartic centrifugal distortion constants. Centrifugal distortion is not large in this compound, and only two sextic constants,  $\Phi_{JK}$  and  $\Phi_K$ , were necessary to obtain a fit with a root-mean-square deviation comparable to the experimental uncertainty. The remaining sextic constants were preset at zero in the least-squares fits.

It is seen from Table 1 that changes of the rotational constants and  $P_c$  are much larger from the ground vibrational state to the first excited state of the puckering vibration than for other successively excited puckering states, a behavior typical for compounds possessing a nonplanar ring.<sup>2,3</sup> The variations of the rotational constants upon excitation of  $\nu_{24}$  are illustrated in Figure 2.

**Potential Function.** The  $A$  and  $B$  constants of the potential function  $V(z) = A(z^4 + Bz^2)$  were determined in the following manner: The rotational constants in Table 1 were least-squares fitted to eq 3 using values of  $\langle z^2 \rangle_v$  and  $\langle z^4 \rangle_v$  calculated for a series of values of  $B$ . The rotational constants were given unit weights in the fitting procedure. The residuals of these fits were found to be very sensitive to the value of  $B$ . The best overall fit was obtained with a negative value of  $B = -0.65$ , whereas positive values of this constant resulted in a significantly poorer fits. The following expressions (in MHz) for the rotational constants were obtained from the seven sets of the rotational constants (Table 1) using  $B = -0.65$ :

$$A_v = 8470.46(54) + 10.19(82)\langle z^2 \rangle - 2.58(17)\langle z^4 \rangle \quad (8a)$$

$$B_v = 8122.25(67) + 27.6(10)\langle z^2 \rangle - 3.14(21)\langle z^4 \rangle \quad (8b)$$



**Figure 2.** Deviation of the rotational constants from their ground-state values as a function of the ring-puckering ( $\nu_{24}$ ) quantum number.

$$C_v = 4367.63(11) + 14.31(17)\langle z^2 \rangle - 0.530(35)\langle z^4 \rangle \quad (8c)$$

The numbers in parentheses represent one standard deviation. The calculated values of the rotational constants and their residuals are listed in Table 2 in boldface, where the residuals of the fits obtained by Durig et al.<sup>1</sup> are included for comparison. The error square sum of the residuals of all entries (seven vibrational states) is 1.058 MHz<sup>2</sup>, compared to an almost four times larger sum, 3.872 MHz<sup>2</sup>, calculated from the entries of the six states reported previously in their Table 9.<sup>1</sup>

It is seen from Table 2 that the present fit generally has much smaller residuals than the previous fit.<sup>1</sup> The improvement is especially true for the lowest puckering states, which are most sensitive to the existence of a barrier to planar ring. There are variations among the fits of the rotational constants. The fit of the  $C_v$  rotational constants is best. All these constants are fitted almost to within their experimental uncertainties. The  $A$  and  $B$  rotational constants of the four lowest puckering states are also very well reproduced. The  $A$  and  $B$  constants of the fifth excited puckering state deviate by  $-0.464$  and  $-0.579$  MHz, respectively. It is possible that this deviation is due to interaction of this excited state with another vibrational mode.

The puckering fundamental vibration was determined by relative intensity measurements using selected transitions in the MW spectrum. 2-Oxazoline has a dense MW spectrum, and it is therefore not easy to find isolated lines which are completely unperturbed by overlapping transitions or Stark components. The intensities of nine selected pairs of ground-state lines and the first excited puckering state lines were compared in the manner described by Wilson and Esbitt.<sup>15</sup> A value of  $92 \text{ cm}^{-1}$  with a comparatively large uncertainty (three estimated standard deviations) of  $\pm 15 \text{ cm}^{-1}$  was obtained for the puckering fundamental. This frequency should be compared to  $79 \pm 8 \text{ cm}^{-1}$  found previously in a similar manner.<sup>1</sup> The two determinations agree within their uncertainty limits.

