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# Van der Waals Complexes in 1,3-Dipolar Cycloaddition Reactions: Ozone-Ethylene

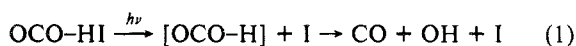
C. W. Gillies,<sup>\*,†</sup> J. Z. Gillies,<sup>†</sup> R. D. Suenram,<sup>§</sup> F. J. Lovas,<sup>§</sup> E. Kraka,<sup>‡</sup> and D. Cremer<sup>‡</sup>

Contribution from the Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180, Department of Chemistry, Union College, Schenectady, New York 12308, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, and Theoretical Chemistry, University of Göteborg, Kemigården 3, S-41296 Göteborg, Sweden. Received August 8, 1990

**Abstract:** Microwave spectra of  $\text{O}_3\text{-CH}_2\text{=CH}_2$ ,  $\text{O}_3\text{-CD}_2\text{=CH}_2$ ,  $\text{O}_3\text{-trans-CHD=CHD}$ , and  $\text{O}_3\text{-cis-CHD=CHD}$  have been observed with a pulsed-beam Fabry-Perot cavity, Fourier transform microwave spectrometer. Internal motions in the van der Waals complex give two states for the normal, 1,1-dideuterated and trans-1,2-dideuterated isotopic forms. The  $c$ -type transitions of the two states for the isotopic species above, as well as the one observed isotopic form of  $\text{O}_3\text{-cis-CHD=CHD}$ , independently fit to an asymmetric top Watson Hamiltonian. Stark effect measurements for  $\text{O}_3\text{-CH}_2\text{=CH}_2$  give  $\mu_a = 0.017$  (1) D and  $\mu_c = 0.466$  (2) D. The microwave data are only consistent with a structure having  $C_s$  symmetry in which the nearly parallel planes of ethylene and ozone have a center of mass separation of  $R_{\text{cm}} = 3.290$  (3) Å. Ab initio calculations at the MP4 level indicate that the preferred geometry corresponds to small tilts of the ozone and ethylene planes, which place an exo-oriented pair of hydrogens toward the terminal oxygens of ozone. Both the theoretical and microwave results suggest the tunneling splitting arises at least in part from a  $180^\circ$  rotation of ethylene about its  $C_2$  axis, which is perpendicular to the ethylene plane. 1,3-Dipolar cycloaddition theory, orbital symmetry rules, and ab initio calculations of the complex and transition states are used to argue that  $\text{O}_3\text{-CH}_2\text{=CH}_2$  lies in a shallow minimum on the reaction coordinate prior to the transition state in the reaction of ozone plus ethylene, which produces the primary product 1,2,3-trioxolane.

## Introduction

A number of experimental studies have shown that reactant orientation plays an important role in the dynamics of bimolecular gas-phase chemical processes by influencing reaction probabilities and internal state distributions of products. Hexapole fields<sup>1</sup> and photoselection<sup>2</sup> have been used to orient the reacting species. Recently, reactant orientation in the  $\text{H} + \text{CO}_2$  reaction was achieved by producing the van der Waals  $\text{CO}_2\text{-HBr}$  complex in a nozzle expansion followed by laser photodissociation of the covalent  $\text{H-Br}$  bond.<sup>3</sup> The same reaction has been studied with the  $\text{CO}_2\text{-HI}$  van der Waals complex as shown in eq 1.<sup>4</sup> In this case, the existence of a collision complex ( $[\text{OCO-H}]$ ) was inferred and its lifetime measured from the delay time of the laser-induced fluorescence signal of the OH product.



This paper reports a direct approach to the problem of obtaining reactant orientation in a bimolecular gas-phase chemical reaction. Here, a reacting mixture of ethylene and ozone is sampled by a modified pulsed-beam nozzle. The van der Waals complex between the reactants  $\text{O}_3$  and  $\text{C}_2\text{H}_4$  is formed in the expansion and detected in the Fabry-Perot cavity of a Fourier transform microwave spectrometer<sup>5</sup> of the Balle-Flygare type.<sup>6</sup> Both microwave spectral data and ab initio calculations are used to obtain the complex geometry, describe the internal motion, and determine the stability of the complex with respect to ethylene plus ozone. Since the van der Waals complex falls on the reaction potential surface of ozone plus ethylene, the structural results obtained in this research provide detailed structural information about the geometry of a species at large distances along the reaction coordinate. 1,3-Dipolar cycloaddition theory, orbital symmetry rules, and ab initio calculations of the complex and transition state are used to show that the complex lies in a shallow minimum on the reaction coordinate prior to the transition state, which leads to 1,2,3-trioxolane (primary ozonide,  $\text{CH}_2\text{OOOCH}_2$ ), the primary product of the cycloaddition between  $\text{O}_3$  and  $\text{C}_2\text{H}_4$ .

