

# Rotational spectrum, structure, and modeling of the HCCH-(OCS)<sub>2</sub> trimer: Observation of a polar OCS dimer fragment

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The rotational spectra of eight isotopomers of the HCCH-(OCS)<sub>2</sub> trimer have been assigned by pulsed nozzle, Fourier-transform microwave spectroscopy. The rotational constants and dipole moment components are consistent with a nonplanar, triangular-twisted structure of C<sub>1</sub> symmetry which aligns the three monomer axes approximately 3°–27° away from perpendicular to a triangle formed by the center of HCCH and the carbons of OCS. The OCS dimer portion of the trimer has the two OCS monomers aligned in an almost parallel fashion such that the monomer dipole moments reinforce, rather than in the antiparallel arrangement observed in the well-known OCS dimer. This configuration has been obtained using a semiempirical model which employs a distributed multipole representation of the electrostatic interaction and analytical atom-atom terms to describe the dispersion and repulsion terms in the interaction potential. © 1999 American Institute of Physics. [S0021-9606(99)01147-2]

## I. INTRODUCTION

The study of the spectra of van der Waals dimers in the gas phase is a fertile field for investigating the nature of weak interaction forces. Spectroscopists begin with a working model of the structure of the weakly bound complex to explore these spectra and learn about the interaction. This model results from reasoning covering the gamut from intuition and analogy to semiempirical calculations and *ab initio* theory.

Intuition and analogy are not yet sufficiently well developed to always infer a good approximation to the structure of a new complex. For example, the differences in the equilibrium configurations for the dimers: (HCN)<sub>2</sub>, (HF)<sub>2</sub>, (HCCH)<sub>2</sub>, and (CO<sub>2</sub>)<sub>2</sub>, (respectively: linear, V-shaped, T-shaped, and slipped parallel planar) suggest subtle interactions which are not readily transferable using simple rules. For many dimer systems, routine and reliable *ab initio* calculations are beyond the scope of most experimental groups unlike the situation for covalently bonded molecules. Semiempirical calculations are growing in usage as a means of filling the gap since they are computationally much less formidable. In our experience, a simple electrostatic interaction model with hard sphere repulsions<sup>1,2</sup> has often proven useful after the fact to qualitatively understand configurations and trends. The question remains as to how quantitatively accurate and useful such modeling can become in assisting in the assignment of high resolution spectra of dimers, trimers and tetramers formed in supersonic expansions. While the basic interaction mechanisms are thought to be understood, it is only when a calculation gives a useful structure prediction to guide in the assignment of the spectrum, that we will have made practical progress. In the ideal world, this would entail an accuracy of 2%–3% in structural parameters to assist

spectral assignments of the high resolution pure rotational spectra arising in the mixture of species usually found in a supersonic expansion.

Our recent efforts have been directed at assigning the high resolution spectra of more complex dimers and trimers, and exploring a more sophisticated modeling program (ORIENT) to improve the understanding of weak binding forces and the structures of weak complexes. This paper discusses a novel trimer system. An increasing number of high resolution studies of trimeric or higher clusters have been reported in recent years. As weakly bound dimers are becoming better understood and the factors governing the structural patterns in dimers are determined, the systematic study of the effects of a third body becomes an attractive and logical next step. The growing body of information on trimers or even larger clusters provides a valuable resource for the development and improvement of the theoretical models that seek to rationalize such clusters. Successful models must ultimately be able to predict and quantify the effects of adding a third body to a two body system if the model is to be useful for the description of interactions in larger aggregates and in condensed phases.

Recently, the HCCH-OCS dimer was studied in this laboratory by Fourier transform microwave spectroscopic techniques.<sup>3</sup> The goal was to obtain a well defined structure for the dimer before attempting an assignment of one of the two possible mixed trimers that should be present in a HCCH-OCS gas mixture: HCCH-(OCS)<sub>2</sub> or OCS-(HCCH)<sub>2</sub>. This would allow us to extend our recent study of trimers comprised of linear monomers to some acetylene containing systems. The assignment of CO<sub>2</sub>-(OCS)<sub>2</sub> (Ref. 4) and the structural similarity between HCCH and CO<sub>2</sub> made the HCCH-(OCS)<sub>2</sub> system an attractive target for study. Also, the molecular quadrupole moments for HCCH and CO<sub>2</sub> are opposite in sign [ $\Theta(\text{HCCH}) = +25.1 \times 10^{-40} \text{ C m}^2$ ,  $\Theta(\text{CO}_2) = -14.8 \times 10^{-40} \text{ C m}^2$ ].<sup>5</sup> It

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was of interest to see if this would lead to significant differences between the HCCH-(OCS)<sub>2</sub> and CO<sub>2</sub>-(OCS)<sub>2</sub> trimers.

In the present study we report on the identification and characterization of the HCCH-(OCS)<sub>2</sub> trimer. This species is found to possess a somewhat surprising parallel arrangement of the dipole moments of the OCS monomers, in contrast to the CO<sub>2</sub>-(OCS)<sub>2</sub> trimer<sup>4</sup> and the isolated OCS dimer.<sup>6</sup> Despite searches for the polar form of the OCS dimer,<sup>7</sup> it has not yet been observed by high resolution techniques. However, evidence for its existence in molecular beam electric resonance experiments has been reported.<sup>8</sup> The HCCH-(OCS)<sub>2</sub> structure will be discussed in light of recent results for (OCS)<sub>3</sub>,<sup>9</sup> the HCCH-OCS dimer,<sup>3</sup> and other closely related systems. Results obtained from a semiempirical model (ORIENT) will also be discussed. A preliminary report of the rotational spectrum of the normal species of HCCH-(OCS)<sub>2</sub> has already been given.<sup>10</sup>

## II. EXPERIMENT

The rotational spectrum of the HCCH-(OCS)<sub>2</sub> trimer was observed using a Fourier transform microwave spectrometer similar to the type originally developed by Balle and Flygare.<sup>11</sup> Previous searches for the HCCH-OCS dimer in the region from 6.5 to 7.8 GHz revealed a large number of unassigned transitions of reasonable intensity once the HCCH-OCS dimer transitions had been assigned. The initial spectral searches were then further extended to a total of approximately 3.5 GHz up to 9.9 GHz, facilitated by the autoscan facility of the University of Michigan spectrometer. The spectrometer uses hardware and software developments from the University of Kiel<sup>12</sup> which enable it to scan several hundreds of megahertz unassisted. Known (OCS)<sub>3</sub> (Ref. 7) and (HCCH)<sub>2</sub> (Ref. 13) transitions were used as a guide to optimum conditions. Upon completion of mixing tests on the unassigned transitions to determine the composition of the spectrum carrier. Stark effect measurements were made on 25 or so of the most intense transitions to determine their *J* quantum numbers, Stark effect experiments were carried out by the application of voltages up to ±8 kV to a pair of parallel 50 cm × 50 cm steel mesh plates that are separated by about 30 cm and situated just outside the Fabry-Perot cavity. The electric field was calibrated daily by measurement of the Stark effect of the OCS monomer 1←0 transition at 12 162.980 MHz, assuming a dipole moment of 0.7152 D.<sup>14</sup>

The HCCH-(OCS)<sub>2</sub> trimer was generated in a supersonic expansion using a gas mixture comprised of approximately 1.5% HCCH and 1.5% OCS seeded in a 97% He-Ne "first-run" mixture (90% Ne, 10% He). The He-Ne gas mixture was kept at pressures of between 2.5 and 3 atm to obtain the best transition intensity. It was expanded into the evacuated cavity through a modified Bosch fuel injector valve. The expansion was perpendicular to the direction of microwave propagation which eliminates Doppler doublets for the measured transitions but broadens them slightly. Linewidths were approximately 30 kHz full-width at half-maximum, and the measured transition frequencies were typically reproducible to within 4 kHz. Microwave pulses of 1.5–2 μs duration were optimal for the observation of the HCCH-(OCS)<sub>2</sub> transitions. The most intense of the mea-

sured *c*-type transitions were easily visible in 100 gas pulses with a signal to noise ratio in excess of 14. Some of the weaker *a*- and *b*-type lines required averaging for several thousand shots to achieve a respectable signal to noise. None of the observed lines showed any evidence of tunneling splittings or other perturbations.

