

# Rotational spectra, conformational structures and dipole moments of 2-(ethylthio)ethanol by jet-cooled FTMW and ab initio calculations<sup>☆</sup>

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## Abstract

The rotational spectra of three low-energy conformers of 2-(ethylthio)ethanol also known as ethyl 2-hydroxyethylsulfide or hydroxyethyl ethyl sulfide (HOEES), together with the monosubstituted <sup>13</sup>C and <sup>34</sup>S isotopic forms of the two lowest energy conformers, have been measured in a molecular beam using a pulsed-nozzle Fourier-transform microwave spectrometer. To search for the likely conformational structures, ab initio calculations were performed at the MP2/6-31G\* level for reduced dimensionality potential energy mapping and at the MP2 = FULL/6-311G\*\* and B3LYP = FULL/6-311G\*\* levels for full structural optimization and electronic energy calculations of possible lower energy conformers. In all, five low-energy conformers, each of C<sub>1</sub> point group symmetry, were located in the ab initio search with complete information obtained on rotational constants, dipole moments, and structures. Rotational constants for three of the conformers agree well with the experimental observations, leaving the other two with no experimental partners. The three having experimental matches display relatively open “chain-like” structures corresponding to TG-, and GG-like forms, while the two with no experimental matches display relatively closed or “folded” structures with significantly different rotational constants. Although results using different ab initio level theories with and without zero point energy corrections alter the conformer energy ordering slightly, the no-match conformers always stay in the lower energy group, leaving an unsolved question as to why these lower energy conformers with “folded-like” structures were not observed in the jet-cooled FTMW spectra.

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## 1. Introduction

This work describes an experimental jet-cooled Fourier transform microwave (FTMW) study and ab initio conformational analysis of 2-(ethylthio)ethanol, also known as ethyl 2-hydroxyethylsulfide or hydroxyethyl ethyl sulfide (HOEES). This species is a hydrolysis/degradation product of mustard gas. Since HOEES is

among the family of compounds related to the mustard gas chemical agents, it is therefore of interest from both a theoretical and practical viewpoint. The present study is part of an ongoing effort aimed at setting up a microwave database for chemical agents and families of related compounds (simulents, degradation products, hydrolysis, and oxidation products).

These molecules are relatively large, and can exist in the gas phase as distinct conformational isomers associated with internal torsional rotations about the bonds joining the heavy atoms forming the molecular backbone. Typically these conformational changes are hindered by substantial potential barriers, thus permitting the molecules to exist as a variety of different conformers with differing energies. Tunneling between the

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conformations is very slow on the timescale of the rotational motions, hence the different conformers are quasi-stable in the FTMW experiments and appear as distinct isomeric species with separate and well-defined spectra and molecular structures.

The internal potential energy of a molecule of this size is a complicated function of the internal torsional degrees of freedom, for which current levels of chemical intuition cannot reliably predict the relative depths of the potential minima corresponding to the stable conformations. Thus, to connect the different conformers observed experimentally in the microwave spectrum to their corresponding conformational structures, *ab initio* calculations can be of great assistance. By mapping the internal potential as a function of a subset of the molecular internal coordinates, one can locate local minima in the potential corresponding to stable conformers, calculate the conformer rotational constants and dipole moment components, and then seek to match them against the experimental results. With *ab initio* calculations, once the conformational isomers are matched, estimates of the molecular structures are obtained without additional effort. This dual approach has been used successfully in the previous study of the parent molecule, diethyl sulfide [1].

In the present work, we report on observations and assignments in the jet-cooled FTMW spectrum of HOEES and its  $^{13}\text{C}$  and  $^{34}\text{S}$  monosubstituted isotopomers. We discuss the experimental identification of three distinct conformers, and then describe *ab initio* calculations that have produced good structural matches for the three observed conformers but which have also raised intriguing questions about the failure to observe two other predicted low-lying species.

## 2. Experimental

A commercially-available sample of HOEES (CAS#110-77-0) was used at its stated purity of 97%. Since the vapor pressure of HOEES is rather low ( $< 1 \times 10^2$  Pa), a small sample of approximately 200  $\mu\text{l}$  was transferred to a reservoir in the pulsed molecular beam valve [2]. The reservoir was then heated to 40–70  $^{\circ}\text{C}$  in order to increase the vapor pressure of the sample in the carrier gas. The compact FT spectrometer described by Suenram et al. [3] was used to record survey scans from 10.5 to 26 GHz. The composite of these scans is shown in Fig. 1. Spectral assignments were obtained using the jb95 spectral fitting program [1]. The most intense transitions in the spectrum are *a*-type, *R*-branch transitions that belong to two different conformers. Both conformers are prolate rotors so these *R*-branches occur at intervals spaced by approximately the  $B + C$  values of the rotational constants. A computer simulation of these is also shown in Fig. 1. Other transitions in the spectrum arise from additional selection rules for the two conformers,

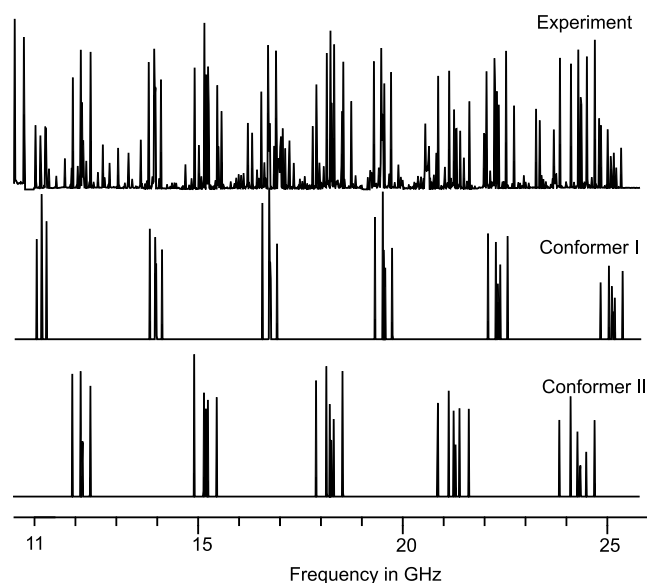


Fig. 1. Survey scan of HOEES. The upper trace shows the experimental spectrum. The lower two traces show only the prominent *a*-type, *R*-branch patterns for the two lowest energy conformers; Conformer I and Conformer II. The characteristic triplet patterns (most noticeable at the lower frequency end of the spectrum) are formed by the lower  $K_{-1} = 1$ ,  $K_{-1} = 0$ , and the upper  $K_{-1} = 1$  transitions.

i.e., *b*- and *c*-type transitions. Weaker transitions in the spectrum result from the  $^{13}\text{C}$  and  $^{34}\text{S}$  isotopomers of the two low-energy conformers. Transitions of a second TG conformer (Conformer III) with higher energy are relatively weak and were assigned only after the  $^{13}\text{C}$  and  $^{34}\text{S}$  transitions of the other two conformers were assigned and subtracted from the spectrum. It is believed that Conformer III lies at higher energy than the other two and thus has only a minimal population in the 1K molecular beam. The assigned transitions of the three conformers are available as supplemental material. The rotational parameters are given in Tables 1–3.