## Experimental Methods

A Fabry-Perot cavity, Fourier transform microwave spectrometer described previously<sup>5,6</sup> was used to obtain the rotational spectra of the  $\text{O}_3\text{-C}_2\text{H}_4$  complex.<sup>7</sup> Since ethylene reacts rapidly with ozone in the gas phase, mixtures of  $\sim 1\%$  ozone in argon and  $1\%$  ethylene in argon were independently passed through capillary tubing leading to the high-pressure side of the 0.5-mm orifice of a modified pulsed-solenoid valve.<sup>7,8</sup> Formaldehyde was produced as a product of the ethylene-ozone reaction by means of this flow arrangement. Hence, the pulsed valve serves as a flow reactor as well as a device to sample the reacting gas mixture for spectral analysis in the Fabry-Perot cavity. Two digital flow controllers were used to regulate the gas flows through the pulsed valve. Ozone was prepared by passing molecular oxygen through a Welsbach ozonator into a silica gel trap maintained at dry ice temperature. One of the flow controllers located between a cylinder of compressed argon and the ozone trap regulated the ozone-argon gas flow into the pulsed solenoid valve. The second controller was used to regulate the  $1\%$  ethylene in argon through a second gas inlet of the pulsed valve. Gas pulses of 200–400- $\mu\text{s}$  duration from the reacting gas mixture were delivered into the Fabry-Perot cavity at repetition rates up to 35 Hz. Short microwave pulses polarized molecular species in the cavity when the microwave frequency was nearly resonant ( $\Delta\nu \leq 0.5$  MHz) with a rotational transition. Free induction emission from the cavity was digitized (512 points, 0.5  $\mu\text{s}$ /point), and typically 200–2000 pulses were averaged. Fourier transforms of the averaged data yielded the power spectrum in the frequency domain

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<sup>†</sup> Rensselaer Polytechnic Institute.

<sup>‡</sup> Union College.

<sup>§</sup> National Institute of Standards and Technology.

<sup>‡</sup> University of Göteborg.

Table I. Rotational Transitions of  $O_3-CD_2=CH_2$ 

transition ( $J'_{K_1K_2}-J''_{K_1K_2}$ )	low-frequency state <sup>a,b</sup>		high-frequency state <sup>a,b</sup>	
	$\nu_{obsd}^c$ (MHz)	$\Delta\nu^d$ (kHz)	$\nu_{obsd}^c$ (MHz)	$\Delta\nu^d$ (kHz)
1 <sub>10</sub> -0 <sub>00</sub>	10 105.245	-1	10 106.925	6
4 <sub>04</sub> -3 <sub>12</sub>	10 245.490	0	10 243.940	2
5 <sub>05</sub> -4 <sub>13</sub>	13 266.367	0	13 264.910	-2
4 <sub>23</sub> -4 <sub>13</sub>	14 352.878	-7	14 355.980	-9
2 <sub>11</sub> -1 <sub>01</sub>	14 919.935	1	14 921.610	-5
3 <sub>22</sub> -3 <sub>12</sub>	15 213.464	21	15 216.567	27
2 <sub>21</sub> -2 <sub>11</sub>	15 868.944	-19	15 872.054	-5
2 <sub>20</sub> -2 <sub>12</sub>	17 234.544	2	17 237.633	2
3 <sub>21</sub> -3 <sub>13</sub>	18 023.409	-1	18 026.455	-1
3 <sub>12</sub> -2 <sub>02</sub>	19 966.106	0	19 967.763	0

<sup>a</sup> The intensities of the two states are almost the same, which makes it difficult to assign one to the lowest energy state. Most of the lines of the state designated low-frequency are at lower frequency than lines from the second state designated high-frequency. <sup>b</sup> Nuclear spin weight 1. <sup>c</sup> The transition frequencies are estimated to have measurement uncertainties of  $\sim 8$  kHz. <sup>d</sup>  $\Delta\nu$  is the observed minus calculated frequency (kHz) from the least-squares fit.

with a resolution element of 3.9063 kHz/point. The precision and accuracy of the transition frequency measurements for  $O_3-C_2H_4$  lines (15-kHz full widths at half-peak intensity) were estimated to be 4 kHz.