<sup>13</sup>C<sub>2</sub>H<sub>2</sub> (99% <sup>13</sup>C<sub>2</sub>, Isotec), O<sup>13</sup>CS (99% <sup>13</sup>C, Isotec), and DCCD (98% D, MSD Isotopes) were used to observe the spectra of the <sup>13</sup>C<sub>2</sub>H<sub>2</sub>-(OCS)<sub>2</sub>, HCCH-(O<sup>13</sup>CS)<sub>2</sub>, and DCCD-(OCS)<sub>2</sub> species. The two singly substituted H<sup>13</sup>CCH-(OCS)<sub>2</sub> species were observed using singly substituted H<sup>13</sup>CCH purchased from CDN Isotopes (99.2% <sup>13</sup>C). The singly substituted HCCH-O<sup>13</sup>CS-OCS species were observed by combining 25% O<sup>13</sup>CS with 25% normal OCS and 50% HCCH.

## III. RESULTS

### A. Spectra

*a*, *b*, and *c*-type transitions were observed for all eight isotopic species, with the *c*-type lines being the most intense. The location of a pair of doublets with a constant splitting at approximately 7961, 7963 and 7981, 7983 MHz (identified by Stark effects as a 3←2 transition) and another set at 9477, 9492 and 9582, 9597 MHz (identified as a 4←3 transition), provided a useful starting point in the fitting process. Attempts to fit these lines as *a*, *b* *K*-doublet pairs failed. Inspection of the numerous possible models that resulted from the semiempirical program (to be discussed later) suggested the correct *b*, *c* pair assignments. A least-squares fit of these 8 lines with a rigid rotor program proved to be more than sufficient for the prompt identification of the remaining transitions, typically to within a few hundred kilohertz of the rigid rotor predictions. This good performance of the rigid rotor model can be easily understood by noting the small distortion constants for all of the species. Frequencies for the 42 transitions belonging to the normal isotopic species are listed in Table I along with the residuals that result from a fit of the observed transitions to a Watson *A*-reduction Hamiltonian in the *I'* representation.<sup>15</sup> Spectra for an additional seven isotopomers were observed: H<sup>13</sup>C<sup>13</sup>CH-(OCS)<sub>2</sub>, H<sup>13</sup>CCH-(OCS)<sub>2</sub>, HC<sup>13</sup>CH-(OCS)<sub>2</sub>, DCCD-(OCS)<sub>2</sub>, HCCH-(O<sup>13</sup>CS)<sub>2</sub>, HCCH-O<sup>13</sup>CS-OCS, and HCCH-OCS-O<sup>13</sup>CS. The fitted rotational and centrifugal distortion constants for the normal species and the seven isotopomers are listed in Table III. The value of Δ<sub>*JK*</sub> was held fixed in the fits of the singly substituted isotopomers since the smaller number of lines was not sufficient to adequately determine this parameter; this procedure does not introduce any significant worsening of the fit since the distortion constants are all small in magnitude. Transition frequencies for the additional isotopic species are given in Tables I and II, and the spectroscopic constants are given in Table III.

### B. Dipole moment

Measurement of the Stark effects for fourteen components selected from six rotational transitions allowed a least-squares fitting of the dipole moment components to be carried out. Table IV lists the observed Stark coefficients and

TABLE I. Transition frequencies for the normal and doubly substituted isotopomers of the HCCH-(OCS)<sub>2</sub> trimer.

		$\nu_{\text{obs}}/\text{MHz}$			
$J'_{KaKc}$	$J''_{KaKc}$	Normal	HCCH-(O <sup>13</sup> C) <sub>2</sub>	DCCD-(OCS) <sub>2</sub>	<sup>13</sup> C <sub>2</sub> H <sub>2</sub> -(OCS) <sub>2</sub>
3 <sub>12</sub>	2 <sub>02</sub>	5763.504	...	...	...
3 <sub>22</sub>	2 <sub>11</sub>	6449.510	...	...	...
3 <sub>21</sub>	2 <sub>11</sub>	6554.133	6516.906	6336.629	6384.879
3 <sub>22</sub>	2 <sub>12</sub>	6863.734	6821.511	6642.675	6699.985
3 <sub>21</sub>	2 <sub>12</sub>	6968.354	...	...	...
3 <sub>31</sub>	2 <sub>20</sub>	7961.749	7935.799	7623.839	7692.437
3 <sub>30</sub>	2 <sub>20</sub>	7963.890	7937.741	7626.596	7695.411
3 <sub>31</sub>	2 <sub>21</sub>	7983.328	7956.100	7648.611	7718.638
3 <sub>30</sub>	2 <sub>21</sub>	7985.467	7958.048	7651.368	7721.609
4 <sub>14</sub>	3 <sub>13</sub>	5933.381	...	...	...
4 <sub>04</sub>	3 <sub>03</sub>	6056.919	...	...	...
4 <sub>14</sub>	3 <sub>03</sub>	9268.330	...	...	...
4 <sub>23</sub>	3 <sub>22</sub>	...	...	6145.274	6170.466
4 <sub>22</sub>	3 <sub>21</sub>	...	6341.671	6357.448	6393.688
4 <sub>13</sub>	3 <sub>12</sub>	6473.004	6399.479	6389.640	...
4 <sub>13</sub>	3 <sub>03</sub>	7634.233	7549.728	7519.217	...
4 <sub>23</sub>	3 <sub>12</sub>	7801.909	...	...	...
4 <sub>22</sub>	3 <sub>12</sub>	8096.413	...	...	...
4 <sub>23</sub>	3 <sub>13</sub>	8628.196	8563.411	8391.313	8462.766
4 <sub>22</sub>	3 <sub>13</sub>	8922.704	...	...	...
4 <sub>32</sub>	3 <sub>21</sub>	9477.837	9437.205	9112.807	9185.023
4 <sub>31</sub>	3 <sub>21</sub>	9492.599	9450.630	9131.745	9205.456
4 <sub>32</sub>	3 <sub>22</sub>	9582.456	9535.822	9232.030	9310.947
4 <sub>31</sub>	3 <sub>22</sub>	9597.219	9549.246	9250.986	9331.376
5 <sub>14</sub>	4 <sub>23</sub>	6707.249	...	...	...
5 <sub>05</sub>	4 <sub>14</sub>	7267.688	7185.934	7176.905	7194.172
5 <sub>15</sub>	4 <sub>14</sub>	7388.517	7314.853	7267.557	7282.941
5 <sub>05</sub>	4 <sub>04</sub>	7479.094	7407.619	7345.288	7360.860
5 <sub>15</sub>	4 <sub>04</sub>	7599.921	7536.540	7435.938	7449.630
5 <sub>24</sub>	4 <sub>23</sub>	7760.730	7676.818	7650.819	7680.557
5 <sub>33</sub>	4 <sub>32</sub>	7863.021	7773.604	7765.939	...
5 <sub>32</sub>	4 <sub>31</sub>	7905.628	7812.444	7820.049	...
5 <sub>14</sub>	4 <sub>13</sub>	8036.163	7947.935	7922.131	7959.616
5 <sub>23</sub>	4 <sub>22</sub>	8088.816	7989.805	8009.239	8056.083
5 <sub>24</sub>	4 <sub>13</sub>	9089.643	...	...	...
5 <sub>14</sub>	4 <sub>04</sub>	9613.477	9500.186	9489.085	9575.885
5 <sub>23</sub>	4 <sub>13</sub>	9712.223	9627.840	9494.547	9566.057
6 <sub>15</sub>	5 <sub>24</sub>	8501.340	...	...	...
6 <sub>16</sub>	5 <sub>15</sub>	...	8745.662	8685.095	8701.958
6 <sub>06</sub>	5 <sub>05</sub>	8889.357	8804.906	8730.432	8746.838
6 <sub>25</sub>	5 <sub>24</sub>	9274.617	9176.096	...	9170.787
6 <sub>34</sub>	5 <sub>33</sub>	9438.781	...	...	...
6 <sub>43</sub>	5 <sub>42</sub>	9441.428	...	...	...
6 <sub>15</sub>	5 <sub>14</sub>	9554.822	9454.694	9403.193	9441.985
6 <sub>24</sub>	5 <sub>23</sub>	9749.168	...	9644.918	...

