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Rotationally Resolved Electronic Excitation Spectra of the Ethoxy  $\tilde{B} \leftarrow \tilde{X}$  TransitionXue Qing Tan,<sup>†</sup> James M. Williamson,<sup>†</sup> Stephen C. Foster,<sup>‡</sup> and Terry A. Miller<sup>\*†</sup>

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High-resolution electronic excitation spectra of the  $0_0^0$  and the  $9_0^2$  bands of the near-UV electronic transition of the ethoxy radical have been recorded. The ethoxy radical was produced in a free-jet expansion by photodissociation of ethyl nitrite ( $C_2H_5ONO$ ). Both spectra have a linewidth of about 400 MHz. A complete rotational analysis of the spectrum indicates that the electronic transition of ethoxy is c-type (perpendicular) and the ground-state spin-rotation splittings are fully resolved, while the excited state spin-rotation splittings are not resolved. The spin-rotational parameters are compared to the corresponding spin-rotational parameters of the closely related radicals, methoxy and vinoxy.

## I. Introduction

The simple alkoxy and alkenyloxy radicals have both great fundamental and practical significance. They are often implicated as reactive intermediates in important combustion and atmospheric reactions. For example, methoxy,  $CH_3O$ , is ubiquitous in flame chemistry. Ethoxy,  $C_2H_5O$ , is thought to be a product in the reaction of methyl radical and formaldehyde,<sup>1–4</sup> and similarly vinoxy,  $C_2H_3O$ , likely is a product of the reaction of oxygen atoms and acetylene.<sup>5,6</sup>

Recently the detailed spectroscopy, and thereby geometric and electronic structure, of the simplest of these radicals,  $CH_3O$ , has been investigated in detail by microwave<sup>7</sup> and laser-induced fluorescence<sup>8–10</sup> (LIF) techniques. However, it is clear that, even with methoxy, some fundamental aspects of its spectroscopy and structure are not yet fully understood.<sup>11</sup> Spectroscopic work on the other radicals is considerably less advanced. Vinoxy is probably the next most studied; it has been detected by kinetic absorption spectroscopy,<sup>12</sup> LIF spectroscopy,<sup>5,13,14</sup> and IR spectroscopy<sup>15</sup> in a matrix. A rotational analysis<sup>14</sup> of its LIF spectrum has yielded considerable information about the radical's geometric and electronic structure.

The ethoxy radical and the next member of the series, isopropoxy radical,  $C_3H_7O$ , have received less detailed attention. Several years ago, vibronically resolved electronic spectra in the near-UV for each radical were reported.<sup>16–18</sup> Somewhat more recently partially rotationally resolved LIF spectra were reported<sup>19</sup> for each species. However, that resolution was insufficient to provide any significant amount of structural information.

In this paper, we report the jet-cooled LIF spectra of the  $\tilde{B}^2A' \leftarrow \tilde{X}^2A''$  electronic transition in the near-UV, with sufficient resolution to observe individual spin-rotation components of rotational lines. Our analysis provides accurate values for all three rotational constants in both the ground and excited  $\tilde{B}$  state, as well as the principal components of the spin rotation tensor in the ground state. The rotational constants are compared with *ab initio* structural predictions<sup>20</sup> for the ground state and are used to infer the geometric changes in the excited  $\tilde{B}$  state for which no *ab initio* calculations exist. (Note that we shall refer to the excited state in this transition as the  $\tilde{B}$  state, even though it has been sometimes referred to as the  $\tilde{A}$  state. As our analysis shows, there should be an as yet unobserved low-lying  $\tilde{A}^1A'$  state of ethoxy.)

The components,  $\epsilon_{ij}$ , of the spin-rotation tensor of ethoxy are compared with the previously measured values of the analogous quantities in methoxy<sup>7,21</sup> and vinoxy radicals.<sup>14</sup> Numerically, the values in ethoxy are much closer to those of methoxy than vinoxy. At first glance, this is quite surprising because in the ground state of methoxy, particularly  $\epsilon_{aa}$ , is thought<sup>21</sup> to be uniquely large because of an effect associated with the Jahn–Teller distortion of a degenerate electronic state. Since the substitution of a methyl group for hydrogen in methoxy to form ethoxy removes the electronic degeneracy, the value of  $\epsilon_{aa}$  in ethoxy might be expected to be much closer to that of the nondegenerate ground state of vinoxy. However, the converse experimental finding can be rationalized, given certain reasonable assumptions about the electronic structure of ethoxy and vinoxy.