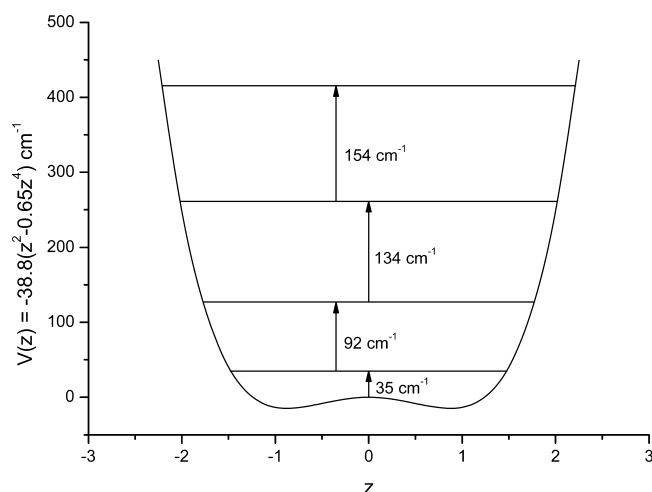
An  $A$  constant of  $38.8 \text{ cm}^{-1}$  reproduces  $92 \text{ cm}^{-1}$  for the fundamental puckering vibration, and the potential function now becomes  $V(z) = 38.8(z^4 - 0.65z^2) \text{ cm}^{-1}$  compared to the previous determination<sup>1</sup>  $V(z) = 22.2(z^4 + 1.31z^2) \text{ cm}^{-1}$ . Our potential function is drawn in Figure 3, where the first few energy levels are indicated. The barrier height is only  $4.10 \text{ cm}^{-1}$  ( $49 \text{ J/mol}$ ). The ground-state energy level is  $35 \text{ cm}^{-1}$  above the maximum of the barrier to planar ring. It is difficult to say exactly how accurate this barrier height is, but taking the fundamental puckering frequency to be  $77$  or  $107 \text{ cm}^{-1}$ , the two extremes of the uncertainty interval ( $92 \pm 15 \text{ cm}^{-1}$ ), one finds that  $A = 32.4$  in the first case ( $77 \text{ cm}^{-1}$ ) and  $A = 45.0 \text{ cm}^{-1}$  for the higher frequency ( $107 \text{ cm}^{-1}$ ). The associated barrier heights are  $3.42 \text{ cm}^{-1}$  ( $41 \text{ J/mol}$ ) and  $4.75 \text{ cm}^{-1}$  ( $57 \text{ J/mol}$ ), compared to  $4.10 \text{ cm}^{-1}$  ( $49 \text{ J/mol}$ ) for  $92 \text{ cm}^{-1}$ . A value

**Table 2.** Results of the Fits of the Rotational Constants

$\nu$	$A_v$			$B_v$			$C_v$		
	calc. <sup>a</sup>	obs. - calc. <sup>a</sup>	obs. - calc. <sup>b</sup>	calc. <sup>a</sup>	obs. - calc. <sup>a</sup>	obs. - calc. <sup>b</sup>	calc. <sup>a</sup>	obs. - calc. <sup>a</sup>	obs. - calc. <sup>b</sup>
0	<b>8473.516</b>	-0.072	-0.15	<b>8122.271</b>	-0.101	-0.33	<b>4384.102</b>	-0.005	-0.43
1	<b>8476.648</b>	0.014	0.48	<b>8134.745</b>	0.004	0.85	<b>4406.507</b>	-0.026	1.25
2	<b>8476.393</b>	0.167	-0.21	<b>8139.337</b>	0.213	-0.32	<b>4418.766</b>	0.042	-0.45
3	<b>8476.038</b>	-0.150	-0.24	<b>8143.692</b>	-0.191	-0.30	<b>4430.713</b>	-0.017	-0.46
4	<b>8474.164</b>	0.337	-0.03	<b>8145.726</b>	0.387	-0.14	<b>4441.156</b>	0.073	-0.19
5	<b>8473.050</b>	-0.464	0.17	<b>8148.374</b>	-0.579	0.28	<b>4450.989</b>	-0.093	0.41
6	<b>8470.044</b>	0.167	- <sup>c</sup>	<b>8148.490</b>	0.227	- <sup>c</sup>	<b>4459.834</b>	0.025	- <sup>c</sup>

<sup>a</sup>This work (boldface) using  $B = -0.65$ . The observed rotational constants are given in Table 1. <sup>b</sup>Taken from Table 9 of ref 1, who used  $B = 1.31$ .

<sup>c</sup>Not obtained.