the computed dipole moment components. The dipole moment components are calculated to be  $\mu_a=0.666(10)$  D,  $\mu_b=0.48(6)$  D, and  $\mu_c=0.913(6)$  D, resulting in a total dipole moment,  $\mu_{\text{total}}$ , of 1.227(23) D. The higher uncertainty associated with the  $\mu_b$  component arises from the smaller contribution that this component makes to the frequency shifts in the observed transitions. The total dipole moment of 1.227(23) D was an early indication that the OCS molecules were aligned almost parallel, with their dipole moments reinforcing one another.

### C. Structure

The measured experimental rotational constants for eight isotopomers provided more than sufficient moments of iner-

TABLE II. Transition frequencies for the singly substituted isotopomers of the HCCH-(OCS)<sub>2</sub> trimer.

		$\nu_{\text{obs}}/\text{MHz}$			
$J'_{KaKc}$	$J''_{KaKc}$	HCCH-O <sup>13</sup> CS-OCS	HCCH-OCS-O <sup>13</sup> CS	H <sup>13</sup> CCH-(OCS) <sub>2</sub>	HC <sup>13</sup> CH-(OCS) <sub>2</sub>
3 <sub>12</sub>	2 <sub>02</sub>	...	...	...	...
3 <sub>22</sub>	2 <sub>11</sub>	...	...	...	...
3 <sub>21</sub>	2 <sub>11</sub>	6535.805	6535.191	6467.668	6466.634
3 <sub>22</sub>	2 <sub>12</sub>	6843.341	6841.895	6777.580	6782.150
3 <sub>21</sub>	2 <sub>12</sub>	...	...	...	...
3 <sub>31</sub>	2 <sub>20</sub>	7953.117	7944.456	7825.586	7822.163
3 <sub>30</sub>	2 <sub>20</sub>	7955.150	7946.506	7828.009	7824.808
3 <sub>31</sub>	2 <sub>21</sub>	7974.030	7965.416	7848.753	7846.663
3 <sub>30</sub>	2 <sub>21</sub>	7976.058	7967.468	7851.172	7849.307
4 <sub>14</sub>	3 <sub>13</sub>	...	...	...	...
4 <sub>04</sub>	3 <sub>03</sub>	...	...	...	...
4 <sub>14</sub>	3 <sub>03</sub>	...	...	...	...
4 <sub>23</sub>	3 <sub>22</sub>	...	...	...	...
4 <sub>22</sub>	3 <sub>21</sub>	...	...	...	...
4 <sub>13</sub>	3 <sub>12</sub>	...	...	...	...
4 <sub>13</sub>	3 <sub>03</sub>	7587.552	7596.323	7597.281	7619.312
4 <sub>23</sub>	3 <sub>12</sub>	...	...	...	...
4 <sub>22</sub>	3 <sub>12</sub>	...	...	...	...
4 <sub>23</sub>	3 <sub>13</sub>	8594.981	8596.597	8358.243	8548.728
4 <sub>22</sub>	3 <sub>13</sub>	...	...	...	...
4 <sub>32</sub>	3 <sub>21</sub>	9460.266	9468.966	9331.157	9325.287
4 <sub>31</sub>	3 <sub>21</sub>	9474.296	9454.846	9347.856	9343.446
4 <sub>32</sub>	3 <sub>22</sub>	9561.718	9556.554	9443.091	9443.443
4 <sub>31</sub>	3 <sub>22</sub>	9575.746	9570.671	9459.791	9461.607
5 <sub>14</sub>	4 <sub>23</sub>	...	...	...	...
5 <sub>05</sub>	4 <sub>14</sub>	...	...	...	...
5 <sub>15</sub>	4 <sub>14</sub>	7343.143	7360.316	7341.419	7329.030
5 <sub>05</sub>	4 <sub>04</sub>	7435.184	7451.656	7426.417	7412.477
5 <sub>15</sub>	4 <sub>04</sub>	...	...	...	...
5 <sub>24</sub>	4 <sub>23</sub>	...	...	...	...
5 <sub>33</sub>	4 <sub>32</sub>	7809.854	7826.743	...	...
5 <sub>32</sub>	4 <sub>31</sub>	7850.399	7867.556	...	...
5 <sub>14</sub>	4 <sub>13</sub>	7984.121	8000.048	7996.405	7999.647
5 <sub>23</sub>	4 <sub>22</sub>	...	...	...	...
5 <sub>24</sub>	4 <sub>13</sub>	...	...	...	...
5 <sub>14</sub>	4 <sub>04</sub>	9550.994	9562.568	9577.222	9611.456
5 <sub>23</sub>	4 <sub>13</sub>	9666.184	9673.680	9630.596	9642.025
6 <sub>15</sub>	5 <sub>24</sub>	...	...	...	...
6 <sub>16</sub>	5 <sub>15</sub>	...	...	8774.817	8758.570
6 <sub>06</sub>	5 <sub>05</sub>	...	...	8826.288	8808.216
6 <sub>25</sub>	5 <sub>24</sub>	...	...	...	...
6 <sub>34</sub>	5 <sub>33</sub>	...	...	...	...
6 <sub>43</sub>	5 <sub>42</sub>	...	...	...	...
6 <sub>15</sub>	5 <sub>14</sub>	...	...	9499.796	9497.759
6 <sub>24</sub>	5 <sub>23</sub>	...	...	...	...

tia to determine an unambiguous structure by least-squares fitting methods. Single substitution data for the carbon atoms on the OCS molecules and on the HCCH molecule allowed the calculation of Kraitchman substitution coordinates,<sup>16</sup> and hence a direct determination of the principal axis coordinates of these atoms. The absolute values of the substitution coordinates are given in brackets in Table V, along with the coordinates that result from the least-squares inertial fit.