At this point we had assigned three conformational isomers of HOEES but even with the additional information available from the  $^{13}\text{C}$  and  $^{34}\text{S}$  isotopomers it was difficult to relate the assigned spectra to a particular conformational isomer. In order to ameliorate the situation, a detailed *ab initio* search was carried out to locate the low-energy conformers of HOEES. The details of this work are discussed below. Following the *ab initio* section the experimental structural details will be presented and compared with the *ab initio* results.

## 3. Theoretical results

The quantum chemistry calculational tool selected for use in this work is the GAUSSIAN 98 *ab initio* package [4,5] installed on the NIST SGI computers. The internal Z-matrix was used to define the molecular configuration and for all GAUSSIAN calculations.

Table 1  
Rotational parameters for the low energy TG conformer (Conformer I) of HOEES

Rotational parameters	Normal species	2- <sup>13</sup> C	3- <sup>13</sup> C	<sup>34</sup> S	5- <sup>13</sup> C	6- <sup>13</sup> C <sup>a</sup>
A (MHz)	5513.9584(3) <sup>b</sup>	5481.781(3)	5449.244(5)	5436.3208(5)	5484.168(3)	5489.576(4)
B (MHz)	1424.01194(7)	1408.672(1)	1418.882(2)	1420.6220(4)	1413.8472(9)	1392.818(1)
C (MHz)	1363.95091(7)	1350.884(1)	1357.392(2)	1359.1765(4)	1355.4039(8)	1333.883(1)
$\Delta_J$ (kHz)	0.8334(3)	0.810(2)	0.813(3)	0.824(1)	0.828(2)	0.797(3)
$\Delta_{JK}$ (kHz)	−8.000(2)	−7.75(3)	−7.68(3)	−7.87(1)	−7.92(2)	−7.84(3)
$\Delta_K$ (kHz)	43.63(3)	44.2(7)	43.0(1)	42.64(8)	43.6(6)	44.1(7)
$\delta_J$ (kHz)	0.2086(1)	0.199(1)	0.206(2)	0.2065(6)	0.202(2)	0.197(2)
$\delta_K$ (kHz)	6.74(2)	6.8(6)	6.7(7)	7.0(1)	7.0(4)	6.6(7)
$\Delta = I_c - I_b - I_a$ (uÅ <sup>2</sup> )	−76.026	−76.845	−76.608	−76.881	−76.740	−76.030
$\kappa = (2B - A - C)/(A - C)$	−0.971	−0.972	−0.970	−0.970	−0.972	−0.972
$\sigma$ (kHz) <sup>c</sup>	3.0	1.2	3.3	1.1	1.6	2.1
No. of lines fit <sup>d</sup>	113	18	31	25	25	21

<sup>a</sup> See Fig. 2 for atom numbering and Fig. 5 for conformer geometry.

<sup>b</sup> Numbers in parentheses are Type A uncertainties with  $k = 1$ , i.e.,  $1\sigma$ .

<sup>c</sup> Overall standard deviation of the fit.

<sup>d</sup>  $\mu_a$  and  $\mu_c$  are active, with  $\mu_c$  believed to be larger than  $\mu_a$ . No  $\mu_b$ -type transitions have been observed for this conformer.

Table 2  
Rotational parameters for the GG conformer (Conformer II) of HOEES

Rotational parameters	Normal species	2- <sup>13</sup> C	3- <sup>13</sup> C	<sup>34</sup> S	5- <sup>13</sup> C	6- <sup>13</sup> C <sup>a</sup>
A (MHz)	4916.20067(27) <sup>b</sup>	4876.74725(66)	4865.56173(76)	4824.15886(50)	4886.11485(91)	4881.51429(74)
B (MHz)	1574.72262(13)	1562.04733(41)	1567.80626(47)	1572.94379(28)	1560.75284(49)	1544.52850(37)
C (MHz)	1465.71477(13)	1451.32784(29)	1463.91760(43)	1456.13779(26)	1456.15525(52)	1436.44893(32)
$\Delta_J$ (kHz)	3.7520(9)	3.697(2)	3.685(2)	3.673(2)	3.687(2)	3.714(2)
$\Delta_{JK}$ (kHz)	−44.297(4)	−43.37(1)	−43.33(2)	−42.95(1)	−43.48(2)	−44.75(1)
$\Delta_K$ (kHz)	156.20(2)	151.92(75)	151.98(9)	151.15(5)	153.10(9)	158.97(9)
$\delta_J$ (kHz)	0.4954(5)	0.491(1)	0.458(1)	0.530(1)	0.479(1)	0.506(1)
$\delta_K$ (kHz)	−2.23(2)	−2.0(2)	−2.7(2)	−1.8(1)	−1.9(2)	−2.5(1)
$\Delta = I_c - I_b - I_a$ (uÅ <sup>2</sup> )	−78.930	−78.948	−80.993	−78.987	−80.172	−78.910
$\kappa = (2B - A - C)/(A - C)$	−0.937	−0.935	−0.939	−0.931	−0.939	−0.937
$\sigma$ (kHz) <sup>c</sup>	3.1	2.2	2.6	2.6	2.4	2.2
No. of lines fit <sup>d</sup>	92	36	37	57	32	33

<sup>a</sup> See Fig. 2 for atom numbering and Fig. 5 for the conformer geometry.

<sup>b</sup> The numbers in parentheses are Type A uncertainties with  $k = 1$ , i.e.,  $1\sigma$ .

<sup>c</sup> Overall standard deviation of the fit.

<sup>d</sup> All three selection rules are active with  $\mu_a \approx \mu_b \gg \mu_c$ .