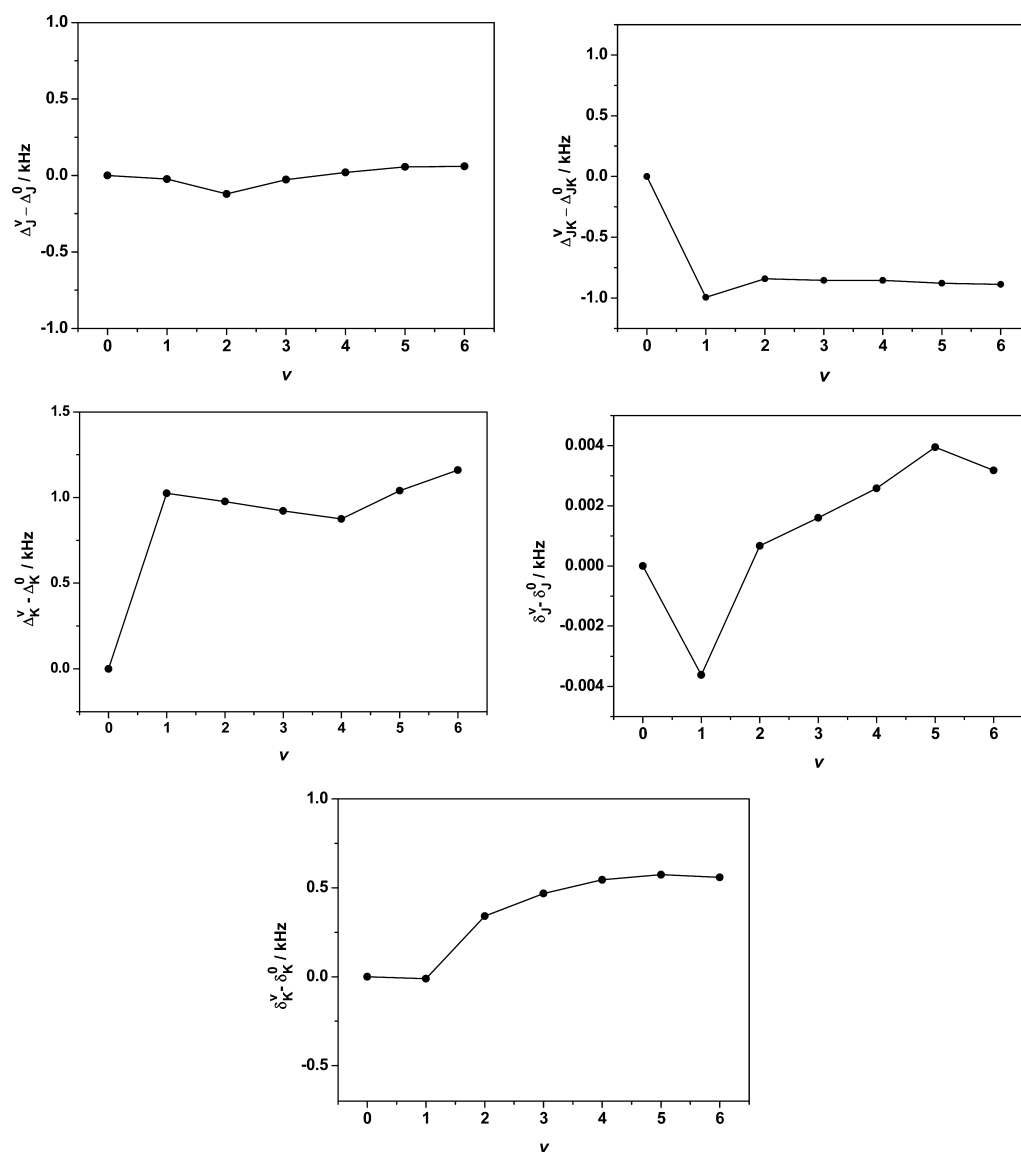


**Figure 3.** Potential function for the ring-puckering vibration. See text for discussion of uncertainties associated with  $A = 38.8 \text{ cm}^{-1}$ .

of  $49(8) \text{ J/mol}$  is our best estimate of the barrier to planar ring. The uncertainty of  $\pm 8 \text{ J/mol}$  corresponds to three standard deviations. This barrier is comparatively small, and it is well below the ground vibrational state.

The previous attempts to directly observe the puckering vibration around  $100 \text{ cm}^{-1}$  using infrared and Raman spectroscopy failed.<sup>1</sup> A series of very weak transitions observed in the low-frequency side in the C–H stretching region was assigned as combination bands of stretching and puckering. No confirmation of the assignments was obtained from the high-frequency side of the stretching bands due to overlapping.<sup>1</sup> No other combination bands seem to have been observed. Relative intensity measurement of the puckering frequency has a comparatively large uncertainty but has the advantage of being unambiguous, and that is why we have preferred this method.

**Centrifugal Distortion and Puckering.** Accurate values have been obtained for most quartic centrifugal distortion constants (Table 1) allowing a comparison with theory.<sup>5,11</sup> The



**Figure 4.** Deviation of the quartic centrifugal distortion constants  $\Delta_J$ ,  $\Delta_{JK}$ ,  $\Delta_K$ ,  $\delta_J$ , and  $\delta_K$  from their ground-state values as a function of the ring-puckering quantum number ( $v_{24}$ ).



variation of the quartic centrifugal distortion constants is illustrated in Figure 4.