Assuming that the monomer geometries are unchanged upon complexation, nine independent parameters are needed to define their orientation. For example, three distances describe the separation of the centers of mass of each mono-

TABLE III. Spectroscopic constants for the eight isotopomers of the HCCH-(OCS)<sub>2</sub> trimer.

Spectroscopic constant	HCCH-(OCS) <sub>2</sub>	H <sup>13</sup> C <sup>13</sup> CH-(OCS) <sub>2</sub>	HCCH-(O <sup>13</sup> CS) <sub>2</sub>	DCCD-(OCS) <sub>2</sub>	HCCH-O <sup>13</sup> CS-OCS	HCCH-OCS-O <sup>13</sup> CS	H <sup>13</sup> CCH-(OCS) <sub>2</sub>	HC <sup>13</sup> CH-(OCS) <sub>2</sub>
A/MHz	1438.0194(5)	1385.9664(8)	1434.4523(8)	1372.7748(11)	1437.2720(13)	1435.2040(12)	1411.6492(12)	1411.0529(14)
B/MHz	849.9422(3)	847.4120(4)	839.4336(4)	841.4956(5)	843.8907(11)	845.4767(10)	847.5943(6)	849.7137(7)
C/MHz	711.8602(3)	700.3955(4)	705.0195(4)	699.7314(5)	707.5515(4)	709.3321(13)	706.9701(7)	705.1468(8)
Δ <sub>J</sub> /kHz	0.900(5)	0.895(6)	0.886(6)	0.854(7)	0.85(2)	0.89(2)	0.912(9)	0.908(11)
Δ <sub>JK</sub> /kHz	0.31(2)	0.35(4)	0.27(3)	0.47(4)	0.31 <sup>a</sup>	0.31 <sup>a</sup>	0.31 <sup>a</sup>	0.31 <sup>a</sup>
Δ <sub>K</sub> /kHz	1.85(4)	1.68(6)	1.88(7)	1.15(10)	2.03(11)	1.64(10)	1.66(10)	1.62(11)
δ <sub>J</sub> /kHz	0.123(2)	0.125(3)	0.115(3)	0.100(4)	0.131(8)	0.140(8)	0.124(4)	0.128(4)
δ <sub>K</sub> /kHz	1.34(5)	1.36(5)	1.43(6)	1.04(7)	1.41(9)	1.63(9)	1.38(7)	1.18(8)
Δν <sub>rms</sub> /kHz <sup>b</sup>	2.17	1.88	2.14	3.00	2.77	2.55	2.43	2.78
N <sup>c</sup>	42	26	30	31	19	19	20	20

<sup>a</sup>Held fixed at the value from the normal isotopomer during the fitting.

<sup>b</sup>Δν<sub>rms</sub>=[Σ(ν<sub>obs</sub>-ν<sub>calc</sub>)<sup>2</sup>/N]<sup>1/2</sup>.

<sup>c</sup>N is the number of fitted transitions.

mer, and define a reference plane. Two angles are then needed to describe the orientation of each monomer relative to the plane. The parameters actually fitted in the least-squares procedure were the two distances  $r(C_2-C_5)$  and  $r(C_2-M_9)$ , the four angles  $(C_2-C_5-M_9)$ ,  $(C_5-M_9-C_{10})$ ,  $(C_2-C_5-O_4)$ , and  $(O_1-C_2-M_9)$  and the three dihedral angles  $(C_2-C_5-M_9-C_{10})$ ,  $(M_9-C_2-C_5-O_4)$ , and  $(O_1-C_2-M_9-C_5)$ . Figure 1 illustrates the numbering of the atoms; M<sub>9</sub> is the center of mass of the HCCH molecule. A least-squares fit of all 24 moments of inertia using Schwendeman's STRFTQ program<sup>17</sup> converged to give the structural parameters listed in Table VI with a standard deviation in the fit, ΔI<sub>rms</sub>, of 0.177 u Å<sup>2</sup>. Attempts to get the program to converge to a starting structure in which the OCS molecules were aligned antiparallel failed and instead resulted in the same converged structure that is listed in Table VI. The data from the doubly substituted HCCH isotopomers (the <sup>13</sup>C<sub>2</sub>H<sub>2</sub> and the DCCD species) show the largest deviation in the

inertial data and this seems to indicate that the HCCH subunit exhibits some floppiness in the trimer.

During the least-squares fitting process, the monomer geometries were held fixed at their literature values [ $r(C\equiv C)=1.203$  Å,  $r(C-H)=1.061$  Å in HCCH and  $r(C=O)=1.1561$  Å, and  $r(C=S)=1.5651$  Å in OCS].<sup>18</sup> Calculation of the C≡C bond length in HCCH from the Kraitchman single substitution coordinates (Table V) gives a value of 1.173 Å, in good agreement with the literature value of 1.203 Å.<sup>18</sup> The calculated value of the C<sub>2</sub>-C<sub>5</sub> distance from the Kraitchman coordinates of these atoms agrees to within 0.035 Å of the value obtained from the inertial fit (Table VI).

The principal axis coordinates that are obtained from the inertial fit are listed in Table V, where it can be seen that the inertial fit coordinates are in generally good agreement with the values from the Kraitchman single substitution calculations. However, an inspection of the *b* coordinates for the C<sub>2</sub>

TABLE IV. Stark coefficients and dipole moment components for the HCCH-(OCS)<sub>2</sub> trimer.

Transition	M	Δν/ε <sup>2a</sup>	Obs-calc <sup>a</sup>
3 <sub>21</sub> -2 <sub>11</sub>	1	2.117	-0.045
	2	9.428	0.093
3 <sub>22</sub> -2 <sub>12</sub>	1	-5.646	-0.152
	2	-23.619	-1.165
3 <sub>22</sub> -2 <sub>11</sub>	1	-3.515	-0.014
	2	-12.608	0.537
4 <sub>13</sub> -3 <sub>03</sub>	1	3.422	0.169
	2	13.165	0.283
	3	29.399	0.469
4 <sub>22</sub> -3 <sub>12</sub>	2	1.937	-0.022
	3	4.358	-0.172
4 <sub>23</sub> -3 <sub>13</sub>	1	-3.172	-0.051
	2	-12.307	0.312
	3	-27.255	1.192
μ <sub>a</sub> =0.666(10) D			
μ <sub>b</sub> =0.48(6) D			
μ <sub>c</sub> =0.913(6) D			
μ <sub>total</sub> =1.227(23) D			

<sup>a</sup>All observed Stark coefficients and residuals in units of 10<sup>-5</sup> MHz/(V cm<sup>-1</sup>)<sup>2</sup>.