Table 3  
Rotational parameters for the high-energy TG conformer (Conformer III) of HOEES

Rotational parameters	Normal species
A (MHz)	4769.3866(5) <sup>a</sup>
B (MHz)	1572.7320(4)
C (MHz)	1479.8687(4)
$\Delta_J$ (kHz)	1.899(2)
$\Delta_{JK}$ (kHz)	−17.65(1)
$\Delta_K$ (kHz)	62.63(7)
$\delta_J$ (kHz)	0.5723(9)
$\delta_K$ (kHz)	15.0(2)
$\Delta = I_c - I_b - I_a$ (uÅ <sup>2</sup> )	−85.799
$\kappa = (2B - A - C)/(A - C)$	−0.944
$\sigma$ (kHz) <sup>b</sup>	1.9
No. of lines fit <sup>c</sup>	43

<sup>a</sup> Numbers in parentheses are Type A uncertainties with  $k = 1$ , i.e.,  $1\sigma$ .

<sup>b</sup> Overall standard deviation of the fit.

<sup>c</sup> All three selection rules are active with  $\mu_a \approx \mu_c \gg \mu_b$ .

### 3.1. Limited-dimension potential energy mapping

For HOEES, there are 42 degrees of freedom; therefore, searching for all possible lower energy conformers by means of a full potential energy (PE) scan is impractical. However, each degree of freedom carries a different weight in its contribution to the overall energy of the whole molecule. Clearly, in the case of HOEES the three backbone dihedral angles,  $D(\text{O1} - \text{C2} - \text{C3} - \text{S4})$ ,  $D(\text{C2} - \text{C3} - \text{S4} - \text{C5})$ , and  $D(\text{C3} - \text{S4} - \text{C5} - \text{C6})$ , arising from the six heavy atoms (O–C–C–S–C–C) of the molecule in Fig. 2, should carry major information for the whole molecule. Unfortunately, a full 3-D PES is also difficult in practice if a relatively fine grid of points is desired in the searching process. Thus, we chose to proceed with two separate 2-D PE scans, namely  $D(1,2,3,4)$  vs.  $D(2,3,4,5)$  and  $D(3,4,5,6)$  vs.  $D(2,3,4,5)$ , at the MP2/6-31G\* level as a starting point in the search for the

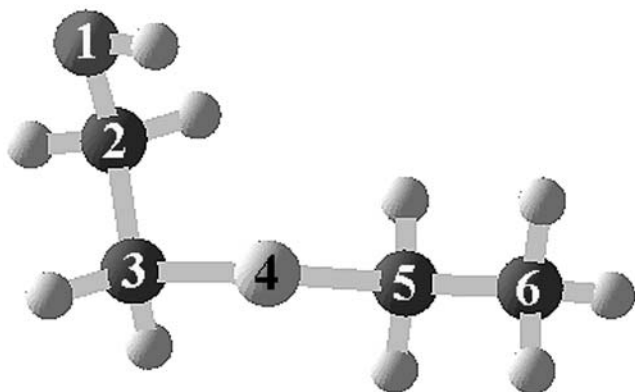


Fig. 2. Numbering from 1 to 6 of the heavy backbone atoms (O1–C2–C3–S4–C5–C6) in the hydroxyethyl ethyl sulfide molecule.

possible lower energy conformers of HOEEs. With  $10^\circ$  grid steps and taking advantage of  $C_2$  symmetry of the 2-D PES to reduce the coordinate ranges scanned, the number of calculation points is  $2 \times 37 \times 19 = 1406$  which becomes a manageable task. In each 2-D scan, the rest of the degrees of freedom were relaxed. In Fig. 3 (A) and (B), we show contour plots of the potential energy surfaces for possible conformational isomerization. The MP2/6-31G\* energies are plotted as a function of the dihedral angles  $D(1,2,3,4)$  and  $D(2,3,4,5)$  in Fig. 3 (A) and  $D(3,4,5,6)$  and  $D(2,3,4,5)$  in Fig. 3 (B). In both scans, the energy was minimized with respect to the other internal coordinates. The contours are spaced by  $399\text{ cm}^{-1}$ , with the darker areas indicating regions of lower energy. As seen from the two contour plots, lower energy valleys were distributed around the  $-60^\circ$ ,  $60^\circ$ , and  $180^\circ$  regions for each dihedral angle, which is consistent with the threefold-like molecular structure about each bond in the heavy-atom backbone. This indicates

that, in principle, one might be able to perform a full 3-D search with three steps only for each backbone dihedral angle spaced by approximately  $120^\circ$ . In practice, however, the ab initio program does not necessarily land on the desired minimum if the starting point is some distance away, likely being diverted by numerous unforeseen barriers between the starting point and the desired minimum in the complicated multi-dimensional potential space. The two 2-D PE scans, though limited in dimensionality, do provide good starting point information about possible lower energy conformers. Structures from some of the lowest energy points in each 2-D PES were first used as initial values for full structural optimization at MP2 = FULL/6-311G\*\*. We arrived at low-energy Conformers I, III, and NM1. Guided by the two 2-D contour plots displayed in Fig. 4 as a hypothetical “3-D” view of the three dihedral angles  $D(1,2,3,4)$ ,  $D(2,3,4,5)$ , and  $D(3,4,5,6)$ , several further 1-D scans were performed to ensure more important degrees of freedom were covered. They are: (i) starting at the Conformer III and first along the  $D(3,4,5,6)$ , (ii) making a  $90^\circ$  right turn at the Conformer NM1 to along the  $D(2,3,4,5)$ , (iii) making another  $90^\circ$  right turn at the Conformer I to along the  $D(3,4,5,6)$ , and (iv) finally making another  $90^\circ$  right turn at the Conformer NM2 back to the starting point to finish the “square walk.”