Rotational transitions of  $Ar-O_3$ ,<sup>9</sup>  $O_3$ ,<sup>10</sup> and  $C_2H_4-H_2O$ <sup>11</sup> were monitored to be certain that both ozone and ethylene were present in the pulsed beam. Optimum signals of the  $O_3-C_2H_4$  complex were obtained at flow rates of 100 cm<sup>3</sup>/min  $O_3/Ar$  and 10 cm<sup>3</sup>/min  $C_2H_4/Ar$ . These signals required the presence of both the ozone and ethylene flows. Formaldehyde lines<sup>12</sup> were observed in the gas pulses by employing the same flow conditions required to see the  $O_3-C_2H_4$  complex. However, spectral lines from the thermally unstable products ethylene primary ozonide,<sup>13</sup> dioxirane,<sup>14</sup> and ethylene secondary ozonide<sup>15</sup> could not be seen in the beam. Deuterium-enriched (99%) samples of  $CD_2=CH_2$ , *cis*-CHD=CHD and *trans*-CHD=CHD were used to obtain the spectra of the three dideuterated isotopes of the  $O_3-C_2H_4$  complex.

## Results

**Spectral Analysis.** Accurate spectral predictions are difficult to make for weakly bound complexes, particularly when both monomer subunits are asymmetric tops because the complex geometries are not very certain. Since the ozone plus ethylene reaction leads to ethylene primary ozonide as expected for a 1,3-dipolar cycloaddition,<sup>13</sup> it is reasonable to assume a parallel plane approach of ethylene to ozone (structure A in Figure 1) in the formation of the  $O_3-C_2H_4$  complex. An  $O_3-C_2H_4$  structure with the two parallel planes of ethylene and ozone separated by 3.0 Å and  $\theta_1 = \theta_2 = 90^\circ$  predicts a nearly prolate rotor spectrum with intense *c*-type transitions.

The *c*-type 2<sub>11</sub>-1<sub>01</sub> and 1<sub>10</sub>-0<sub>00</sub> R-branch transitions were found and assigned by Stark effect measurements. Two  $K_{-1} = 2-1$ , Q-branch series and three additional R-branch lines completed the *c*-type assignment of  $O_3-C_2H_4$ . Each *c*-type transition was accompanied by a satellite line with an intensity about half the intensity of the stronger line. The pairs of transitions are split by 5–10 MHz and have nearly the same Stark effect. A similar doubling of the rotational spectra was observed for the  $O_3-CD_2=CH_2$  and  $O_3-trans-CHD=CHD$  isotopic species. The intensity ratio of transitions from the two states was about 1/1 for  $O_3-CD_2=CH_2$  as compared to 0.7/1.0 for  $O_3-trans-CHD=CHD$ . Extensive spectral searches revealed only one set of transitions for the  $O_3-cis-CHD=CHD$  isotopic species.

Table II. Rotational Transitions of  $O_3-cis-CHD=CHD$ 

transition ( $J'_{K_1K_2}-J''_{K_1K_2}$ )	$\nu_{obsd}^a$ (MHz)	$\Delta\nu^b$ (kHz)
1 <sub>10</sub> -0 <sub>00</sub>	10 122.207	26
4 <sub>04</sub> -3 <sub>12</sub>	10 371.813	1
5 <sub>05</sub> -4 <sub>13</sub>	13 135.435	-5
5 <sub>05</sub> -4 <sub>13</sub>	13 383.837	1
4 <sub>23</sub> -4 <sub>13</sub>	14 212.344	9
2 <sub>11</sub> -1 <sub>01</sub>	14 987.042	-22
3 <sub>22</sub> -3 <sub>12</sub>	15 095.010	12
2 <sub>21</sub> -2 <sub>11</sub>	15 767.694	-14
2 <sub>20</sub> -2 <sub>12</sub>	17 169.784	12
3 <sub>21</sub> -3 <sub>13</sub>	17 982.519	-5
3 <sub>12</sub> -2 <sub>02</sub>	20 089.802	0

<sup>a</sup> The transitions are estimated to have measurement uncertainties of  $\sim 8$  kHz. <sup>b</sup>  $\Delta\nu$  is the observed minus calculated frequency (kHz) from the least-squares fit.