TABLE V. Principal axis coordinates determined from the least squares fit of the inertial data (Å).<sup>a</sup>

Atom <sup>b</sup>	a	b	c
O <sub>1</sub>	2.2946	-0.7333	0.9871
C <sub>2</sub>	2.0611	0.1575	0.2882
	[2.0528]	[0.3515]	[0.2504]
S <sub>3</sub>	1.7450	1.3635	-0.6580
O <sub>4</sub>	-0.9597	0.0997	1.7139
C <sub>5</sub>	-1.6028	0.3524	0.7870
	[1.5794]	[0.1998]	[0.8105]
S <sub>6</sub>	-2.4734	0.6945	-0.4678
H <sub>7</sub>	-0.8038	-2.8745	0.6657
C <sub>8</sub>	-0.3782	-2.5556	-0.2524
	[0.3144]	[2.5847]	[0.2494]
M <sub>9</sub>	-0.1370	-2.3748	-0.7729
C <sub>10</sub>	0.1043	-2.1940	-1.2934
	[0.0000] <sup>c</sup>	[2.2047]	[1.3142]
H <sub>11</sub>	0.5298	-1.8751	-2.2116

<sup>a</sup>Absolute values in brackets for the carbon atoms are the Kraitchman substitution coordinates obtained from the single isotopic substitution data.

<sup>b</sup>See Fig. 1 for the atom numbers. M<sub>9</sub> is the center-of-mass of the acetylene molecule.

<sup>c</sup>The value of *a*<sup>2</sup> for this coordinate was negative in the Kraitchman calculation, hence the zero value for the coordinate.

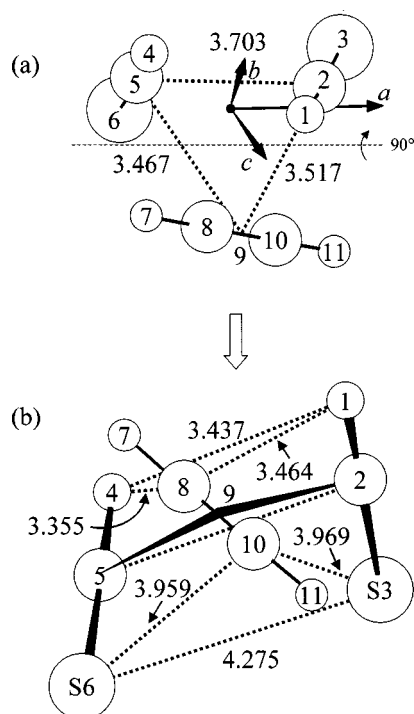


FIG. 1. Interatomic distances in the HCCH-(OCS)<sub>2</sub> trimer. The perspective in (a) places the carbon of the left-hand OCS molecule slightly in front of the plane of the paper and the carbon of the right-hand OCS slightly behind the plane of the paper. The perspective in (b) is obtained by rotating the view in (a) by 90° about the arrow in the direction shown. This will place C<sub>2</sub> and C<sub>5</sub> in the plane of the paper and the HCCH molecule above this plane. Distances are in angstroms.

and C<sub>5</sub> atoms reveals that the coordinates are effectively switched for these atoms, with the calculated Kraitchman coordinate for the C<sub>2</sub> atom much closer in magnitude to the inertial fit value for C<sub>5</sub>, and vice versa. This effect is not completely understood although it may arise simply from the fact that these coordinates are small in magnitude and therefore often subject to a higher uncertainty. A change in the *B* rotational constant of about 0.1 MHz would provide better agreement in the Kraitchman calculation; this is a magnitude

which could readily arise from a vibrational effect. The value of the *a* coordinate for C<sub>10</sub> is calculated to be zero—this arises from the fact that during the Kraitchman calculation the value of *a*<sup>2</sup> was determined to be negative. This is again probably due to the small magnitude of this coordinate. Table VI lists the structural parameters that are calculated from the coordinates in Table V, as well as parameters obtained from a semiempirical model which will be discussed later.

Using the coordinates in Table V and projecting the monomer dipole moments into the principal axis frame, the following dipole moment components are calculated:  $\mu_a = 0.54$  D,  $\mu_b = 0.71$  D, and  $\mu_c = 1.01$  D, giving a total dipole moment,  $\mu_{\text{total}}$ , of 1.34 D. These are in reasonable agreement with the measured dipole moment components of  $\mu_a = 0.666(10)$  D,  $\mu_b = 0.48(6)$  D, and  $\mu_c = 0.913(6)$  D, and the total dipole moment,  $\mu_{\text{total}}$  of 1.227(23) D. It is apparent from a comparison of these two sets of moments that there is a small amount of polarization which serves to decrease  $\mu_b$  and  $\mu_c$  and increase  $\mu_a$ . An *ab initio* calculation was carried out to test whether the discrepancies in the observed and calculated dipole moment components can be attributed to induced moments. GAUSSIAN98 (Ref. 19) was used to calculate the electric fields at the centers of mass of each monomer from the presence of the other two. Using the relation  $\mu_{\text{ind}} = \alpha \cdot F$  (where  $\alpha$  is the polarizability and *F* is the electric field at the point) and polarizabilities taken from Ref. 20 [ $\alpha(\text{HCCH}) = 3.36 \text{ \AA}^3$  and  $\alpha(\text{OCS}) = 5.21 \text{ \AA}^3$ ], the dipole moment components were calculated to change by  $-0.02$  D,  $-0.48$  D, and  $+0.08$  D for  $\mu_a$ ,  $\mu_b$ , and  $\mu_c$ , respectively. Applying these corrections to the projected dipole moments from above leads to  $\mu_a = 0.52$  D,  $\mu_b = 0.23$  D, and  $\mu_c = 1.09$  D. The  $\mu_b$  component of dipole is clearly the only one that is significantly affected by this correction and the effect is to decrease the magnitude of this component. Although this simplistic approach leads to a correction that is too large for the  $\mu_b$  component, it does suggest that the small difference between the measured and projected moments may be explained in part by polarization effects.

TABLE VI. Comparison of calculated structural parameters for the HCCH-(OCS)<sub>2</sub> trimer.

Parameter	Inertial fit	Kraitchman	Model <sup>a</sup>	Model <sup>b</sup>
			$K = 0.001E_h$	$K = 0.001375E_h$
$r(\text{C}_2\text{-C}_5)/\text{\AA}$	3.703(30)	3.678	3.628	3.804
$r(\text{C}_2\text{-M}_9)/\text{\AA}$	3.517(66)	...	3.318	3.490
$r(\text{C}_5\text{-M}_9)/\text{\AA}$	3.467(34)	...	3.351	3.534
$\angle(\text{C}_2\text{-C}_5\text{-M}_9)/\text{deg}$	58.6(11)	...	57.5	57.8
$\angle(\text{C}_5\text{-M}_9\text{-C}_{10})/\text{deg}$	108.8(22)	...	86.9	87.7
$\angle(\text{C}_2\text{-C}_5\text{-O}_4)/\text{deg}$	63.0(15)	...	59.1	59.1
$\angle(\text{O}_1\text{-C}_2\text{-M}_9)/\text{deg}$	75.8(24)	...	82.8	82.0
$\tau(\text{C}_2\text{-C}_5\text{-M}_9\text{-C}_{10})/\text{deg}$	-65.9(23)	...	-102.5	-103.7
$\tau(\text{M}_9\text{-C}_2\text{-C}_5\text{-O}_4)/\text{deg}$	104.4(31)	...	98.5	98.0
$\tau(\text{O}_1\text{-C}_2\text{-M}_9\text{-C}_5)/\text{deg}$	111.0(18)	...	116.0	115.3
$\tau(\text{O}_1\text{-C}_2\text{-C}_5\text{-O}_4)/\text{deg}$	38.0	...	29.5	29.3
$\tau(\text{O}_1\text{-C}_2\text{-M}_9\text{-C}_8)/\text{deg}$	48.9	...	17.9	17.4
$\tau(\text{O}_4\text{-C}_5\text{-M}_9\text{-C}_8)/\text{deg}$	54.3	...	18.1	16.7

<sup>a</sup>Calculated with the ORIENT model [Structure II, Fig. 5(b)] using the default parameters.