## II. Experimental Section

The experimental arrangement has been described before<sup>10,19,22,23</sup> and so will only be briefly outlined here. The ethoxy radical was produced in a free-jet expansion by UV laser photolysis (ArF) of ethylnitrite. The ethylnitrite was synthesized following well-known procedures<sup>24</sup> and stored at  $-78^\circ\text{C}$  until used. A few Torr of ethylnitrite was entrained in the jet flow by passing high-pressure He ( $\sim 200$  psi) over a liquid sample maintained at a low temperature. The ethoxy radical was produced at the tip of the nozzle and then probed  $\sim 9$  mm downstream. The probe laser was a pulse amplified, Ar<sup>+</sup> pumped ring dye laser (Coherent 699-29 Autoscan), frequency doubled by an angle-tuned KDP crystal. The doubled radiation was separated from the fundamental with a UV filter. The total laser-induced fluorescence was collected and imaged through an optical slit to reduce the Doppler width of the spectral lines. Relative peak positions were calibrated by using an external low finesse etalon ( $\sim 475$  MHz FSR), while absolute positions were calibrated with an  $I_2$  spectrum. Both were recorded simultaneously with the ethoxy spectrum by using a portion of the cw dye laser output split off before pulse amplification and harmonic generation. Due to limitations of the Autoscan software in scanning the laser, the entire spectrum consists of about a dozen separate scans, which were combined according to the autoscan's wavemeter frequency readings. In this process an uncertainty of 200 MHz or less in relative fundamental frequency was introduced. This results in an experimental error in the spectral frequency measurements of about 400 MHz (in the UV).

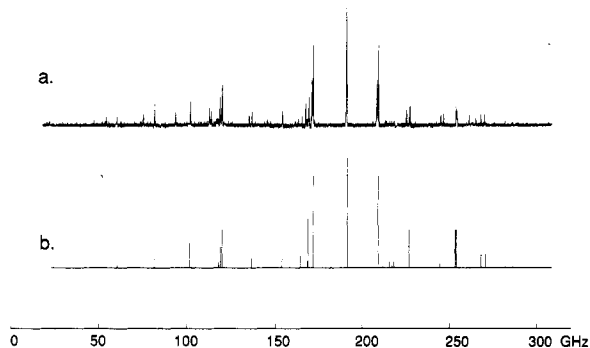
## III. Results and Analysis

The rotationally resolved  $0_0^0$  band of the ethoxy  $\tilde{B} \leftarrow \tilde{X}$  transition is shown in Figure 1a. About 35 lines can be identified

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**Figure 1.** (a) Experimental spectrum of the  $0_0^0$  band of  $\bar{B} \leftarrow \bar{X}$  transition of ethoxy, shown in frequencies relative to 875 552.2 GHz. (b) Rigid rotor simulation of (a) with a c-type transition scheme. Note that most of the rigid rotor transitions are split in the experimental spectrum.

in the spectrum. The gross structure of the band is similar to that observed by Foster *et al.*<sup>19</sup> but the sensitivity and resolution is greatly improved in the current work. To analyze the spectrum, we start with the rigid, asymmetric rotor Hamiltonian,

$$\mathcal{H}_{ROT} = AN_x^2 + BN_y^2 + CN_z^2 \quad (1)$$

where  $N_x$ ,  $N_y$ , and  $N_z$  are components of the rotational angular momentum  $N$ , which satisfies  $N = J - S$ .  $J$  is the total angular momentum of the molecule (excluding nuclear spin) and  $S$  is the electron spin angular momentum.  $A$ ,  $B$ , and  $C$  are rotational constants defined in the usual way. The initial values of  $A$ ,  $B$ , and  $C$  were estimated by using Gonzalez *et al.*'s *ab initio* geometry.<sup>20</sup> Following Foster *et al.*'s<sup>19</sup> suggestion, we first attempted to fit the spectrum by using a c-type transition scheme. As can be seen in Figure 1b, a decent fit of the majority of lines in the spectrum can be achieved. However, as can also be seen in Figure 1, almost all the rigid rotor transitions are further split into two components. These splittings were not observed in previous studies.<sup>16-19</sup> Upon closer examination, the splittings were found to correlate with the ground-state quantum numbers. Those transitions with  $K_a'' = 0$  seem to have splittings around 1 GHz; those with  $K_a'' = 1$  levels seem to have splittings around 9 GHz.

In ethoxy, two mechanisms can cause these additional splittings of the rotationally resolved transitions. One is methyl group internal rotation; the other is the spin-rotation interaction. The former can be likely excluded, since the potential that hinders the methyl group internal rotation in ethoxy is expected to be on the same order as or greater than that in ethane, which is about 1000  $\text{cm}^{-1}$ . Thus the splittings caused by methyl group internal rotation should be very small and could not be resolved under the current resolution. We thus focus our attention on the spin-rotation coupling.