### 3.2. Full structural ab initio optimization

Following the 2-D and 1-D PE scans in Figs. 3 and 4, full geometry optimizations were performed at MP2 = FULL/6-311G\*\*. Altogether, five low-energy conformers, I, II, III, NM1, and NM2, have been found as possible conformers for HOEEs. In order to establish the relative conformer energy ordering and have some idea how such energy ordering is dependent on the

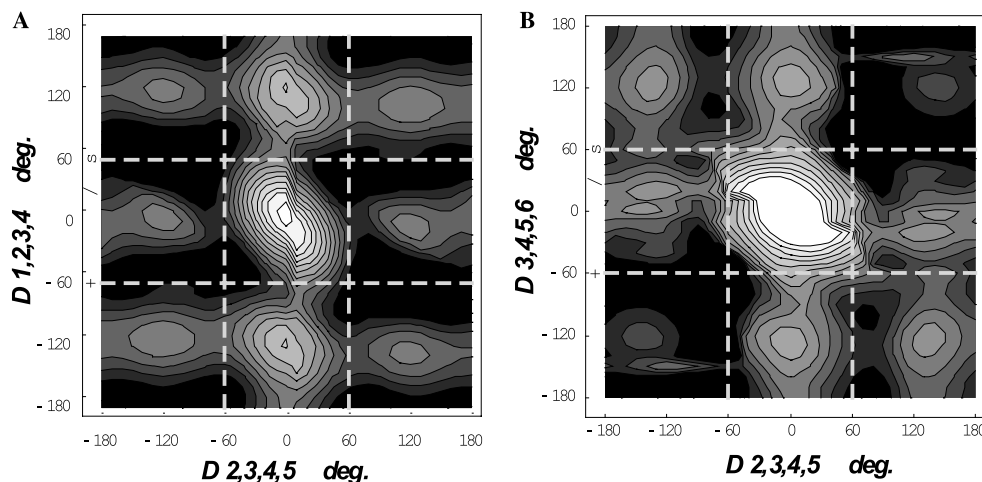


Fig. 3. 2-D contour plots showing the potential energy of HOEEs as a function of dihedral angles for (A)  $D(1,2,3,4)$  vs.  $D(2,3,4,5)$ , and (B)  $D(3,4,5,6)$  vs.  $D(2,3,4,5)$ . Ab initio calculations at the MP2/6-31G\* were used to generate the energies for the plot for  $10^\circ$  increments of the three dihedral angles. For each fixed value of  $D(1,2,3,4)$ ,  $D(2,3,4,5)$ , and  $D(3,4,5,6)$ , the other structural parameters were relaxed to minimize the energy. The contours are spaced by  $399\text{ cm}^{-1}$ , with the darker areas indicating regions of lower energy.

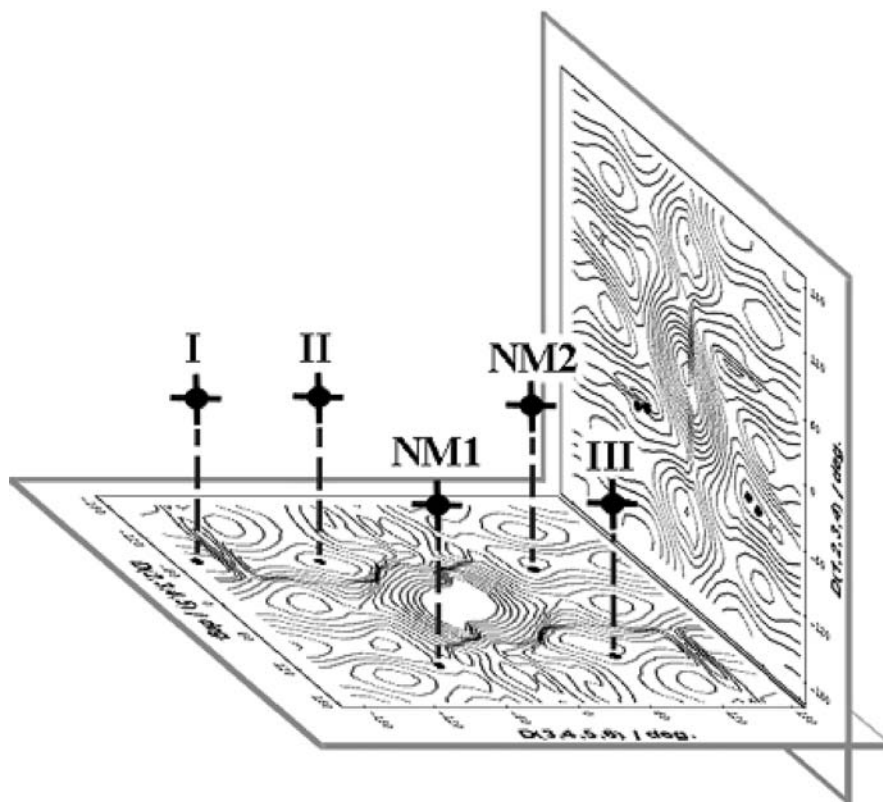


Fig. 4. Hypothetical “3-D” view of the three dihedral angles  $D(1,2,3,4)$ ,  $D(2,3,4,5)$ , and  $D(3,4,5,6)$ . The conformer minima, I, II, III, NM1, and NM2, are indicated.

ab initio level theory, we carried out full structural optimizations at B3LYP=FULL/6-311G\*\* and HF/6-311G\* levels of theory as well. In addition, we carried out harmonic frequency calculations for each lower energy conformer at the HF/6-311G\* and MP2=FULL/6-311G\*\* level in order to apply vibrational zero point energy corrections to the minimized electronic energy for each conformer. Altogether, we arrived at five low-energy conformers, identified as conformers I, II, III, NM1, and NM2 in Fig. 5. The resulting relative energies (zero-point corrected), rotational constants, inertial defects, backbone dihedral angles, and dipole moments are listed in Table 4. Their visualization structures are displayed in Fig. 5. As seen in Table 4, MP2 and B3LYP gave consistent conformer energy ordering as well as approximately the same dihedral angle values and rotational constants, indicating that we can rely to some extent on the structure determination at the current level of ab initio theory. All five low-energy conformers show  $C_1$  point group symmetry, with three displaying relatively open and chain-like structures, while the other two show relatively closed, folded-like structures with very different rotational constants. As seen in Table 4 and Fig. 4, the dihedral angle  $D(1,2,3,4)$  values for the five low-energy conformers are all about  $-60^\circ$  indicating that this half of the molecule favors a *gauche*-ethanol-like structure. The dihedral angle  $D(3,4,5,6)$ , on the

other hand, is distributed approximately evenly among angle values of  $-60^\circ$ ,  $60^\circ$ , and  $180^\circ$ , consistent with a *trans* or *gauche*-ethane-like structure for the other half of the molecule. The dihedral angle  $D(2,3,4,5)$  connecting the two halves of the molecule is either about  $-60^\circ$  or about  $120^\circ$  in order to bring the overall conformational energy for the molecule to a minimum value. In all five conformational isomers, the hydroxyl hydrogen forms a hydrogen bond to one of the lone pairs of electrons on the sulfur atom.