Table III. Rotational Transitions of  $O_3-trans-CHD=CHD$ 

transition ( $J'_{K_1K_2}-J''_{K_1K_2}$ )	$A_1$ state <sup>a</sup>		$A_2$ state <sup>b</sup>	
	$\nu_{obsd}^c$ (MHz)	$\Delta\nu^d$ (kHz)	$\nu_{obsd}^c$ (MHz)	$\Delta\nu^d$ (kHz)
1 <sub>10</sub> -0 <sub>00</sub>	10 081.544	0	10 079.902	-3
4 <sub>04</sub> -3 <sub>12</sub>	10 242.226	0	10 243.774	0
5 <sub>05</sub> -4 <sub>13</sub>	13 203.374	-5	13 200.378	-6
5 <sub>05</sub> -4 <sub>13</sub>			13 246.198	0
4 <sub>23</sub> -4 <sub>13</sub>	14 262.224	10	14 259.213	10
2 <sub>11</sub> -1 <sub>01</sub>	14 898.001	0	14 896.360	1
3 <sub>22</sub> -3 <sub>12</sub>	15 129.613	6	15 126.594	3
2 <sub>21</sub> -2 <sub>11</sub>	15 790.452	-20	15 787.448	-10
2 <sub>20</sub> -2 <sub>12</sub>	17 167.855	18	17 164.837	0
3 <sub>21</sub> -3 <sub>13</sub>	17 964.817	-10	17 961.867	9
4 <sub>22</sub> -4 <sub>14</sub>	19 159.059	1	19 156.156	-6
3 <sub>12</sub> -2 <sub>02</sub>	19 948.008	-1	19 946.391	1
2 <sub>20</sub> -1 <sub>10</sub>			24 999.206	-1

<sup>a</sup> Nuclear spin weight 15. <sup>b</sup> Nuclear spin weight 21. <sup>c</sup> The transitions are estimated to have measurement uncertainties of  $\sim 8$  kHz. <sup>d</sup>  $\Delta\nu$  is the observed minus calculated frequency (kHz) from the least-squares fit.

Table IV. Rotational Constants and Centrifugal Distortion Constants of Ozone-Ethylene Isotopic Species<sup>a</sup>

spectral constant (MHz)	$O_3-CD_2=CH_2$		$O_3-$ <i>cis</i> -CHD=CHD
	low-frequency state	high-frequency state	
<i>A</i>	7697.423 (22)	7699.243 (21)	7689.330 (23)
<i>B</i>	2408.323 (25)	2408.332 (27)	2433.481 (33)
<i>C</i>	1961.439 (33)	1961.451 (36)	1974.958 (52)
$\Delta_J$	0.015 22 (29)	0.015 55 (31)	0.013 73 (23)
$\Delta_{JK}$	0.2056 (14)	0.2062 (15)	0.2465 (22)
$\Delta_K$	-0.2893 (51)	-0.1343 (53)	-0.2380 (46)
$\delta_J$	0.003 13 (15)	0.003 26 (13)	0.002 81 (18)
$\delta_K$	0.152 (13)	0.151 (15)	0.154 (21)

<sup>a</sup> Uncertainties in parentheses are 1 standard deviation from the least-squares fit.

Stark effect measurements were used to assign the two states of  $O_3-CD_2=CH_2$  and  $O_3-trans-CHD=CHD$  as well as the one state of  $O_3-cis-CHD=CHD$ . Each state observed for all the isotopic species of the complex was fit separately to an  $F$  A-reduced Watson Hamiltonian.<sup>16</sup> The frequency measurements for  $O_3-CD_2=CH_2$  and  $O_3-cis-CHD=CHD$  are listed in Tables I and II, and those for  $O_3-trans-CHD=CHD$  are given in Table III. Table IV contains the spectral constants for  $O_3-CD_2=CH_2$  and  $O_3-cis-CHD=CHD$ . The spectral constants for  $O_3-trans-CHD=CHD$  are presented in Table V. A preliminary communication contains the transition frequencies and spectral constants for the normal isotopic species  $O_3-CH_2=CH_2$ .<sup>7</sup> Table V also lists the spectral constants for  $O_3-CH_2=CH_2$ . It is argued in a subsequent section of this paper that the doubling of lines