According to Brown and Sears,<sup>25</sup> the following Hamiltonian can be used to describe the spin-rotation coupling in a  $C_s$  molecule

$$\mathcal{H}_{SR} = \epsilon_{aa}N_xS_z + \epsilon_{bb}N_yS_x + \epsilon_{cc}N_zS_y + \frac{1}{4}(\epsilon_{ab} + \epsilon_{ba})(N_xS_x + S_xN_x + N_yS_y + S_yN_y) \quad (2)$$

The total Hamiltonian is then

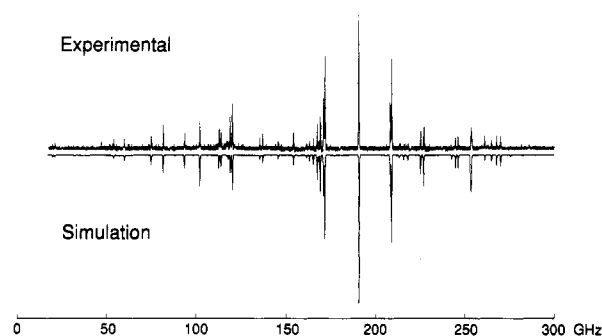
$$\mathcal{H} = \mathcal{H}_{ROT} + \mathcal{H}_{SR} \quad (3)$$

This Hamiltonian can be diagonalized by using either the Hund's case (a) basis set  $|JPM_J, S\Sigma\rangle$  or the Hund's case (b) basis set  $|NKS, JM_J\rangle$ . We performed calculations in both basis sets and as expected the results are identical. Typically it is much easier to program with the case (a) basis set, but the quantum numbers associated with the case (b) basis set are more intuitive in this problem. The matrix elements for  $\mathcal{H}$ , eq 3, have been given in the case (b) basis set by Raynes.<sup>26</sup> The intensity formula can be derived by using tensor algebra and the results are given in the appendix.

**TABLE I: Molecular Constants of Ethoxy<sup>a,b</sup>**

	$0_0^0$	$9_0^2$	calcd <sup>c</sup>
$A''$	$39.52 \pm 0.04$	$39.48 \pm 0.04$	39.32
$B''$	$9.61 \pm 0.06$	$9.59 \pm 0.02$	9.59
$C''$	$8.51 \pm 0.09$	$8.51 \pm 0.03$	8.51
$\epsilon_{aa}''$	$-9.44 \pm 0.26$	$-9.31 \pm 0.15$	
$\epsilon_{bb}''$	$-1.02 \pm 0.26$	$-1.06 \pm 0.14$	
$\epsilon_{cc}''$	$-0.02 \pm 0.20$	$-0.01 \pm 0.13$	
$ \epsilon_{ab}'' + \epsilon_{ba}'' /2$	$2.65 \pm 1.3$	$2.60 \pm 0.36$	
$A'$	$33.49 \pm 0.05$	$34.02 \pm 0.29$	33.48
$B'$	$9.33 \pm 0.04$	$9.33 \pm 0.03$	9.35
$C'$	$8.02 \pm 0.05$	$8.12 \pm 0.03$	8.02
$D_K'$		$0.018 \pm 0.07$	
$D_{NK}'$		$0.25 \pm 0.03$	
$H_{KN}'$		$0.051 \pm 0.007$	
origin, $\text{cm}^{-1}$	$29210.207 \pm 0.006$	$30380.478 \pm 0.006$	

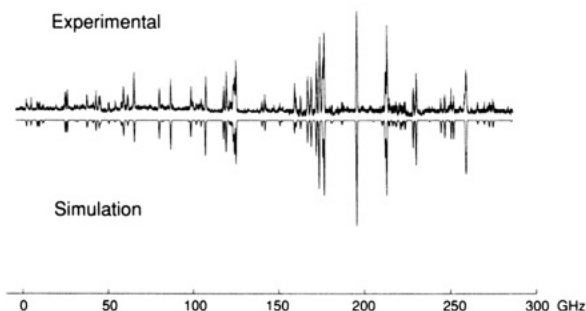
<sup>a</sup> The units are GHz unless otherwise indicated. <sup>b</sup> Indicated errors are one standard deviation. <sup>c</sup> Calculation of the ground-state rotational constants is based on Gonzalez *et al.*'s *ab initio* geometry<sup>20</sup> (at UHF/6-31G\* level) with  $\angle\text{OCC}$  changed from  $113.3^\circ$  to  $114.4^\circ$ . Calculation of the excited-state rotational constants is also based on the above geometry but with  $\angle\text{OCC} = 107.5^\circ$  and the O-C bond length equal to 1.558 Å.



**Figure 2.** Experimental spectrum of the  $0_0^0$  band of  $\bar{B} \leftarrow \bar{X}$  transition of ethoxy (upper half) along with a calculated spectrum (lower half, plotted downward) including ground-state spin-rotation coupling. The frequency scale is the same as in Figure 1.

Based on the dependence of the observed splittings on the ground-state quantum numbers, the ground-state spin-rotation rotation coupling is expected to be dominant. By inspection of the matrix elements of  $\mathcal{H}$ ,  $|\epsilon_{aa}''|$  could be estimated from the spectrum to be about 9 GHz and  $|\epsilon_{bb}'' + \epsilon_{cc}''|$  about 1 GHz. These assumptions were quickly confirmed by the actual simulation. With ground-state spin-rotation terms "turned on", we can account for all the observed transitions in the  $0_0^0$  band. This also means that the excited-state spin-rotation splittings are not resolved in the spectrum. We did, however, note that the experimental widths ( $\approx 400$  MHz) of the lines are about 50% greater than expected and hints of structure are discernible on some of the transitions. We attribute these effects to excited-state spin-rotation splittings just below our experimental resolution.