Theory<sup>5</sup> predicts that  $\Delta_J$  is unaffected by puckering (eq 5a), and this is indeed observed (Table 1), as all seven values of  $\Delta_J$  are constant to within the experimental uncertainties.  $\delta_J$  is also predicted to be unaffected by puckering (eq 5b), but this is not supported by the experimental data. This constant drops from 0.019 883(25) kHz in the ground state to 0.016 268(20) kHz in the first excited state and then increases to 0.023 833(26) kHz in the fifth excited state (Table 1). The maximum variation between the ground and the first excited state is thus more than 40%, which is well outside the experimental uncertainties.

$\Delta_{JK}$ ,  $\Delta_K$ , and  $\delta_K$  depend on the perturbation sum  $\Phi_v$ , according to eqs 7a–7c. These sums are listed in Table 3 for

**Table 3. Calculated Perturbation Sums,  $\Phi_v$ , for  $B = -0.65^a$**

$v_{24}$	$\Phi_v$
0	−0.3473
1	+0.0155
2	−0.0379
3	−0.0291
4	−0.0256
5	−0.0228
6	−0.0207

<sup>a</sup>See eq 4 and text.

$B = -0.65$ .  $\Phi_v$  displays a characteristic zigzagging behavior, which is especially prevalent for the three lowest vibrational states because they are perturbed most by the barrier to planar ring. The variation of  $\Phi_v$  in the fourth, fifth, and sixth excited puckering states is smooth.  $\Delta_{JK}$ ,  $\Delta_K$ , and  $\delta_K$  are connected with  $\Phi_v$  through eqs 7a–7c and should display a similar zigzagging behavior.  $\Delta_{JK}$  and  $\Delta_K$  indeed behave in the predicted manner as shown in Table 1.  $\Delta_{JK}$  decreases by about −1.00 kHz from the ground to the first excited state, from −1.9352(12) to −2.9304(14) kHz. A small increase to −2.7775(25) kHz occurs from the first excited state to the second excited puckering state. A smooth variation is seen for the remaining excited states.  $\Delta_K$ , on the other hand, increases by about 1.00 kHz from the ground to the first excited state. The magnitude of this variation ( $\approx 1.00$  kHz) is the same as for  $\Delta_{JK}$  but with opposite sign in accordance with eqs 7a and 7b. Further variations of  $\Delta_K$  upon excitation are similar in magnitude to the variations seen for  $\Delta_{JK}$ .

$\delta_K$  values of the ground and first excited state are almost identical, 10.9754(10) and 10.9641(10) kHz, respectively. It can be inferred from eqs 5c–5e that the magnitude of the variation of  $\delta_K$  should be almost half of what is the case for  $\Delta_{JK}$  and  $\Delta_K$ , because Ray's asymmetry parameter  $\kappa = 0.828$ . A difference of roughly −0.4 kHz from the ground to the first excited puckering state, compared to approximately −1.0 kHz found for  $\Delta_{JK}$  and +1.0 kHz for  $\Delta_K$ , was therefore expected. Instead a decrease of only 0.0113 kHz from the ground to the first excited state was observed experimentally. This unexpected small difference was followed by a relatively large increase of 0.3514 kHz from the first excited state (10.9641(10) kHz) to the second excited state (11.3155(45) kHz). The variations of  $\delta_K$  of the next excited states are smooth.

Because  $\Delta_{JK}$  and  $\Delta_K$  vary in the expected manner, they were least-squares fitted jointly to eqs 7a and 7b in order to determine  $\Delta_{JK}^*$ ,  $\Delta_K^*$ , and  $c_1$ . The inverse squares of the experimental one-standard deviations in Table 1 were used as

weights with the results shown in Table 4.  $\Delta_{JK}^* = -2.882(5)$ ,  $\Delta_K^* = 0.872(68)$ , and  $c_1 = 2.729(24)$  kHz were obtained from

**Table 4. Determination of  $\Delta_{JK}^*$ ,  $\Delta_K^*$ ,  $\delta_K^*$ ,  $c_1$ , and  $c_2^{a,b}$**

$v_{24}$	$\Delta_{JK}/\text{kHz}$		$\Delta_K/\text{kHz}$		$\delta_K/\text{kHz}$	
	obs.	obs. − calc.	obs.	obs. − calc.	obs.	obs. − calc.
0	−1.9352	−0.001	−0.035	−0.274	10.9754	−0.045
1	−2.9304	−0.006	1.060	0.146	10.9641	−0.0351
2	−2.7775	0.001	0.942	0.174	11.3155	0.044
3	−2.7914	0.011	0.887	0.095	11.4438	0.165
4	−2.7914	0.020	0.840	0.038	11.5190	0.237
5	−2.8143	0.005	1.005	0.195	11.5487	0.265
6	−2.823	0.002	1.13	0.315	11.533	0.247