### 3.3. Ab initio dipole moment in the principal axis system

The dipole moment information obtained from the ab initio frequency calculations is presented in the Z-matrix orientation in which the first atom is at the origin, the second atom is along the +Z-axis, and the third atom is in the XZ plane. Thus, in order to be able to compare the ab initio dipole moment information to the experimental intensity information, we need to rotate the Z-orientation dipole moments into the principal axis system. For this, we can use the same transformation matrix obtained when rotating the Z-orientation Cartesian coordinates to the principal axis system. The dipole moment values in the principal axis system, together with the ab initio rotational constants, and atomic coordinates, form the three criteria used in our attempts to match the ab initio

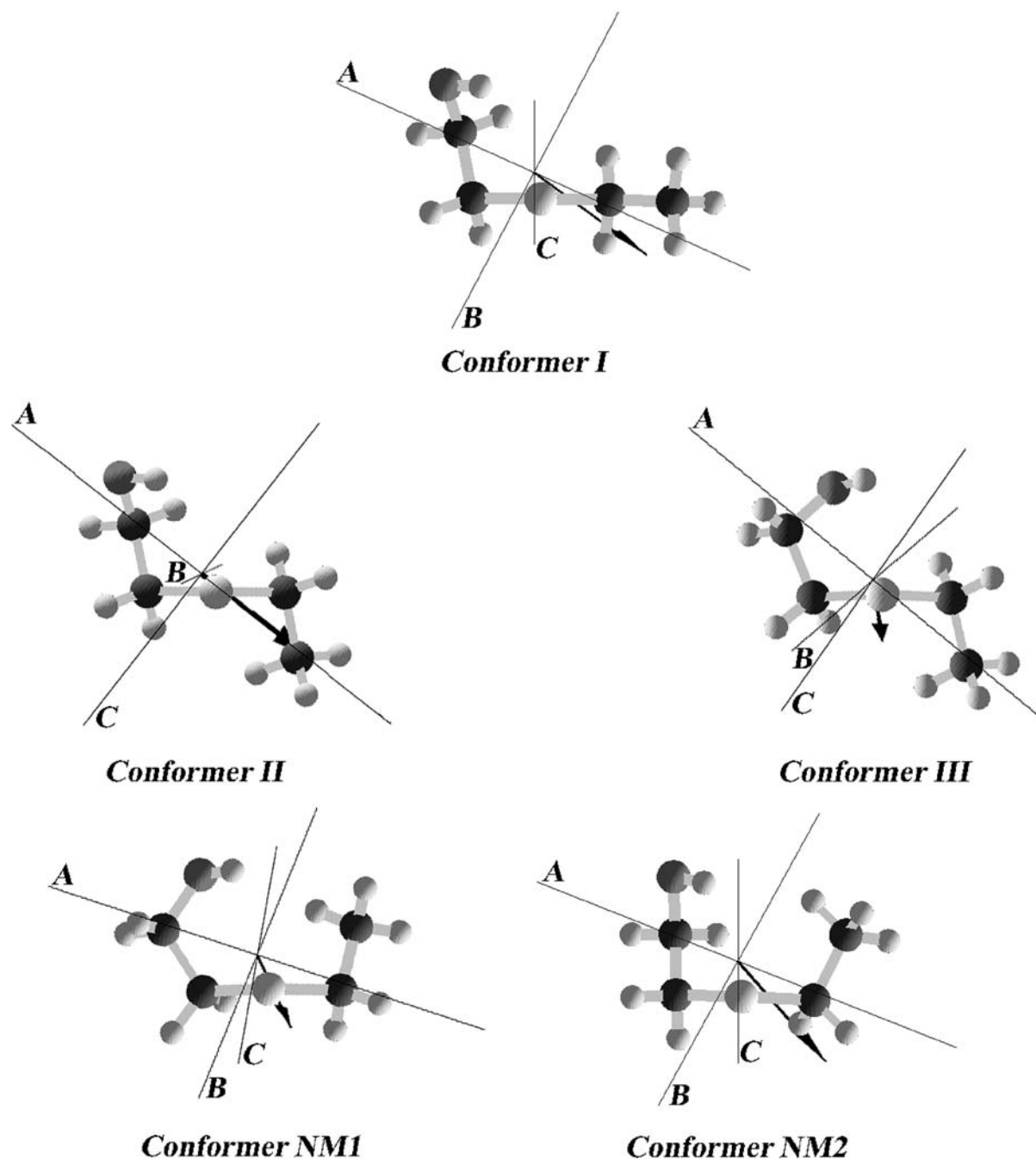


Fig. 5. The lower energy conformational isomers of HOEEs. A, B and C are principle axes, arrow indicates the overall dipole moment. The FTMW spectra of the two conformers with relatively closed structures (folding-like structures) were not experimentally identified in this study.

conformers to the experimentally observed isomers as described in the next section.

#### 4. Experimental structural analysis

##### 4.1. General comments on conformational comparisons

The five low-energy conformers identified in the theoretical section above fall into two groups, char-

acterized by  $A$  values of about 3.5–3.8 and 4.5–5.6 GHz. It should be pointed out that the energy surface is quite flat in that four of the five conformers are calculated to lie within  $104\text{ cm}^{-1}$  at the MP2=FULL/6-311G\*\* level of theory and within  $42\text{ cm}^{-1}$  at the B3LYP=FULL/6-311G\*\* level of theory and therefore reliable energy level ordering is probably not feasible. The fifth conformer NM2 GG' is always calculated to be higher in energy and thus may not be a viable candidate.