The final fit of the  $0_0^0$  band is performed with all the 35 observed transitions included. The maximum  $J$  and  $K$  quantum numbers accessed are 3.5 and 2, respectively, in both states. The excited-state spin-rotation constants were kept at zero since no splittings caused by these terms were resolved. The fit has a standard deviation of 105 MHz. This number is quite acceptable if one considers the 400-MHz linewidths. The molecular constants obtained in the fit are listed in Table I. A simulated spectrum of the  $0_0^0$  band, along with the experimental spectrum, is shown in Figure 2. In the simulation, two different rotational temperatures were used. The portion of the simulation with relative frequencies less than 105 GHz has a rotational temperature of 2.0 K; the portion of the simulation with relative frequencies larger than 105 GHz has a rotational temperature of 1.5 K. The variation of temperature in the spectrum is thought to be the



**Figure 3.** Experimental spectrum of the  $9_0^2$  band of  $\tilde{B} \leftarrow \tilde{X}$  transition of ethoxy (upper half) along with a calculated spectrum (lower half, plotted downward), shown in frequencies relative to 910 581.2 GHz.

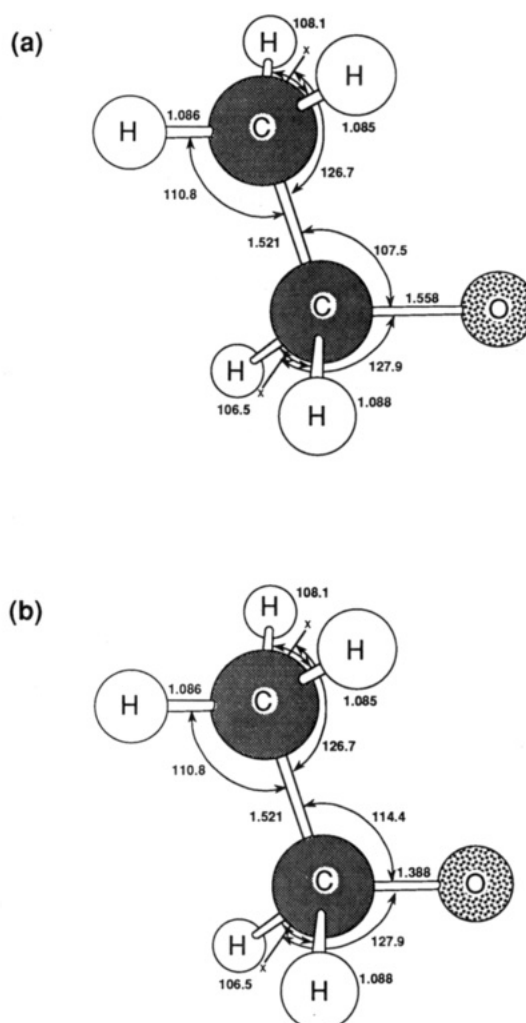
result of variation of the photolysis laser power during the scanning of the spectrum. A Gaussian line profile with FWHM of 400 MHz is used to convolute the stick spectrum. As can be seen in Figure 2, excellent agreement between the experiment and theory is achieved.

Two rotationally resolved spectra of the  $9_0^2$  band (the O–C stretch) of the ethoxy  $\tilde{B} \leftarrow \tilde{X}$  transition were also recorded. One spectrum is relatively cold, with a rotational temperature similar to that of the  $0_0^0$  band. The other spectrum is about 2–3 degrees hotter. The colder  $9_0^2$  spectrum can be analyzed in a straightforward way because it has a structure similar to that of the origin band. Obviously, with two quanta in the vibrational mode, the upper state of the  $9_0^2$  band should also have  $A'$  symmetry; *i.e.*, the rotational band type of the  $9_0^2$  transition is still c-type. This is confirmed in the rotational analysis. Also with a combination of a higher temperature and two quanta in the O–C stretch, the  $9_0^2$  band demonstrates significant distortion effects. To obtain a good fit of the spectra, three distortion terms,  $D_K$ ,  $D_{NK}$ , and  $H_{KN}$ , were added to the excited state Hamiltonian. The Watson  $A$ -reduction formalism<sup>27</sup> for the distortion Hamiltonian was used. The final fit of the  $9_0^2$  band was performed for 52 transitions, with  $J_{\max} = 4.5$  and  $K_{\max} = 2$  for both states. The standard deviation was 92 MHz. A calculated spectrum of the  $9_0^2$  band along with the experimental spectrum (the hotter one) is shown in Figure 3. The molecular constants are listed in Table I. Note that, since the coupling between the methyl group internal rotation and a vibration in a molecule is usually strong and complicated,<sup>28</sup> the Watson  $A$ -reduction Hamiltonian may not be an entirely appropriate description of the rovibrational coupling in ethoxy. Consequently the physical interpretation of the distortion parameters listed in Table I should be regarded with some caution.