<sup>a</sup> $\Delta_{JK}^* = -2.882(5)$  kHz;  $\Delta_K^* = 0.872(68)$  kHz;  $\delta_K^* = 11.30(13)$  kHz;  $c_1 = 2.729(24)$  kHz;  $c_2 = 0.98(85)$  kHz. <sup>b</sup> $c_1$ ,  $\Delta_{JK}^*$ , and  $\Delta_K^*$  were determined from a simultaneous fit of the observed values of  $\Delta_{JK}$  and  $\Delta_K$ , whereas  $c_2$  and  $\delta_K^*$  were determined from a fit of the observed values of  $\delta_K$ ; see text. Uncertainties represent one standard deviation.

this fit. The standard deviation obtained for  $\Delta_{JK}^*$  (0.005 kHz) and  $c_1$  (0.024 kHz) are smaller than the accuracy of  $\Delta_K^*$  (0.068 kHz). This is due mainly to the higher experimental accuracy of the  $\Delta_{JK}$  constants (Table 1).

Because  $\delta_K$  behaves in another way than  $\Delta_{JK}$  and  $\Delta_K$ , this parameter was fitted separately to eq 7c with the results displayed in Table 4.  $\delta_K^* = 11.30(13)$  and  $c_2 = 0.98(85)$  kHz were obtained in this manner. One standard deviation of  $c_2$  (0.85 kHz) is of the same order of magnitude as  $c_2$  (0.98 kHz) itself. However, the fact that  $c_2$  is somewhat less than half the value of  $c_1$  is what one should expect from eqs 5c–5e.

**Quantum Chemical Calculations.** The low barrier to planar ring of 49(8) J/mol motivated us to test several quantum chemical methods to see if they were capable of predicting a barrier this low, as well as the puckering frequency ( $\nu_{24}$ ) of 92(15)  $\text{cm}^{-1}$ . Both ab initio and DFT methods were explored. The calculations were undertaken using the Gaussian 09<sup>16</sup> and Molpro<sup>17</sup> programs running on the Abel cluster in Oslo.

The ab initio methods employed were Hartree–Fock (HF), Møller–Plesset second-order perturbation method, MP2,<sup>18</sup> the coupled cluster method with single and double excitations, CCSD,<sup>19</sup> as well as the CCSD(T)<sup>20</sup> and CCSD(T)-F12<sup>21,22</sup> procedures which include perturbative triplets. The F12 treatment<sup>23</sup> is designed to quickly incorporate the cusp condition<sup>24</sup> and thus converges much more quickly with basis set size. The frozen-core approximation was used in all these calculations. The DFT methods were M06-2X<sup>25</sup> and B3LYP.<sup>26,27</sup> Most of the MP2 and all DFT calculations were performed using Gaussian 09, whereas Molpro was used for the CCSD, CCSD(T), and CCSD(T)-F12 as well as for some MP2 calculations. Dunning's wave functions<sup>28</sup> of double-, triple-, quadruple-, and quintuple- $\zeta$  quality, sometimes augmented with diffuse functions, were employed. The default convergence criteria of Gaussian and Molpro (less than about 1 J/mol) were observed in all calculations.

The planar ring equilibrium conformation, which has  $C_s$  symmetry, must be the maximum of the potential-energy hypersurface, while the minimum has a nonplanar ring ( $C_1$  symmetry), according to the experimental findings above. The energy difference between a planar ring ( $C_s$ ) and a nonplanar ring ( $C_1$ ) conformation is thus the barrier to planar ring. The

lowest vibrational fundamental frequency is the puckering vibration,  $\nu_{24}$ . The computation of vibrational frequencies is considerably more costly than the calculation of an optimized structure, and vibrational frequencies were only obtained for the less demanding calculations.

**HF and MP2 Results.** HF calculations employing the quadruple- $\zeta$  cc-pVQZ wave function and assuming  $C_1$  symmetry for 2-oxazoline refined to a planar-ring  $C_s$  conformation. The resulting structure (in Cartesian coordinates) is shown in Table S8 of the Supporting Information. HF calculations are thus unable to reproduce the barrier to planar ring in this compound.

MP2/cc-pVTZ calculations predicted a *nonplanar* ring for 2-oxazoline. The O2–C3–C4–N5 dihedral angle, which can conveniently be taken to describe deviation from the planar ring, was predicted to be  $6.5^\circ$  (Supporting Information Table S9). The lowest harmonic vibrational frequency essentially associated with the torsion about the C2–C3 bond (puckering) was  $47.7\text{ cm}^{-1}$  compared to the experimental puckering vibration of  $92(15)\text{ cm}^{-1}$ .