<sup>b</sup>Calculated with the ORIENT model [Structure II, Fig. 5(b)] using a value for the pre-exponential factor, *K*, that reproduced the center-of-mass separation in the HCCH-OCS dimer. See text for discussion.

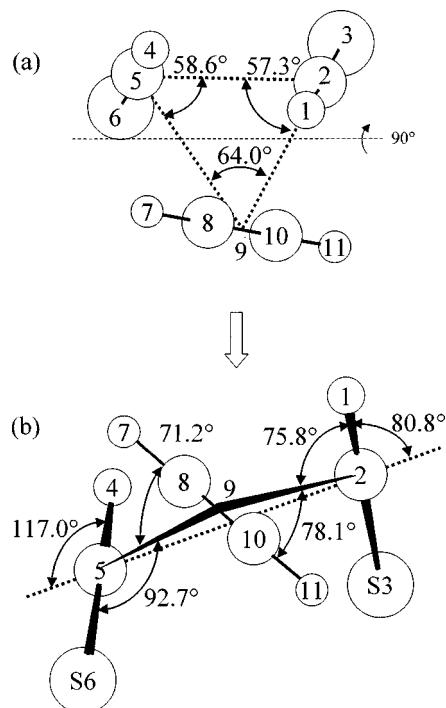


FIG. 2. Planar angles in the HCCH-(OCS)<sub>2</sub> trimer. The perspective is the same as in Fig. 1. (b) May be obtained by a 90° rotation about the arrow.

It should be noted that the structural parameters obtained from the inertial fit are calculated from ground state moments of inertia and hence ignore any vibrational contributions to these moments. The uncertainties that accompany the structural parameters in Table VI are statistical uncertainties that arise from the least-squares fitting process and so will not take into account any errors that may arise from the neglect of vibrational effects in this model. Although an estimate of these errors is well beyond the scope of this study, we conclude that the calculated parameters are a reasonable approximation to the structure due to the consistency of the fit for all eight isotopic species, the small magnitude of the centrifugal distortion constants and the good agreement between the coordinates from the inertial fit and those derived from the Kraitchman calculations. It is reasonable to assume that the equilibrium parameters would fall within  $\pm 0.05$  Å for the distances and  $\pm 5^\circ$  for the angles given in the tables and figures.

#### IV. DISCUSSION

Figures 1 and 2 illustrate the triangular-twisted structure of the trimer. The center of acetylene and the two carbons in OCS form a triangle with the linear axes of the monomers deviating from perpendicular to the edges of the triangle by  $3^\circ$ – $27^\circ$ . The twisting of the linear axes is more pronounced than in the more cylindrical, barrel-like structures recently observed for the mixed trimers OCS-(CO<sub>2</sub>)<sub>2</sub>,<sup>21,22</sup> N<sub>2</sub>O-(CO<sub>2</sub>)<sub>2</sub>,<sup>23</sup> and CO<sub>2</sub>-(OCS)<sub>2</sub>,<sup>4</sup> as well as for homotrimers such as (CO<sub>2</sub>)<sub>3</sub>,<sup>24</sup> (N<sub>2</sub>O)<sub>3</sub>,<sup>25</sup> and (OCS)<sub>3</sub>.<sup>7,9</sup> In marked contrast to the CO<sub>2</sub>-(OCS)<sub>2</sub> complex,<sup>4</sup> the two OCS molecules in the HCCH-(OCS)<sub>2</sub> trimer are found to be aligned parallel rather than antiparallel. The polar OCS dimer portion

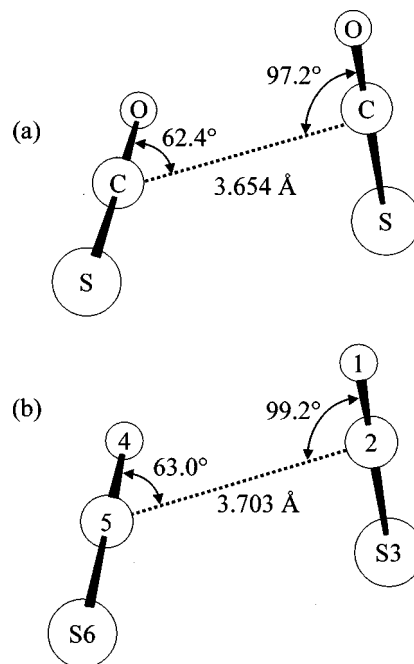


FIG. 3. The polar OCS dimer face (a) in the OCS trimer and (b) in the HCCH-(OCS)<sub>2</sub> trimer. Distances are in angstroms. The dihedral angles (O-C-C-O) in (a) and (b) are  $32.7^\circ$  and  $38^\circ$ , respectively.

of the trimer is clearly not planar (Figs. 1 and 2), with the dihedral angle (O<sub>1</sub>-C<sub>2</sub>-C<sub>5</sub>-O<sub>4</sub>) calculated to be  $38.0^\circ$ . This is consistent with the value of  $34.0^\circ$  found in the CO<sub>2</sub>-(OCS)<sub>2</sub> trimer.<sup>4</sup> Of course, actually the OCS dimer portion is antiparallel in the latter so that in a consistent coordinate system these angles differ by about  $180^\circ$ . The acetylene aligns itself across the OCS monomers with H<sub>7</sub> and C<sub>8</sub> significantly closer to both oxygens than C<sub>10</sub> and H<sub>11</sub> are to the sulfur atoms. The C<sub>10</sub>-S distances are about 0.45 Å greater than the sum of the C, S van der Waals radii. The C<sub>8</sub>-O distances are 0.13 and 0.24 Å larger.

Since no experimental structure determination exists for the polar OCS dimer, we are unable to make direct comparisons of the structural parameters with this dimer. However, it is possible to compare the polar OCS dimer fragment [Fig. 3(b)] with the well-known nonpolar OCS dimer<sup>6</sup> (not shown) and with the polar (OCS)<sub>2</sub> fragment in the OCS trimer<sup>9</sup> [Fig. 3(a)]. The C-C separation in the OCS dimer face of the HCCH-(OCS)<sub>2</sub> trimer is 3.703 Å which is some 0.011 Å shorter than observed for the OCS dimer<sup>9</sup> (in which the OCS molecules are aligned antiparallel). Comparison of the structure in Fig. 3(a) with the (OCS)<sub>2</sub> face from the HCCH-(OCS)<sub>2</sub> trimer [Fig. 3(b)] reveals these two distances are in closer agreement. Hopefully, the structure of the OCS dimer fragment obtained from this trimer system will allow us to accurately predict the structure of the dimer and undertake a search for the elusive polar OCS dimer.