#### IV. Discussion

**A. Rotational Constants and Geometry.** Foster *et al.*<sup>19</sup> have discussed the point group symmetries of the  $\tilde{X}$  and the  $\tilde{B}$  states of ethoxy. On the basis of the correlation with methoxy ( $\text{OCH}_3$ ) and the c-type perpendicular transition observed in the  $\tilde{B} \leftarrow \tilde{X}$  rotational spectrum, they concluded that the ground electronic state of ethoxy has  $A''$  symmetry (in  $C_s$  point group) and the excited  $\tilde{B}$  state has  $A'$  symmetry ( $C_s$ ). The present rotational analysis confirmed their results.

Typically it is not possible to determine the geometry of a polyatomic molecule by using only the three rotational constants. But with a good *ab initio* calculation, it is possible to "fine tune" the theoretical geometry with measured rotational constants so that it could be very close to the real geometry of the molecule. In the case of ethoxy, Gonzalez *et al.*'s *ab initio* geometry<sup>20</sup> gives  $A = 38.73$  GHz,  $B = 9.70$  GHz, and  $C = 8.57$  GHz for the ground electronic state, very close to the corresponding measured values listed in Table I. Thus only slight corrections are needed to improve the *ab initio* geometry. By examination of the discrepancies between the theoretical rotational constants and the



**Figure 4.** Suggested "best" geometries for ethoxy, (a)  $\tilde{B}$  state; (b)  $\tilde{X}$  state. "Dummy" atoms (marked as "x") are used to illustrate certain angles for the convenience of constructing  $Z$  matrices. These dummy atoms lie at the intersection of the OCC plane and HCH plane of the carbon to which x is bonded. Bond lengths are in angstroms and angles in degrees.

measured rotational constants, it is quickly realized that a small change in  $\angle\text{OCC}$  is sufficient to make the calculated and experimental rotational constants agree. The  $\angle\text{OCC}$  was determined to be  $114.4^\circ$  instead of  $113.3^\circ$  for the ground state. It is important to remark that this geometry is not a direct experimental determination but represents the best estimation from a combination of experimental and *ab initio* results. The new set of calculated constants are listed in Table I, with the corresponding molecular geometry being depicted in Figure 4.

For the excited state of ethoxy, the above procedure cannot be applied directly because no *ab initio* calculation is available for this state. However, on the basis of considerable evidence for analogous radicals,<sup>19</sup> it is quite likely that the decrease in the  $A$  rotational constant (from 39.48 to 33.49 GHz) observed upon electronic excitation results from a significant increase in the O–C bond length. This kind of decrease can hardly be explained by the lengthening of the C–C bond or the C–H bonds since the electronic transition is mostly localized near the oxygen atom. To have a rough idea of how much the O–C bond has increased in the  $\tilde{B} \leftarrow \tilde{X}$  transition, we performed a calculation to reproduce the measured  $\tilde{B}$  state, vibrationless level rotational constants by varying only the O–C bond length and  $\angle\text{OCC}$  while keeping all other geometric parameters the same as those found in the ground-state *ab initio* calculation. We found that with an O–C bond length of 1.558 Å and an  $\angle\text{OCC}$  of  $107.5^\circ$ , the measured  $\tilde{B}$  state rotational constants can be satisfactorily reproduced (see Table

I). The corresponding geometry is depicted in Figure 4. Obviously this geometry should be regarded with the same caution as or greater caution than that for the  $\tilde{X}$  state, but we do see an increase of the O—C bond length by the amount of 0.17 Å, which is likely close to reality. Concurrent with the lengthening of the O—C bond, its strength should be reduced. Consequently the excited-state O—C stretch vibrational frequency  $\nu_9$  should be significantly less than the corresponding ground-state vibrational frequency. Inoue *et al.*<sup>16</sup> measured  $\omega_e'' = 1074 \text{ cm}^{-1}$  and  $\omega_e' = 606 \text{ cm}^{-1}$  for  $\nu_9$ , in accord with the above argument.

**B. Spin-Rotation Interaction.** Since ethoxy can be considered as methoxy with one of its hydrogen atoms substituted by a methyl group, it is helpful to refer to methoxy when discussing the electronic properties and molecular parameters of ethoxy. In this case, substitution of a hydrogen by a methyl group does not alter the gross features of the transition. But the substitution can be expected to significantly alter the fine structure, since the methyl group addition breaks the  $C_{3v}$  point group symmetry of methoxy. Any effect should be more pronounced in the ground electronic state, since the  $\tilde{X}$  state of methoxy is orbitally degenerate and this degeneracy must be lifted when the symmetry is broken. The  $\tilde{X}^2E$  state in methoxy is predicted to split into an  $A'$  and an  $A''$  state after the H/CH<sub>3</sub> replacement to form ethoxy. The rotational analysis shows that the  $A''$  state is the ground state of ethoxy. Furthermore, the breaking of the  $C_{3v}$  symmetry will quench the electronic angular momentum and there should be no observable first-order spin-orbit coupling in ethoxy.