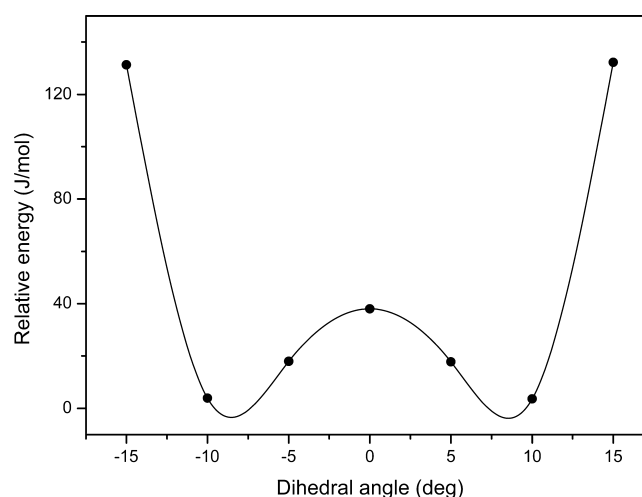
The transition state was searched for using the transition-state option of Gaussian 09. This state must have a planar ring ( $C_s$  symmetry), which was indeed found (Supporting Information Table S10). This first-order transition state has one imaginary frequency of  $-33.8i\text{ cm}^{-1}$  (Supporting Information Table S10). The electronic MP2 barrier height is as low as 11 J/mol, as calculated from entries in Supporting Information Tables S9 and S10, lower than experiment ( $49(8)\text{ J/mol}$ ).

The encouraging result obtained by the MP2 method with a wave function of triple- $\zeta$  quality prompted us to test the dependency of this method on the quality of the basis set by performing computations using basis functions of quadruple- and quintuple- $\zeta$  qualities.

The MP2/cc-pVQZ results for the  $C_1$  symmetry conformation are shown in Supporting Information Table S11, while the results of the  $C_s$  computations are listed in Supporting Information Table S12. Not only the optimized structure but also vibrational frequencies and the quartic centrifugal distortion constants were calculated for the  $C_1$  species (Supporting Information Table S11) at this level of theory. The O2–C3–C4–N5 dihedral angle is  $8.8^\circ$  (Supporting Information Table S11), the barrier to planar ring is 39.6 J/mol, and the puckering frequency is  $65.5\text{ cm}^{-1}$ . This barrier is close to experimental value ( $49(8)\text{ J/mol}$ ), whereas the puckering frequency deviates from experiment ( $92(15)\text{ cm}^{-1}$ ).

The energy dependence of the O2–C3–C4–N5 dihedral angle was computed at this level of theory. The dihedral angle was stepped from  $-15^\circ$  to  $+15^\circ$  in  $5^\circ$  intervals. All other structural parameters were optimized. The resulting potential function is shown in Figure 5. This function has its maximum at the expected  $C_s$  symmetry (planar ring conformation).

The results of the quintuple- $\zeta$  MP2/cc-pVSZ computations are displayed in Supporting Information Tables S13 and S14. They predict 61 J/mol for the barrier,  $61\text{ cm}^{-1}$  for the puckering vibration, and  $9.9^\circ$  for the O2–C3–C4–N5 dihedral angle. It turned out (see also below) that the MP2 method is the only method that unambiguously predicts a nonplanar ring conformation for 2-oxazoline. We consider the MP2/cc-pVSZ structure of the  $C_1$  conformation to be the best structure obtained in the present calculations, and it is therefore listed in Table 5 together with the rotational constants calculated from



**Figure 5.** Relative MP2/cc-pVQZ energy versus the O2–C3–C4–N5 dihedral angle. Note that the energy is given in J/mol. It is seen that a dihedral angle of about  $8^\circ$  ( $C_1$  conformation) represents the minimum. The  $C_s$  conformation (O2–C3–C4–N5 dihedral angle is zero) is 39.6 J/mol higher in energy than the  $C_1$  conformation; see text.

this structure and the MP2/cc-pVQZ quartic centrifugal distortion constants.

Some comments are warranted: The MP2/cc-pVSZ rotational constants (Table 5) are *larger* than the ground-state rotational ( $r_0$ ) shown in Table 1 by 92.1, 65.1, and 44.4 MHz in the cases of A, B, and C, respectively. Larger  $r_e$  rotational constants than the  $r_0$  counterparts are expected because  $r_e$  bond lengths, which are close to the MP2/cc-pVSZ bond lengths, are generally shorter than the  $r_0$  bond lengths resulting in larger  $r_e$  rotational constants.

It has not been possible for cost reasons to calculate the differences between the  $r_e$  and  $r_0$  rotational constants at the very high MP2/cc-pVSZ level of theory. However, such calculations were performed above at the much lower MP2/cc-pVTZ level (Supporting Information Table S9). These differences obtained from this table are 86.7, 97.1, and 77.1 MHz in the cases of the A, B, and C rotational constants, respectively, quite different from observations (92.1, 65.1, and 44.4 MHz).