Table 4

Calculated ab initio (HF/6-31G\*, MP2 = FULL/6-311G\*\* and B3LYP = FULL/6-311G\*\*) rotational constants ( $A$ ,  $B$ ,  $C$ ), inertial defects ( $\Delta$ ), relative energies ( $E_{\text{rel}}$ ), and dihedral angles ( $D$ ) for HOEES

Conformer No.	No match 1	II	I	III	No match 2
HF/6-31G*					
$A$ (MHz)	3862	5513	5893	4622	3862
$B$ (MHz)	1936	1443	1339	1590	1814
$C$ (MHz)	1483	1355	1305	1459	1496
$\Delta$ (uÅ <sup>2</sup> ) <sup>a</sup>	−51	−69	−76	−81	−72
$D(1,2,3,4)^\circ$	−64	−62	−62	−59	−60
$D(2,3,4,5)^\circ$	118	−79	−79	99	−73
$D(3,4,5,6)^\circ$	−75	−76	−178	79	100
$\mu_a$ (D) <sup>b</sup>	0.8	2.1	−1.7	0.6	−1.7
$\mu_b$ (D)	0.3	1.7	−0.6	0.0	−0.4
$\mu_c$ (D)	1.0	−0.4	2.0	0.6	2.0
Erel(el) (cm <sup>−1</sup> )	267	145	0	234	492
Erel(el + zpe) (cm <sup>−1</sup> )	300	138	0	250	476
MP2 = FULL/6-311G**					
$A$ (MHz)	3818	4558	5656	4592	3545
$B$ (MHz)	2044	1673	1419	1645	2154
$C$ (MHz)	1548	1530	1364	1516	1649
$\Delta$ (uÅ <sup>2</sup> ) <sup>a</sup>	−53	−83	−75	−84	−71
$D(1,2,3,4)^\circ$	−62	−59	−60	−58	−56
$D(2,3,4,5)^\circ$	118	−66	−72	100	−62
$D(3,4,5,6)^\circ$	−73	−64	−171	78	98
$\mu_a$ (D) <sup>b</sup>	−0.9	1.9	−1.6	0.8	−1.2
$\mu_b$ (D)	0.4	1.4	−0.5	0.0	0.0
$\mu_c$ (D)	1.1	0.3	1.8	0.8	1.8
Erel(el) (cm <sup>−1</sup> )	0	79	144	172	124
Erel(el + zpe) (cm <sup>−1</sup> )	0	37	88	104	150
B3LYP = FULL/6-311G**					
$A$ (MHz)	3712	5341	5658	4466	3568
$B$ (MHz)	1998	1453	1350	1612	2003
$C$ (MHz)	1496	1364	1312	1468	1567
$\Delta$ (uÅ <sup>2</sup> ) <sup>a</sup>	−51	−72	−78	−82	−72
$D(1,2,3,4)^\circ$	−60	−60	−60	−57	−55
$D(2,3,4,5)^\circ$	113	−78	−78	96	−65
$D(3,4,5,6)^\circ$	−76	−76	−179	80	97
$\mu_a$ (D) <sup>b</sup>	−0.7	2.0	−1.6	0.6	−1.3
$\mu_b$ (D)	0.3	1.6	−0.3	0.0	−0.1
$\mu_c$ (D)	1.0	−0.2	2.0	0.7	1.9
Erel(el) (cm <sup>−1</sup> )	0	58	54	108	277
Erel(el + zpe) (cm <sup>−1</sup> ) <sup>c</sup>	2	18	0	42	305

<sup>a</sup> Inertial defect  $\Delta$  is defined as ( $I_{cc} - I_{aa} - I_{bb}$ ) where  $I_{xx}$  is the moment of inertia of the molecule about the  $x$  principal axis of the inertia tensor.

<sup>b</sup> PAM dipole moments obtained using transformation matrixes when structures from Z-matrix orientation were rotated to PAM.

<sup>c</sup> Zero point energy corrections are from MP2 = FULL/6-311G\*\*.

The conformers with the larger  $A$  values are those which are either *trans gauche* (TG) or *gauche gauche* (GG) with the two ethyl type subunits on opposite sides of the C<sub>3</sub>–S–C<sub>5</sub> plane. The two conformers with the lower  $A$  values are *gauche gauche* with the two ethyl subunits on the same side of the C<sub>3</sub>–S–C<sub>5</sub> plane, hereafter referred to as “GG'” conformers. The GG' conformer labeled as NM1 in Fig. 5 is calculated to be one of the lowest energy forms in both the MP2 = FULL/6-311G\*\* calculations and in the B3LYP = FULL/6-311G\*\* calculations whereas the GG' conformer labeled NM2 is always calculated to be the highest energy of the five considered and thus is probably not a

likely candidate. It is interesting to note that in the previous work on diethyl sulfide, the analogous GG' conformer was not observed either and it was always calculated to be the highest energy of the four considered in that case [1]. Here we believe that in reality the NM1 GG' conformer probably lies at somewhat higher energy than one or more of the more prolate forms (larger  $A$  values) and gets cooled out in the expansion process. This would imply that the barrier to conversion is <400 cm<sup>−1</sup>. Ruoff, et. al. have discussed this in detail in an earlier paper [6].

In Table 4, the TG Conformer I has the largest  $A$  value and we would tentatively map this to the

experimental Conformer I. In addition, a comparison of the observed transition strengths vs the calculated dipole moment components from the ab initio work also agree well for this conformer. It is interesting that we actually get a better match with the rotational constants for Conformer II at the B3LYP=FULL/6-311G\*\* level but, relatively speaking, Conformer I retains the largest  $A$  value. Furthermore, the calculated dipole moment components for Conformer II do not agree with the experimental data for the experimental conformer with the largest  $A$  value.

For the second experimentally observed conformer with the intense spectrum, the  $A$  value could be mapped to either Conformer II or Conformer III of the ab initio results. Here again, we can use the relative intensities of the  $a$ -type,  $b$ -type, and  $c$ -type transitions to aid in the selection process. Experimentally, for the observed conformer, we have intense  $a$ -type and  $b$ -type transitions and very weak  $c$ -type transitions. This correlates nicely with Conformer II from the ab initio work. Based on these general considerations we can map the experimentally observed conformers with Conformers I and II of the ab initio work.

As alluded to previously, the spectrum of the third experimentally observed conformer was found only after the  $^{13}\text{C}$  species of Conformer II had been assigned. In fact it was initially thought that this spectrum was a  $^{13}\text{C}$  isotopomer of Conformer II based on the intensity of the spectrum and the similarity of the rotational constants. However, after closely looking at the selection rule behavior and the relative intensities of the transitions ( $a$ -type,  $b$ -type, and  $c$ -type) it was found that for

this spectrum the  $a$ -type and  $c$ -type transitions were equally intense whereas for Conformer II the  $a$ -type and  $b$ -type were the most intense and the  $c$ -types were quite weak. Based on these facts, we mapped the carrier of this spectrum to that of Conformer III of the ab initio work. Since this spectrum is so weak, we were not able to observe any  $^{13}\text{C}$  or  $^{34}\text{S}$  isotopomers which would help to elucidate the conformation. Experimentally, this conformer must lie at higher energy than Conformers I and/or II and have a low barrier to interconversion as discussed above [6].