Despite these differences in electronic structure, methoxy and ethoxy are observed to have larger than normal spin-rotation coupling constants in the ground state. In fact, a simple isotopic scaling relationship, derived by Brown *et al.*,<sup>29</sup> can be used to demonstrate a surprising similarity between the spin rotation constants of the two radicals. If the replacement of a hydrogen atom by a methyl group is viewed as an "isotopic substitution", the following relation holds:

$$\mathbf{I}^* \cdot \boldsymbol{\epsilon}^* = \mathbf{I} \cdot \boldsymbol{\epsilon} \quad (4)$$

where  $\mathbf{I}$  and  $\boldsymbol{\epsilon}$  are respectively the moment of inertia and spin-rotation tensors of methoxy and the asterisks denote the equivalent tensors for ethoxy. Since the  $a$ -principal axis of ethoxy is rotated from that of methoxy by 35.6° in the O—C—C plane, the matrix product on the right-hand side of eq 4 must also be rotated by 35.6°. Thus in the principal axis system of ethoxy, eq 4, should be rewritten as

$$\mathbf{I}^* \cdot \boldsymbol{\epsilon}^* = \mathbf{R}^{-1} \cdot \mathbf{I} \cdot \boldsymbol{\epsilon} \cdot \mathbf{R} \quad (5)$$

where  $\mathbf{R}$  is the three-dimensional rotation matrix. For methoxy, Liu *et al.*<sup>21</sup> have shown that  $\epsilon_{aa} = -40.57 \text{ GHz}$  and  $\epsilon_{bb} = \epsilon_{cc} = -1.30 \text{ GHz}$  in the  $\tilde{X}$  state. In the  $\tilde{A}$  state,  $\epsilon_{aa} = -0.01 \text{ GHz}$  and  $\epsilon_{bb} = \epsilon_{cc} = 0.37 \text{ GHz}$ . By use of eq 5 and the corresponding rotational constants of both methoxy and ethoxy, the "isotopic" spin-rotational parameters for ethoxy can be computed. The results are summarized in Table II.

As can be seen in Table II, the "calculated" spin-rotation parameters for the ground state of ethoxy are actually very close to those corresponding experimentally determined values. Considering the fact that methyl substitution is not strictly an isotopic substitution, the agreement is remarkably good. Since the isotopic transformation we performed accounts for the kinematic aspect of the spin-rotation interaction, it then seems that the electronic aspect of the spin-rotation interaction in the two radicals is very similar. However, as discussed earlier, the electronic structure of methoxy is rather different from that of ethoxy. As a matter of fact, Liu *et al.*<sup>21</sup> have invoked a significant Jahn-Teller interaction (presumably in the  $\nu_6$  vibration) in order to explain the abnormally large spin-rotation constant  $\epsilon_{aa}$  in the ground state of methoxy. This type of interaction is obviously absent in

**TABLE II: Spin-Rotation Coupling Constants for Ethoxy<sup>a</sup> (GHz)**

	exptl	calcd
$\epsilon_{aa}''$	$-9.44 \pm 0.26$	-7.57
$\epsilon_{bb}''$	$-1.02 \pm 0.26$	-1.18
$\epsilon_{cc}''$	$-0.02 \pm 0.20$	-0.40
$ \epsilon_{ab}'' + \epsilon_{ba}'' /2$	$2.60 \pm 1.30$	2.47
$\epsilon_{aa}'$		0.19
$\epsilon_{bb}'$		0.10
$\epsilon_{cc}'$		0.0
$ \epsilon_{ab}' + \epsilon_{ba}' /2$		0.17

<sup>a</sup> The experimental data are those measured for the  $0_0^0$  band. The calculated results are based on an isotopic transformation of the spin-rotation parameters of methoxy (see text). According to Brown and Sears,<sup>25</sup> the measurable spin-rotation coupling parameters,  $\epsilon_{aa}$  etc., should be written as  $\tilde{\epsilon}_{aa}$  etc., in order to distinguish them from the Cartesian components of the spin-rotation tensor. But in the case of ethoxy, the differences between  $\epsilon_{aa}$  and  $\tilde{\epsilon}_{aa}$  etc. are expected to be smaller than the experimental errors so that there is no need to distinguish between them.

ethoxy. Why then is there good agreement between the calculated and experimentally determined spin-rotation parameters for ethoxy?

This question is even more perplexing when one considers another closely related radical, vinoxy. The spin-rotation parameter  $\epsilon_{aa}$  for vinoxy has also been determined in a rotational analysis.<sup>14</sup> A calculation similar to that performed for ethoxy would predict  $|\epsilon_{aa}''| = 14 \text{ GHz}$ , while the measured value is only 0.75 GHz, a discrepancy of more than an order of magnitude. Obviously the "isotopic" prediction fails for vinoxy. This is not particularly surprising, since the electronic structure of vinoxy differs significantly from that of methoxy, due to its resonance structure with formyl methyl,<sup>30</sup> and we expect the components of the spin-rotation tensor to be sensitive to the electronic structure of a molecule.