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Table V. Rotational Constants and Centrifugal Distortion Constants of Ozone–Ethylene Isotopic Species<sup>a</sup>

spectral constant (MHz)	O <sub>3</sub> –CH <sub>2</sub> =CH <sub>2</sub> <sup>b</sup>		O <sub>3</sub> – <i>trans</i> -CHD=CHD	
	A <sub>1</sub>	A <sub>2</sub>	A <sub>1</sub>	A <sub>2</sub>
<i>A</i>	8246.841 (2)	8241.897 (4)	7673.001 (51)	7671.214 (8)
<i>B</i>	2518.972 (4)	2518.941 (9)	2409.216 (54)	2409.214 (11)
<i>C</i>	2044.248 (5)	2044.287 (11)	1958.598 (37)	1958.581 (13)
Δ <sub><i>J</i></sub>	0.015 96 (3)	0.015 77 (6)	0.0151 (12)	0.014 768 (68)
Δ <sub><i>JK</i></sub>	0.2333 (2)	0.2350 (4)	0.2116 (20)	0.211 20 (58)
Δ <sub><i>K</i></sub>	–0.0524 (6)	–0.405 (1)	–0.127 (14)	–0.2813 (19)
δ <sub><i>J</i></sub>	0.003 16 (2)	0.003 28 (3)	0.002 98 (17)	0.002 955 (51)
δ <sub><i>K</i></sub>	0.168 (2)	0.147 (5)	0.152 (19)	0.1554 (59)

<sup>a</sup>Uncertainties in parentheses are 1 standard deviation from the least-squares fit. <sup>b</sup>Obtained from Table II in ref 7.

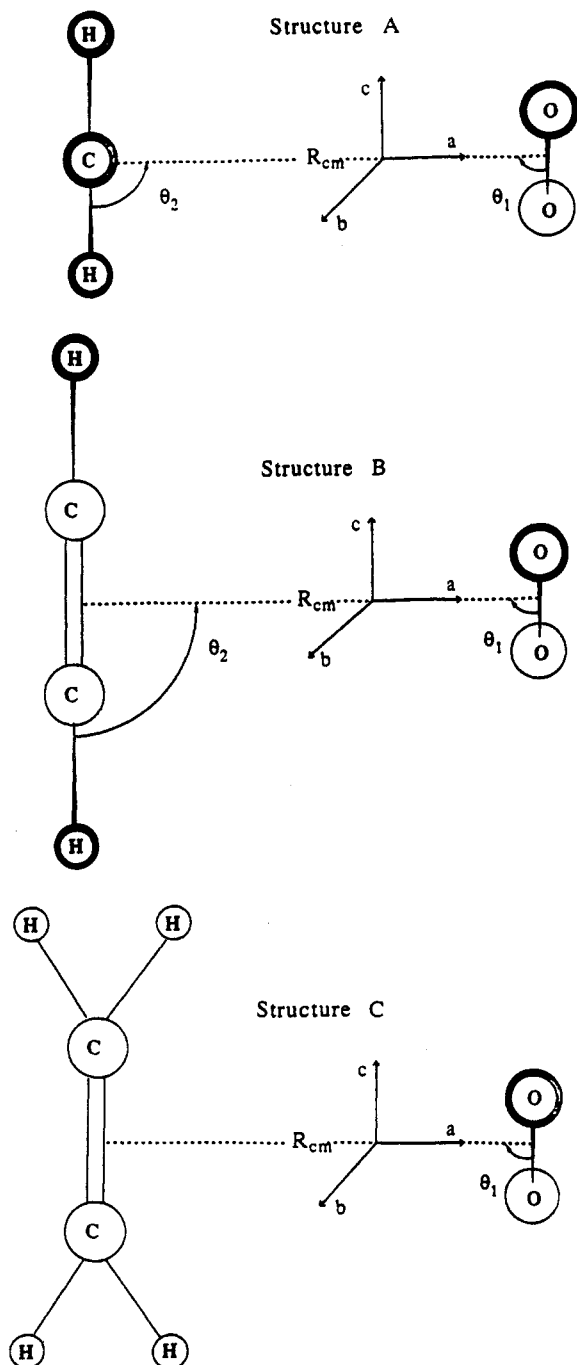


Figure 1. Projections of structures A, B, and C in the *a,c* symmetry plane of O<sub>3</sub>–CH<sub>2</sub>=CH<sub>2</sub>. *R*<sub>cm</sub> is the distance of the center of mass of ozone to the center of mass of ethylene, *θ*<sub>1</sub> is the angle between the local *C*<sub>2</sub> axis of ozone and *R*<sub>cm</sub>, and *θ*<sub>2</sub> is the angle between *R*<sub>cm</sub> and the molecular plane of ethylene.