#### 4.2. Kraitchman analysis

The spectra for both Conformer I and Conformer II are quite intense and thus have allowed us to observe and assign the spectra of all the monosubstituted  $^{13}\text{C}$  and  $^{34}\text{S}$  forms for both conformers in natural abundance. With the substitution data that is available, it is possible to determine the atomic coordinates of each substituted atom using the method described by Kraitchman [7]. In Table 5 the atomic coordinates are given for the carbon and sulfur atoms of both conformers. The uncertainties in the atomic coordinates given in Table 5 are Type B uncertainties that are calculated from the formula  $\Delta(\text{\AA})/0.0015/(\text{absolute value of the atomic coordinate})$ . These uncertainties are much larger than the Type A uncertainties propagated from the uncertainties in the rotational constants through the least squares fit and are thought to be a more accurate representation of the true uncertainties in the coordinates. As can be seen from the formula, once the

Table 5  
Sulfur and carbon atom Kraitchman coordinates for Conformers I and II

Parameter	TG Conformer I			GG Conformer II		
	$a$	$b$	$c$	$a$	$b$	$c$
	<i>Experimental values<sup>a</sup></i>			<i>Experimental values<sup>a</sup></i>		
C <sub>2</sub>	+1.8627(8) <sup>b</sup>	−0.3574(42)	+0.6484(23)	−1.6128(9)	+0.9150(16)	+0.0970(155)
C <sub>3</sub>	+0.9972(15)	+0.8892(17)	+0.5553(27)	−0.6207(24)	+0.1932(78)	+1.0202(15)
S	−0.4618(32)	+0.6622(23)	−0.4803(31)	+0.4115(36)	−0.9936(15)	+0.1250(120)
C <sub>5</sub>	−1.4847(10)	−0.3744(40)	+0.6039(25)	+1.5031(10)	+0.1090(138)	−0.7943(19)
C <sub>6</sub>	−2.8254(5)	−0.6483(23)	−0.0399(376)	+2.5102(6)	+0.8758(17)	+0.1124 <sup>c</sup>
	<i>Ab initio values<sup>d</sup></i>			<i>Ab initio values<sup>d</sup></i>		
C <sub>2</sub>	+1.847587	−0.438703	+0.610137	−1.549067	+0.906422	+0.165186
C <sub>3</sub>	+0.979012	+0.811112	+0.666870	−0.635524	+0.066201	+1.047003
S	−0.470329	+0.707161	−0.415135	+0.431396	−1.048114	+0.094723
C <sub>5</sub>	−1.459589	−0.503206	+0.504473	+1.481065	+0.135842	−0.791547
C <sub>6</sub>	−2.853896	−0.587038	−0.106083	+2.357601	+0.991726	+0.112445

<sup>a</sup> The signs on the experimental numbers are derived from the ab initio values in Angstrom (Å) unit.

<sup>b</sup> The values in parentheses are Type B uncertainties that are calculated from the formula  $\Delta(\text{\AA}) = 0.0015/(\text{absolute value of the atomic coordinate})$ . These uncertainties are much larger than the Type A uncertainties propagated from the least squares fit and are thought to be a more accurate representation of the true uncertainties in the coordinates.

<sup>c</sup> Value from the MP2/6-311G\*\* ab initio calculations, see text for discussion.

<sup>d</sup> Six digits are given here for the MP2=FULL/6-311G\*\* ab initio parameters to minimize round off errors when calculating bond lengths and angles from these coordinates. See Table 6.



Table 6  
Comparison of bond lengths and angles for the TG and GG conformers of HOEES

Parameter <sup>a</sup>	TG Conformer I			GG Conformer II		
	Kraitchman	$r_0$	Ab Initio <sup>b</sup>	Kraitchman	$r_0$	Ab Initio <sup>b</sup>
C <sub>2</sub> –C <sub>3</sub>	1.521(4) <sup>c</sup>	1.529(4)(4) <sup>d</sup>	1.523	1.536(10)	1.544(3)(14) <sup>d</sup>	1.522
C <sub>3</sub> –S	1.804(4)	1.817(2)(4) <sup>e</sup>	1.812	1.810(8)	1.815(1)(8) <sup>e</sup>	1.813
S–C <sub>5</sub>	1.816(4)	1.817(2)(4)	1.814	1.803(10)	1.815(1)(8)	1.814
C <sub>5</sub> –C <sub>6</sub>	1.512(14)	1.533(6)(8)	1.524	1.558(11) <sup>f</sup>	1.542(7)(13)	1.523
C <sub>2</sub> –C <sub>3</sub> –S	113.10(6)	112.9(2)(2)	113	112.29(51)	112.54(9)(69)	113
C <sub>3</sub> –S–C <sub>5</sub>	100.65(6)	100.44(13)(17)	100	101.33(39)	101.56(14)(41)	101
S–C <sub>5</sub> –C <sub>6</sub>	110.4(11)	108.4(4)(5)	109	113.31(52) <sup>f</sup>	113.4(4)(6)	114
$D(\text{C}_2\text{--C}_3\text{--S--C}_5)$	–73.5(1)	–73.6(3)	–72	–72.2(02)	–70.45(7)	–66
$D(\text{C}_3\text{--S--C}_5\text{--C}_6)$	–177.2(6)	–178.1(6)	–171	–69.2(8)	–70.3(2)	–64

<sup>a</sup> Bond lengths are in Å and angles are in degrees.

<sup>b</sup> From the coordinate values of Table 5 (MP2 = FULL/6-311G\*\*).

<sup>c</sup> These are Type A ( $k = 1$ ) uncertainties propagated from the Type B uncertainties in the coordinate values of Table 5.

<sup>d</sup> First uncertainty value is the standard deviation of fit, the second value is the Costain uncertainty.

<sup>e</sup> The CS values were nearly equal when fit independently, so they were constrained to fit equally.