As noted by Liu *et al.*,<sup>21</sup> the major contributions to the spin-rotation tensor are generally second-order. These second-order contributions,  $\epsilon_{xx}^{(2)}$ , to the diagonal spin-rotation tensor element can be written

$$\epsilon_{xx}^{(2)} = \epsilon_{xx}^{(2e)} + \epsilon_{xx}^{(2v)} \delta_{xx} \quad (6)$$

where

$$\epsilon_{xx}^{(2e)} = -2 \sum_{\alpha' \neq \alpha} \frac{\langle \alpha | a L_x | \alpha' \rangle \langle \alpha' | X L_x | \alpha \rangle + \langle \alpha | X L_x | \alpha' \rangle \langle \alpha' | a L_x | \alpha \rangle}{(E_\alpha - E_{\alpha'})} \quad (7)$$

and

$$\epsilon_{xx}^{(2v)} = -2 X_a a_{\alpha\alpha} \sum_{N' \neq N} \frac{[2|d_{NN'}|^2 \xi_{\alpha\alpha} + d_{NN'}(g_{NN'}^x)^* + (d_{NN'})^* g_{NN'}^x]}{(E_{\alpha N} - E_{\alpha N'})} \quad (8)$$

In the above  $a$  = spin-orbit coupling constant,  $\mathbf{L}$  = electronic orbital angular momentum with the expectation value of  $\mathbf{L}_z = \xi_{\alpha\alpha}$ , in the electronic state  $\alpha$ , and  $x$  = a principal inertial axis,  $a$ ,  $b$ , or  $c$ , and with  $X$  the corresponding rotational constant. Electronic states are denoted  $\alpha$  and vibrational ones  $N$ . The parameters  $d_{NN'}$  and  $g_{NN'}$  are defined in terms of integrals over vibronic eigenfunctions in a Jahn-Teller distorted state and vanish for a vibronically non-degenerate state. For a small or moderate Jahn-Teller effect as is expected in methoxy  $d_{NN'}$  is less than but approaches unity.

Physically, eqs 7 and 8 can be explained as follows. All three components of the spin-rotation tensor along the principal inertial axis<sup>31</sup> are dominated by second-order cross terms of the spin-

orbit and rotational coriolis interactions between different electronic states as was shown by Hougen.<sup>32</sup> Uniquely for Jahn–Teller distorted degenerate electronic states there is a second contribution,  $\epsilon_{aa}^{(2v)}$ , to the spin–rotation tensor component along the symmetry axis. Effectively this term arises from a cross product of the spin–orbit perturbation with electronic and vibrational coriolis perturbations between different vibrational states.

Since vibrational energy denominators are much smaller than the electronic ones,  $\epsilon_{aa}^{(2v)}$  is expected to be much larger than  $\epsilon_{aa}^{(2e)}$  when the former does not vanish. Indeed, Liu *et al.* explained the observed value of  $\epsilon_{aa}$  in methoxy (–40.5 GHz) by estimating  $\epsilon_{aa}^{(2v)} \approx -39.5$  GHz and  $\epsilon_{aa}^{(2e)} \approx -1.1$  GHz. For vinyloxy  $\epsilon_{aa}^{(2v)}$  vanishes and  $\epsilon_{aa}^{(2e)}$  would then be equivalent to  $\epsilon_{aa}^{(2e)}$ . The separation<sup>30</sup> between the lowest excited  $A'$  state and the  $A''$  ground state is roughly 10 000  $\text{cm}^{-1}$ . Using this value along with  $A = 2.1 \text{ cm}^{-1}$  and  $a = -145 \text{ cm}^{-1}$  (the OH value—likely an upper limit<sup>21</sup>) yields  $|\epsilon_{aa}| = 0.12 \text{ cm}^{-1}$ , in rough agreement with the observed value of 0.025  $\text{cm}^{-1}$ .

For ethoxy  $\epsilon_{aa}^{(2v)}$  must also vanish, but we note that in the limit of  $d$  tending to unity  $\epsilon_{aa}^{(2v)}$  becomes comparable to  $\epsilon_{aa}^{(2e)}$  except for the energy denominators. Then we conclude that, if the  $\epsilon_{aa}$ 's in methoxy and ethoxy are comparable, the electronic energy separation between the ground  $A''$  and excited low-lying  $A'$  state must be comparable to a vibrational interval. Indeed inserting into eq 7  $\langle A | aL_z | A'' \rangle = -145 \text{ cm}^{-1}$  and  $A = 1.3 \text{ cm}^{-1}$  yields the experimental value of  $\epsilon_{aa}$  if the summation is replaced by a one-term contribution with the energy denominator  $\approx 2300 \text{ cm}^{-1}$ . Since the posited value for  $\langle A | aL_z | A'' \rangle$  is likely an upper limit, this establishes a rough upper limit on the  $A'-A''$  splitting in ethoxy, a quantity of considerable interest, but one yet to be measured directly.