The planar moment,  $P_c$ , calculated from the MP2/cc-pVSZ rotational constants of Table 5, is  $3.31 \times 10^{-20}\text{ u m}^2$ , close to the experimental value of the ground vibrational state shown in Table 1 ( $3.295\,660(26) \times 10^{-20}\text{ u m}^2$ ).

The MP2/cc-pVSZ principal axes dipole moment components are  $\mu_a = 1.199$ ,  $\mu_b = 1.328$ ,  $\mu_c = 0.009\text{ D}$ , and the total dipole moment is  $\mu_{\text{tot}} = 1.789\text{ D}$ . The reported experimental values obtained for the ground vibrational state are  $\mu_a = 1.14(1)$ ,  $\mu_b = 1.35(1)$ , and  $\mu_{\text{tot}} = 1.77(1)\text{ D}$ . The  $c$ -component of the dipole moment of 2-oxazoline in the ground vibrational state was found experimentally to be zero,<sup>1</sup> as noted above. This was taken as an indication that 2-oxazoline has a planar ring.<sup>1</sup> The theoretical dipole moment refers to an approximate equilibrium structure that is nonplanar, whereas the experimental dipole moment has been obtained for the ground vibrational state. The dipole moments are thus defined differently. However, the average structure of the zero-point vibrating molecule is effectively planar, and this is likely to lead to an experimental determination of a value of zero for  $\mu_c$  and the absence of  $c$ -type rotational transitions.

Table 5. MP2 Structure,<sup>a</sup> Rotational Constants,<sup>a</sup> and Quartic Centrifugal Distortion Constants<sup>b</sup> of 2-Oxazoline

bond length (pm)		angle (deg.)		dihedral angle (deg.)	
C1–O2	135.4	O2–C1–N5	120.1	N5–C1–O2–C3	−5.1
C1–C5	126.9	O2–C1–H6	114.5	H6–C1–O2–C3	175.3
C1–H6	107.9	N5–C1–H6	125.3	O2–C1–N5–C4	−1.6
O2–C3	144.8	C1–O2–C3	104.8	H6–C1–N5–C4	177.9
C3–C4	153.5	O2–C3–C4	104.0	C1–O2–C3–C4	8.9
C3–H7	108.7	O2–C3–H7	107.6	C1–O2–C3–H7	−111.0
C3–H8	108.4	O2–C3–H8	107.9	C1–O2–C3–H8	130.5
C4–N5	147.2	C4–C3–H7	112.9	O2–C3–C4–N5	−9.9
C4–H9	108.6	C4–C3–H8	114.1	O2–C3–C4–H9	−129.3
C4–H10	108.8	H7–C3–H8	109.8	O2–C3–C4–H10	108.0
		C3–C4–N5	104.8	H7–C3–C4–N5	106.4
		C3–C4–H9	112.6	H7–C3–C4–H9	−12.9
		C3–C4–H10	112.6	H7–C3–C4–H10	−135.7
		N5–C4–H9	109.9	H8–C3–C4–N5	−127.3
		N5–C4–H10	108.7	H8–C3–C4–H9	113.4
		H9–C4–H10	108.2	H8–C3–C4–H10	−9.3
		C1–N5–C4	105.3	C3–C4–N5–C1	7.2
				H9–C4–N5–H1	128.4
				H10–C4–N5–C1	−113.4
Rotational Constants (MHz)					
A = 8565.5		B = 8187.3		C = 4428.5	
Centrifugal Distortion Constants (kHz)					
$\Delta_{\text{I}} = 2.81$		$\Delta_{\text{JK}} = -1.47$		$\Delta_{\text{K}} = -0.491$	
				$\delta_{\text{I}} = 0.0147$	
				$\delta_{\text{I}} = 10.63$	

<sup>a</sup>cc-pV5Z basis set. <sup>b</sup>cc-pVQZ basis set; see text.

The vibration–rotation constants (the  $\alpha$ 's)<sup>29</sup> obtained from the entries of Table 1 by subtracting the rotational constants of the first excited state from the rotational constants of the ground vibrational state, are  $\alpha_A = -3.20$ ,  $\alpha_B = -12.62$ , and  $\alpha_C = -22.38$  MHz. The corresponding MP2/cc-pVTZ values are all positive and have much larger absolute values (Supporting Information Table S9) leaving a comparison meaningless.