<sup>f</sup> All values involving atom C<sub>6</sub> employ the ab initio calculated value for the  $c$ -coordinate given in Table 5.

absolute value of the coordinate becomes small ( $\leq 0.1$  Å) the uncertainty goes up rapidly. Since one can only obtain the absolute value of the atomic coordinate from the Kraitchman analysis, the signs on the coordinates were determined using the values from the ab initio results. The ab initio results are given to six figures to minimize round off errors in the calculation of bond lengths and angles in Table 6. It is clear from comparison of the absolute values of the coordinates that the experimental data correlates well with the conformational geometries of Conformer I and Conformer II, respectively. For Conformer I, the only small coordinate is the  $c$ -coordinate of C<sub>6</sub>. The same is true for Conformer II except in this case in the Kraitchman analysis, the coordinate turns out to be imaginary (not determinable) so in the Kraitchman analysis for Conformer II, the ab initio calculated value was used. The only other alternative would be to set the  $c$ -coordinate of C<sub>6</sub> to zero. When this is done, the C<sub>5</sub>–C<sub>6</sub> bond length that is calculated is unreasonably small (1.49 Å) for a C–C single bond. As can be seen from Table 5, there are several other small coordinates for the atoms of Conformer II so in general the bond lengths and angles calculated in Table 6 are not as good as those for Conformer I.

### 4.3. $r_0$ analysis

In order to circumvent the problem associated with the small coordinate values encountered with the Kraitchman analysis, a second analysis was carried out using Schwendeman's  $r_0$  method and his fitting program STRFTQ [8]. Since this method involves fitting bond lengths and angles, it is not possible to compare the atomic coordinates directly. In Table 6 the bond lengths and angles are compared for both the Kra-

itchman and  $r_0$  methods as well as the values obtained from the ab initio calculations. Generally speaking, the agreement between the experimental results and the ab initio results are excellent. It appears that the ab initio calculations tend to make both C–C bonds and C–S bonds more nearly equal than is actually found experimentally in the Kraitchman analysis. In the  $r_0$  fits however, the two CS bonds also fit to nearly equal values. In the final  $r_0$  fits, the best fit was obtained when the two CS bonds were constrained to fit to equal values. In general, the  $r_0$  fits are probably the more accurate of the two experimentally determined values since for both conformers, there was at least one small value for one of the atomic coordinates (see Table 5). This translates to large uncertainties in the values of bond lengths and angles which employ this coordinate. In the  $r_0$  fits, other parameters were fixed as follows:  $r_{\text{CH}} = 1.093$  Å,  $r_{\text{CO}} = 1.41$  Å,  $r_{\text{OH}} = 0.97$  Å,  $\angle\text{CCO} = 109.5^\circ$ , and  $\angle\text{COH} = 113.0^\circ$ .

## 5. Discussion and conclusions

One of the perplexing issues that remains is the failure to observe the no-match GG' conformers. This is particularly true for the NM1 conformer which is predicted to lie at very low energy at all levels of the *ab initio* calculations. Fig. 6 shows the residual transitions remaining after all the transitions of the other three conformers have been subtracted from the observed spectrum. A predicted spectrum for the NM1 conformer was generated using ab initio calculated rotational constants and dipole moment values at the MP2 = FULL/6-311G\*\* level. Although the ab initio  $\mu_a$  and  $\mu_c$  values for the no-match conformer are about half of the observed conformer I, they are still sizable

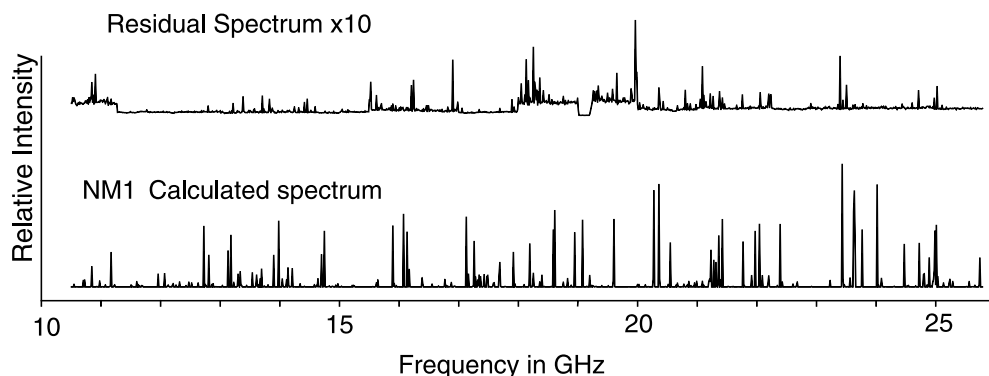


Fig. 6. Comparison of the residual transitions in the HOEES spectrum with the calculated spectrum of the NM1 conformer.

and transitions should be observable if the conformer was present.

With the *ab initio* approach, five lower energy conformers were found. Three of them match well with the experimental findings both in rotational constants and dipole moment information. However, the lowest and the fifth lowest energy conformers found in *ab initio* work at the MP2 = FULL/6-311G\*\* level of calculation with “folded-liked” structures of very different A/B/C rotational constant values do not have experimental matches. The reason for this is most likely the fact that four of the five conformers found at the highest level of theory (B3LYP = FULL/6-311G\*\*) are all calculated to lie within  $42\text{ cm}^{-1}$  of the lowest energy form. This is such a small energy difference that theory cannot discern among the group as to which is the lowest energy. Furthermore the NM1 GG' conformer must lie above Conformer I and/or II and must have a low barrier to interconversion ( $<400\text{ cm}^{-1}$ ) [6] down to Conformer I or II in the molecular beam expansion.

It is interesting to compare the conformational geometries found here for HOEES with the geometries found for the parent molecule, diethylsulfide [1]. In that work, three conformational isomers were also observed. A *trans trans* (TT) form, a *trans gauche* (TG) form, and a *gauche gauche* (GG) form were identified with the TT form estimated to be at higher energy than the later two. The TG form corresponds directly to the TG Conformer I form found here for HOEES. The GG form likewise corresponds to the overall conformational geometry of Conformers II and III of HOEES. No analogue of the TT form was found in this work and likewise no conformational form where the terminal methyls are located on the same side of the  $\text{C}_3\text{--S--C}_5$  plane was found in either case. For diethyl sulfide this GG' form was calculated to be at higher energy and was not expected to be observable in the cold molecular beam. This is contrary to the case for HOEES where the GG' Conformer labeled NM1

was always calculated to be one of the lowest energy conformers.

We are in the process of investigating other similar molecular species in this series. Three conformational isomers have also been observed and assigned for thiodiglycol, [9] ( $\text{HOCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{OH}$ ). Two conformational isomers have also been identified for the chloro analogue of HOEES, i.e., chloroethyl ethylsulfide, [10] ( $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_3$ ).

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