## V. Conclusion

We have recorded and analyzed LIF spectra of the jet-cooled ethoxy radical. We have obtained values for the three rotational constants in both the excited  $\tilde{B} A'$  state and the ground  $\tilde{X} A''$  state. The combination of our experimental rotational constants with recent *ab initio* calculations yields geometries for both electronic states.

In addition to the rotational structure, the fine structure is well resolved in our spectrum, leading to a determination of several components of the spin–rotation tensor in the ground state. The observed values are compared with previous results for the methoxy and vinyloxy radicals and the observed variations rationalized.

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## Appendix. The Intensity Formula

To derive the intensity formula (using the case b basis set) for transitions between rotational states described by eq 3 we start with asymmetric rotor transitions without spin splittings. Suppose the wavefunctions of two asymmetric rotor levels can be written as

$$|\tau' N' M'\rangle = \sum_{K'} a_{\tau' K'} |N' K' M'\rangle \quad (9)$$

$$|\tau'' N'' M''\rangle = \sum_{K''} a_{\tau'' K''} |N'' K'' M''\rangle$$

the line strength of the transition between these two levels is then

given by<sup>33</sup>

$$S(\tau' N'; \tau'' N'') = (2N'' + 1) \left| \sum_{K', K''} \sum_q a_{\tau' K'}^* a_{\tau'' K''} \mu(1, q) \langle N'' K'', 1q | N' K' \rangle \right|^2 \quad (10)$$

where  $\mu(1, q)$  is a spherical tensor component of the transition dipole moment and  $\langle N'' K'', 1q | N' K' \rangle$  are Clebsch–Gordan coefficients. Obviously only terms satisfying  $K' - K'' = q$  can contribute to the sum. For pure c-type transitions, the transition dipole moment lies in the y-axis direction. So  $\mu_x = \mu_z = 0$ , and  $\mu_y = \mu$ . Thus,  $\mu(1, 1) = -(\mu_x + i\mu_y)/2^{1/2} = -i\mu_y/2^{1/2}$ , and  $\mu(1, -1) = (\mu_x - i\mu_y)/2^{1/2} = -i\mu_y/2^{1/2}$ . The line strength becomes

$$S(\tau' N'; \tau'' N'') = \frac{1}{2} (2N'' + 1) \left| \sum_{K''} a_{\tau' K''-1} a_{\tau'' K''} \langle N'' K'', 1-1 | N' K''-1 \rangle + \sum_{K''} a_{\tau' K''+1} a_{\tau'' K''} \langle N'' K'', 11 | N' K''+1 \rangle \right|^2 \quad (11)$$

where  $|\mu|$  was set equal to 1 since its value does not affect the relative intensity. Now if the spin–rotation coupling is taken into account, the wavefunctions for the two rotational levels involved in the transition should be written as

$$|\tau' J' M'_j\rangle = \sum_{K'} a_{\tau' K'} \left| N' = J' - \frac{1}{2} K'; J' M'_j \right\rangle + \sum_{K'} b_{\tau' K'} \left| N' = J' + \frac{1}{2} K'; J' M'_j \right\rangle \quad (12)$$

$$|\tau'' J'' M''_j\rangle = \sum_{K''} a_{\tau'' K''} \left| N'' = J'' - \frac{1}{2} K''; J'' M''_j \right\rangle + \sum_{K''} b_{\tau'' K''} \left| N'' = J'' + \frac{1}{2} K''; J'' M''_j \right\rangle$$

By use of well-known tensor algebra,<sup>34</sup> it can be shown that the line strength of the transition between these two states is

$$S(\tau' J'; \tau'' J'') = \left| \sum_{N', N''} (-1)^{N''+S+J'+1} [(2J'+1)(2J''+1)]^{1/2} \times \left\{ \begin{matrix} N'' & J'' & S \\ J' & N' & 1 \end{matrix} \right\} S^{1/2}(\tau' N'; \tau'' N'') \right|^2 \quad (13)$$

where the quantity in braces is a 6- $j$  symbol.  $S(\tau' N'; \tau'' N'')$  is calculated by using eq 11. Note that  $N''$  and  $N'$  have to satisfy  $|N' - N''| \leq 1$  as well as  $N'' = J'' \pm 1/2$  and  $N' = J' \pm 1/2$ , respectively. So for  $J' = J''$ , four terms occur in the summation. For  $J' - J'' = \pm 1$ , only three terms occur in the summation. Finally, the relative intensity of the transition is given by the line strength multiplied by the Boltzmann factor  $\exp(-(E - E_0)/kT)$ , where  $E_0$  is the lowest ground-state rotational energy and  $E$  is the ground-state rotational energy of the transition.

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