The HCCH subunit is located above a plane defined by C<sub>2</sub>, C<sub>5</sub>, and O<sub>4</sub> and lies approximately parallel to this plane (Fig. 1). Comparison of the two HCCH-OCS faces in the trimer [Fig. 4(b) and 4(c)] with that of the HCCH-OCS dimer<sup>3</sup> in Fig. 4(a) reveals that they are both distorted approximately equally from the structure of the isolated

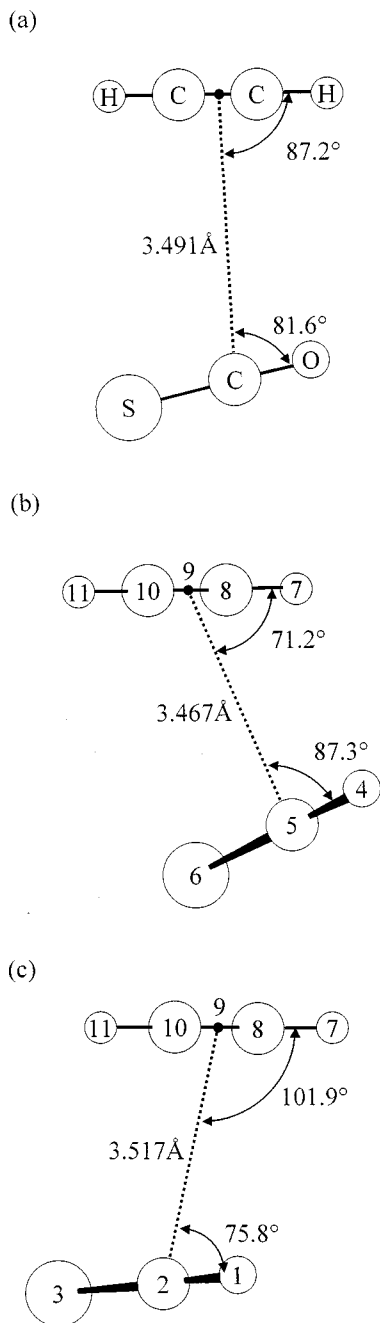


FIG. 4. Comparison of (a) the HCCH-OCS dimer with (b), (c) the HCCH-OCS dimer fragments in the HCCH-(OCS)<sub>2</sub> trimer. Distances are in angstroms. The dihedral angles (O-C-M-C) in (b) and (c) are 48.9° and 54.3°, respectively.

HCCH-OCS dimer.<sup>3</sup> However, compared to the dimer, these fragments are no longer planar, having dihedral angles of  $(O_4-C_5-M_9-C_8)=54.3^\circ$  and  $(O_1-C_2-M_9-O_8)=48.9^\circ$ . This loss of planarity results in some deviation in the planar angles from those of the HCCH-OCS dimer.<sup>3</sup> In spite of these angular deviations, the trimer structure might be described as approximating two HCCH-OCS dimer fragments. This is unlike the CO<sub>2</sub>-(OCS)<sub>2</sub> trimer where two dimerlike CO<sub>2</sub>-OCS fragments are not seen. This contrast arises from the near parallel orientation of the two OCS monomers in HCCH-(OCS)<sub>2</sub>. Recently, a second planar T-shaped isomer (with the sulfur pointing to the C≡C bond) has been

identified<sup>26</sup> which bears no close resemblance to HCCH-(OCS)<sub>2</sub>.

As with previous recent studies in this lab, a semiempirical model was employed to investigate possible structures and to make spectral predictions to aid in the initial assignment. The ORIENT model<sup>27</sup> of Anthony Stone allows for a distributed multipole representation of the electrostatic interaction and includes a combined dispersion-repulsion term that is provided by atom-atom parameters of the exp-6 form. Distributed multipole moments (DMM's) were calculated using a TZ2P basis set at the SCF level using the CADPAC suite of programs.<sup>28</sup> Multipole moments up to and including hexadecapole level were placed at atom centers; the DMM's used are listed in Ref. 3. The model interaction potential for an interaction between two molecules *A* and *B* may be written<sup>5</sup>

$$U_{\text{exp-6}} = \sum_{i,j} K \exp[-\alpha_{ij}(R_{ij}-\rho_{ij})] - \frac{C_6^{ij}}{R_{ij}^6}. \quad (1)$$

*i* and *j* represent sites on the two molecules *A* and *B*, respectively and  $R_{ij}$  is the distance between these sites.  $\alpha_{ij}$  is a parameter that describes the hardness of the exponential repulsion,  $\rho_{ij}$  is a sum of the effective radii of the atoms and  $C_6^{ij}$  is an empirical site-site dispersion term. The term *K* is a convenient energy unit and may be used to adjust the repulsion part of the potential in order to better reproduce experimental separations. The default value of *K* [ $=0.001 \text{ hartrees}(E_h)$ ] was used in this study. Values for  $\alpha_{ij}$ ,  $\rho_{ij}$ , and  $C_6^{ij}$  were taken from the tabulated values of Mirsky<sup>29</sup> that are given in Table 11.2 of Ref. 5. Values for atom-atom pairs not in this table were obtained by the use of the following combining rules: harmonic mean for  $\alpha(1/\alpha_{ij} \approx 1/\alpha_i + 1/\alpha_j)$ , arithmetic mean for  $\rho$  and geometric mean for  $C_6$ .

Using this default model, the global minimum species ( $-1748.9 \text{ cm}^{-1}$ , Structure I) was found to be a much more cylindrical or barrel-like structure in which the OCS monomers were aligned antiparallel and the HCCH situated above and almost parallel to the OCS monomers [Fig. 5(a)]. The second minimum was again a more barrel-type structure in which the two OCS monomers were aligned almost parallel to one another as was found experimentally. This species was some  $38 \text{ cm}^{-1}$  higher in energy ( $-1710.7 \text{ cm}^{-1}$  Structure II). It is illustrated in Fig. 5(b) and the structural parameters calculated from this species are given in the next to last column of Table VI. Predicted rotational constants and dipole moment components for this model are given in Table VII, where they are compared with the experimentally determined values. A third, much higher energy structure ( $-1397.2 \text{ cm}^{-1}$ , Structure III), was also obtained from the model calculation and this structure is shown in Fig. 5(c). Once the initial assignment was made and rotational constants and dipole moment data were in hand, Structure I and III were effectively ruled out, so the remainder of this discussion will focus on exploring how closely Structure II reproduces the experimental structural parameters. An initial, modified version of Structure II was used to predict isotopic shifts which resulted in a relatively straightforward identification of their spectra.