arises from a tunneling motion, which involves internal rotation of ethylene. The state designations in Tables I–IV are symmetry

Table VI. Electric Dipole Moment of Ozone–Ethylene Complex<sup>a</sup>

component (D)	O <sub>3</sub> –CH <sub>2</sub> =CH <sub>2</sub>	O <sub>3</sub>
μ <sub>a</sub>	0.017 (1)	
μ <sub>c</sub>	0.466 (2)	
μ <sub>T</sub>	0.466 (2)	0.5324 (24) <sup>b</sup>

<sup>a</sup>The uncertainties given in parentheses are 1 standard deviation of the least-squares fit. All dipole components have units of debye. <sup>b</sup>The total dipole moment μ<sub>T</sub> = μ<sub>b</sub> for free ozone (see ref 12).

labels related to this internal motion in the complex.

**Electric Dipole Moment.** The frequency shifts as a function of applied electric field were measured for a number of components of O<sub>3</sub>–CH<sub>2</sub>=CH<sub>2</sub> transitions. As described previously,<sup>17</sup> positive and negative dc voltages were applied to 25 × 25 cm square parallel plates spaced at about 26 cm apart in the cavity. The Δ|*M<sub>J</sub>*| = 0 Stark transitions were observed by orienting the applied dc electric and microwave electric field vectors parallel in the cavity. The effective electric field between the plates was calibrated with use of the *J* = 1–0 transition of OCS and its known dipole moment.<sup>18</sup>

A combination of 25 measurements on the A<sub>1</sub> and A<sub>2</sub> states of O<sub>3</sub>–CH<sub>2</sub>=CH<sub>2</sub> was used to determine the electric dipole moment of the complex. The Stark effect data include the |*M<sub>J</sub>*| = 0, 1 components of the 2<sub>11</sub>–1<sub>01</sub> transition, the *M<sub>J</sub>* = 0 component of the 1<sub>10</sub>–0<sub>00</sub> transition, the |*M<sub>J</sub>*| = 2 component of the 2<sub>21</sub>–2<sub>11</sub> transition and the |*M<sub>J</sub>*| = 2, 3 components of the 3<sub>22</sub>–3<sub>12</sub> transition. Frequency shifts (Δ*ν*) of the Stark components were quadratic with respect to the applied electric field.

Linear least-squares fits of the Stark data to second-order perturbation theory<sup>19</sup> gave the results in Table VI. The residual of the fit is 5 kHz with μ<sub>a</sub> = 0.017 (1) D and μ<sub>c</sub> = 0.466 (2) D. The quality of the fit, as well as the absence of *b*-type transitions, indicates that μ<sub>b</sub> = 0. Isotopic moment of inertia data discussed in a subsequent section of this paper confirm the presence of an *a,c* symmetry plane with μ<sub>b</sub> = 0 in the complex. The small nonzero value of μ<sub>a</sub> derived from the Stark effect data was confirmed by observation of a weak line at 13 576 MHz assigned to the 3<sub>03</sub>–2<sub>02</sub> *a*-type transition. Due to the poor signal to noise of 2/1 (5000 pulses at full microwave power) obtained for this transition, no attempts were made to measure additional *a*-type transitions and include them in the spectral least-squares fits.