The experimental quartic centrifugal distortion constants of the ground vibrational state are (Table 1)  $\Delta_J = 2.664(45)$ ,  $\Delta_{JK} = -1.9352(12)$ ,  $\Delta_K = -0.035(23)$ ,  $\delta_J = 0.019883(25)$ , and  $\delta_K = 10.9754(10)$  kHz for the ground vibrational state. Their MP2/cc-pVQZ equivalents are 2.81, –1.47, –0.491, 0.00147, and 10.63 kHz, respectively (Table 5). Two of the theoretical centrifugal distortion constants,  $\Delta_J$  and  $\delta_K$ , are thus in good agreement with their experimental equivalents, while large differences are seen for the three remaining constants  $\Delta_{JK}$ ,  $\Delta_K$ , and  $\delta_J$ . More refined calculations than MP2/cc-pVQZ are clearly needed to reproduce the experimental centrifugal distortion constants, but this is beyond our present possibilities.

**CCSD Results.** CCSD/cc-pVTZ, CCSD/cc-pVQZ, CCSD/aug-cc-pVQZ, CCSD(T)/cc-pVTZ, and CCSD(T)/cc-pVQZ, computations yielded practically the same energies (differences less than 2 J/mol) for the  $C_1$  and  $C_s$  conformations (Supporting Information Tables S15–S24). There is a tendency in these calculations that the planar-ring form has a slightly lower energy than the nonplanar conformation. The  $C_1$  and  $C_s$  structures are identical within the round-off criteria of Molpro. Vibrational frequencies could be obtained in several cases (Supporting Information Tables S15–S16 and S18). The lowest vibrational fundamental (puckering) varied from 40.3 to 66.9  $\text{cm}^{-1}$  in these calculations. It is concluded that CCSD and CCSD(T) calculations with triple- and quadruple- $\zeta$  wave functions erroneously tend to predict a  $C_s$  conformation for 2-oxazoline.

The CCSD(T)-F12 method using a double- $\zeta$  wave function augmented with diffuse functions (aug-cc-pVDZ) predicts that  $C_1$  structure is 8.5 J/mol lower in energy than  $C_s$  structure (Supporting Information Table S25 and S26). However, the same method using the aug-cc-pVTZ wave function predicts that the barrier to planar ring is 5.5 J/mol (Supporting Information Tables S27 and S28) and the O2–C3–C4–N5 dihedral angle is 6.4°, almost the same as the MP2/cc-pVTZ result. It remains to be seen whether this method with larger basis sets than employed here will lead to a more correct value for the barrier.

**DFT Calculations.** B3LYP/cc-pVQZ (Supporting Information Table S29) and M06-2X/cc-pVQZ (Supporting Information Table S30) calculations both refined to a planar ring conformation.

## CONCLUSIONS

Previously, 2-oxazoline was determined to have a planar ring equilibrium conformation.<sup>1</sup> Our present microwave analysis of the rotational constants of the ground and six excited states of the ring puckering vibration reveals that 2-oxazoline has a nonplanar ring equilibrium conformation in contrast to the earlier work.<sup>1</sup> A potential function  $V(z) = 38.8(z^4 - 0.65z^2)$   $\text{cm}^{-1}$ , where  $z$  is a dimensionless reduced puckering coordinate, has been derived. This function yields very good agreement between calculated and observed rotational constants, especially for the lowest puckering states. The barrier to ring planarity is determined to be 49(8) J/mol. The ground-state energy level is 35  $\text{cm}^{-1}$  above the barrier maximum. 2-Oxazoline is thus a rather rare example of a compound where the ground state is above the barrier maximum.

The microwave spectrum has been largely extended to include more than 4600 transitions of the ground state and six excited states of the ring-puckering vibration, and accurate



centrifugal distortion constants have been obtained for the first time. Three of the five Watson centrifugal distortion constants, namely,  $\Delta_{JK}$ ,  $\Delta_K$ , and  $\delta_K$ , should vary with the puckering state, whereas  $\Delta_J$  and  $\delta_J$  should be unaffected.  $\Delta_{JK}$  and  $\Delta_K$  indeed behave in accordance with theory, while deviations were seen for the three other centrifugal distortion constants.

The ability of HF, MP2, CCSD, CCSD(T), and CCSD(T)-F12 ab initio methods and several DFT methods to reproduce the rather low barrier to planar ring was explored. Only the MP2 method yielded a satisfactory prediction of the barrier. The CCSD and the CCSD(T) calculations predict a planar ring, whereas the energy differences between a planar and a nonplanar ring obtained in the CCSD(T)-F12 computations are so small that a definite conclusion cannot be made.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Microwave spectra of the ground and seven vibrationally excited states; results of the theoretical calculations, including electronic energies, molecular structures, dipole moments, harmonic and anharmonic vibrational frequencies, rotational and centrifugal distortion constants, rotation–vibration constants, and  $^{14}\text{N}$  nuclear quadrupole coupling constants. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b02528.

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### Notes

The authors declare no competing financial interest.

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