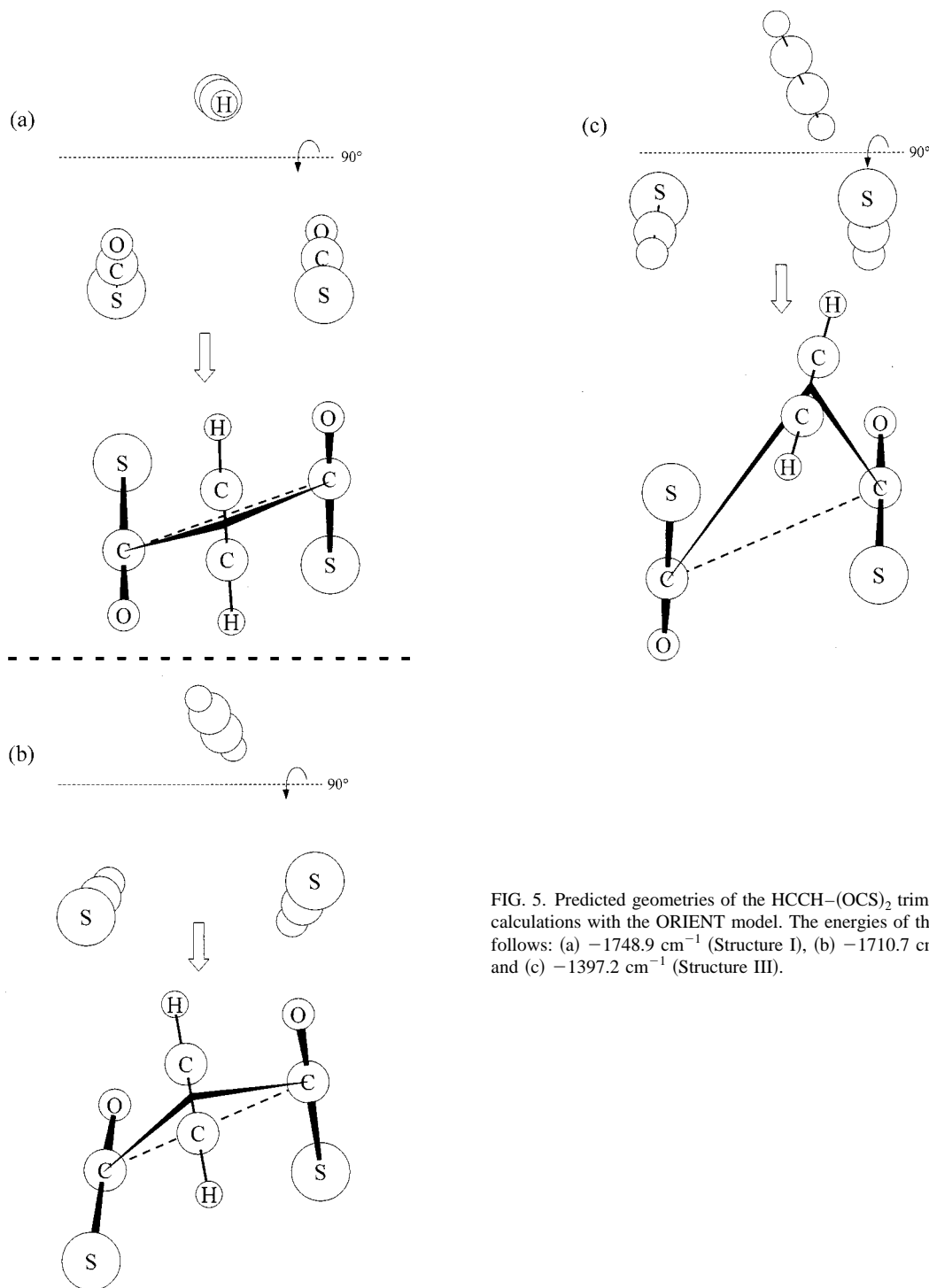


FIG. 5. Predicted geometries of the HCCH-(OCS)<sub>2</sub> trimer that result from calculations with the ORIENT model. The energies of the structures are as follows: (a)  $-1748.9 \text{ cm}^{-1}$  (Structure I), (b)  $-1710.7 \text{ cm}^{-1}$  (Structure II), and (c)  $-1397.2 \text{ cm}^{-1}$  (Structure III).

The values for the ORIENT structure given in the next to last column of Table VI reveals that the default model underestimates the intermolecular separations, in one case by  $0.2 \text{ \AA}$ . This is a fairly typical result when using the model with its default parameters. Previous studies<sup>3,30,31</sup> have shown that the use of the default value of the pre-exponential factor,  $K$ , underestimates the interatomic separations. In the study of the HCCH-OCS dimer, it was necessary to use a value of the  $K$  of  $0.001375E_h$  to reproduce the center-of-mass separation of the two monomers. The default model parameters do a credible job of predicting the approximate angular geometry of this complex. The angles and dihedrals

are typically within  $8^\circ$  or  $9^\circ$  with the notable exceptions of the  $C_5-M_9-C_{10}$  and  $C_2-C_5-M_9-C_{10}$  angles which are underestimated by  $22^\circ$  and overestimated by  $37^\circ$ , respectively. This indicates that the model predicts the HCCH to be aligned much less crossed to the (OCS)<sub>2</sub> portion than the experimental determination indicates. This is clearly visible by a comparison of Figs. 1 and 5(b). Increasing the value of the pre-exponential factor  $K$  to the value used to reproduce the center of mass separation in the HCCH-OCS dimer gave a much better reproduction of the distances in the HCCH-OCS faces of the trimer, although the C-C distance in the (OCS)<sub>2</sub> face is now overestimated by approximately  $0.1 \text{ \AA}$ .



TABLE VII. Comparison of experimental and predicted constants for the HCCH-(OCS)<sub>2</sub> trimer.

Parameter	Experiment	Model <sup>a</sup>	Model <sup>b</sup>
		$K = 0.001E_h$	$K = 0.001375E_h$
A/MHz	1438.0194(5)	1580.450	1477.68
B/MHz	849.9422(3)	888.005	824.13
C/MHz	711.8602(3)	748.487	689.41
$\mu_a/D$	0.666(10)	0.84	0.79
$\mu_b/D$	0.48(6)	0.74	0.71
$\mu_c/D$	0.913(6)	0.94	0.99

<sup>a</sup>See footnote a, Table VI.<sup>b</sup>See footnote b, Table VI.

As can be seen from the last column of Table VI, the angles are changed by very little by the increase of the value of  $K$ , although two of the three distances now resemble the experimental values much more closely. The last column of Table VII illustrates that the better reproduction of these distances results in a significantly better prediction of the rotational constants. The calculated dipole moments arise from the distributed multipole moments of the monomers and do not include induction effects. We have not exhaustively explored whether closer agreement in the details can be obtained by improving the DMM's, introducing distributed polarizabilities or using other atom-atom parameters in the dispersion and repulsion terms.

## V. CONCLUSIONS

The HCCH-(OCS)<sub>2</sub> trimer has been found to possess a triangular-twisted structure similar to that observed in a number of trimer systems to date. The OCS-(CO<sub>2</sub>)<sub>2</sub>,<sup>21,22</sup> (CO<sub>2</sub>-(OCS)<sub>2</sub>),<sup>4</sup> N<sub>2</sub>O-(CO<sub>2</sub>),<sup>23</sup> (CO<sub>2</sub>)<sub>3</sub>,<sup>24</sup> (N<sub>2</sub>O)<sub>3</sub>,<sup>25</sup> and (OCS)<sub>3</sub> (Refs. 7,9) systems have all been determined to possess this type of structure.

For the present trimer system, the structural parameters obtained for the trimer faces are found to uniformly bracket those observed in the isolated dimers. The unexpected parallel alignment of the OCS dipoles and the symmetric nature of the HCCH subunit allows it to align in such a way as to allow both dimer fragments to resemble the isolated dimer. This is in contrast to the observations in CO<sub>2</sub>-(OCS)<sub>2</sub> (Ref. 4) and OCS-(CO<sub>2</sub>)<sub>2</sub>,<sup>21,22</sup> where one of the dimer fragments of the trimer closely resembled the isolated dimer while the other face was significantly perturbed from this geometry. A comparison of the (OCS)<sub>2</sub> fragment with the corresponding face in the OCS trimer reveals that the two are also very similar. This enables a prediction of the spectrum of the polar OCS dimer and work to identify this species is underway, as are attempts at locating the other mixed trimer, OCS-(HCCH)<sub>2</sub>, and the other isomer of HCCH-(OCS)<sub>2</sub> predicted by the semiempirical model in which the OCS monomers are aligned antiparallel.

## ACKNOWLEDGMENTS

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