**Structural Analysis.** Since μ<sub>b</sub> was found to be zero from the electric dipole moment measurements, O<sub>3</sub>–CH<sub>2</sub>=CH<sub>2</sub> has an *a,c* symmetry plane. The second moment *P*<sub>bb</sub> = 1/2(*I*<sub>a</sub> + *I*<sub>b</sub>) is proportional to the square of the out of plane *b* coordinates. For the normal isotopic species, *P*<sub>bb</sub> = 53.94 uÅ<sup>2</sup> in the A<sub>1</sub> state, which demonstrates that the complex cannot be planar and that a number of heavy atoms are located out of the *a,c* plane. Only three structural forms of O<sub>3</sub>–CH<sub>2</sub>=CH<sub>2</sub> have heavy atoms out of an *a,c* symmetry plane. Structure A (shown in Figure 1) has four heavy atoms, two terminal oxygens of ozone, and the two ethylene carbons, located symmetrically out of the *a,c* plane. For structures B and C (also shown in Figure 1), the two carbon atoms fall in

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**Table VII.** Structural Parameters of Ozone–Ethylene Complex

Monomer Geometry				
$O_3^a$	$R(O-O) =$ 1.276 Å	$\theta(O-O-O) =$ 116.97°		
$CH_2=CH_2^b$	$R(C=C) =$ 1.339 Å	$R(C-H) =$ 1.086 Å	$\theta(H-C-H) =$ 121.1°	
$O_3-CH_2=CH_2$				
geometry	syn a	syn b	anti a	anti b
$R_{cm}$ (Å)	3.291 (3)	3.291 (3)	3.291 (2)	3.291 (3)
$\theta_1$ (deg)	111 (4)	68 (4)	112 (4)	69 (4)
$\theta_2$ (deg)	107 (4)	106 (3)	74 (3)	73 (4)
$\sigma$ (uÅ <sup>2</sup> )	0.39	0.39	0.39	0.39

<sup>a</sup>  $R(O-O)$  and  $\theta(O-O-O)$  were determined from an  $r_0$  fit of the moments of inertia of the normal isotopic species of ozone obtained from rotational constants reported in ref 12. <sup>b</sup> The ethylene  $r_0$  parameters were determined from an  $r_0$  fit in the  $CH_2=CHD$  frame with use of the  $CH_2=CD_2$ ,  $CH_2=CHD$ , and *cis*- $CHD=CHD$  second moments  $P_{aa}$  and  $P_{bb}$  reported by: Hirota, E.; Endo, Y.; Saito, S.; Yoshida, K.; Yamaguchi, I.; Mochida, K. *J. Mol. Spectrosc.* **1981**, 89, 223.

the  $a,c$  plane while the two terminal oxygens of ozone lie symmetrically out of this plane.

Structure C is not consistent with the moment of inertia data of the three deuterated isotopic species. For structure C, the four hydrogen atoms are located in the  $a,c$  plane, which means that  $\Delta P_{bb} = P_{bb}(d_2\text{-isotope}) - P_{bb}(\text{normal isotope}) = 0$ . The moment of inertia data determine  $\Delta P_{bb}$  to be 2.7968, 3.0342, and 3.0315 uÅ<sup>2</sup> for  $O_3-CD_2=CH_2$ ,  $O_3\text{-cis-}CHD=CHD$ , and  $O_3\text{-trans-}CHD=CHD$ , respectively. These values of  $\Delta P_{bb}$  for the three deuterated isotopic species show that the deuterium atoms are located symmetrically out of the  $a,c$  plane.

Four heavy atoms are located out of the  $a,c$  plane for structure A, while B has only two heavy atoms out of this plane. Hence, a comparison of calculated values of  $P_{bb}$  with the experimental value for the normal isotopic species provides a way to distinguish A from B. The geometries of free ozone and ethylene listed in Table VII were used to calculate  $P_{bb}$  for the two forms. The center of mass separation ( $R_{cm}$ ) and the angles  $\theta_1$  and  $\theta_2$  shown in Figure 1 do not affect the calculated values of  $P_{bb}$  because the out of plane  $b$  coordinates are not functions of these parameters. Structures A and B have calculated values of  $P_{bb} = 54.68$  and  $41.38$  uÅ<sup>2</sup>, respectively.  $P_{bb}$  for structure A is in excellent agreement with the value of  $53.94$  uÅ<sup>2</sup> determined from the experimental rotational constants of the  $A_1$  state. Structure B has a much lower calculated  $P_{bb}$ , as expected for a geometry with only two heavy atoms located out of the  $a,c$  plane. In summary, the electric dipole moment and moment of inertia data are consistent only with structure A, which has  $C_s$  symmetry.

If the monomer geometries are not changed by complexation,  $R_{cm}$  (the center of mass separation),  $\theta_1$  (the angle between  $R_{cm}$  and the local  $C_2$  axis of ozone), and  $\theta_2$  (the angle between  $R_{cm}$  and the molecular plane of ethylene) are required to determine the geometry of structure A (see Figure 1). The isotopic spectral data of the complex include effective rotational constants of two states for  $O_3-CH_2=CH_2$ ,  $O_3-CD_2=CH_2$ , and *trans*- $CHD=CHD$ . In a subsequent section of this paper, these states are rationalized in terms of a tunneling motion through a barrier that involves internal rotation of ethylene. Differences between the effective rotational constants of the two states for each isotopic species are small. The structural determination used effective rotational constants from the ground  $A_1$  state.

In the case of  $O_3\text{-cis-}CHD=CHD$ , the internal motion does not give rise to two tunneling states. However, two different structural isotopic species of  $O_3\text{-cis-}CHD=CHD$  are possible for structure A with  $C_s$  symmetry. These forms are designated *anti*-( $O_3\text{-cis-}CHD=CHD$ ) and *syn*-( $O_3\text{-cis-}CHD=CHD$ ). Experimentally only one form is seen in the supersonic expansion. This form is likely the lower energy species because extensive spectral searches did not reveal the presence of a second set of rotational transitions. In the  $SO_2-CH_2=CH_2$  complex, which has a similar structure with  $C_s$  symmetry and analogous internal motions, two structural forms of  $SO_2\text{-cis-}CHD=CHD$  were observed with use of a helium carrier gas in the supersonic ex-

**Table VIII.** Comparison of Chutjian Substitution Coordinates with  $r_0$  Coordinates for Hydrogen in Ozone–Ethylene Complex

atomic coordinate (Å)	<i>a</i>	<i>b</i>	<i>c</i>
hydrogen (substitution) <sup>a</sup>	1.6931	1.2352	0.8504
hydrogen $r_0$ (syn a) <sup>b</sup>	-1.8084	±1.2305	+0.8831
hydrogen $r_0$ (syn b)	-1.8068	±1.2305	+0.9185
hydrogen $r_0$ (anti a)	-1.8068	±1.2305	-0.9185
hydrogen $r_0$ (anti b)	-1.8084	±1.2305	-0.8831

<sup>a</sup> The magnitude but not the sign of the atomic coordinates is determined by Chutjian's equations (see ref 21). The coordinates were obtained with use of the normal isotopic species as the parent and  $O_3\text{-cis-}CHD=CHD$  for the substituted species. <sup>b</sup> The  $r_0$  coordinates for hydrogen are obtained from the moment fits summarized in Table VII.

pansion as a means of producing a warmer beam.<sup>20</sup> This was not possible in the ozone–ethylene complex due to the lower overall intensity of the spectrum.

The observation of only one form of  $O_3\text{-cis-}CHD=CHD$  makes it difficult to assign the effective rotational constants obtained from the spectral analysis to the anti or syn isotopic species. This problem is due to the similarity of the magnitude of the syn and anti deuterium coordinates. Least-squares fits of the moment of inertia data require an assignment of the observed  $O_3\text{-cis-}CHD=CHD$  isotopic species to either the anti or syn form. Hence, two structural fits were carried out with use of the anti assignment in one and the syn assignment in the other.

Since  $R_{cm}$ ,  $\theta_1$ , and  $\theta_2$  are dependent upon  $P_{aa} = 1/2(I_b + I_c - I_a)$  and  $P_{cc} = 1/2(I_a + I_b - I_c)$  but not  $P_{bb}$ , only  $P_{aa}$  and  $P_{cc}$  for the four isotopic species were used in the least-squares fits. In these fits, the monomer ozone and ethylene geometries were fixed at the  $r_0$  values listed in Table VII. Table VII also gives  $R_{cm}$ ,  $\theta_1$ , and  $\theta_2$  obtained from the fits for the *syn*- and *anti*-( $O_3\text{-cis-}CHD=CHD$ ) assignments. Fits involving both syn and anti assignments of the  $O_3\text{-cis-}CHD=CHD$  isotopic species are equally compatible with supplementary angles of 68° and 112° for  $\theta_1$ . However, the syn assignment fit determines  $\theta_2$  to be 106°, while the supplementary angle of 74° for  $\theta_2$  is found with the fit that assigns the  $O_3\text{-cis-}CHD=CHD$  isotopic species to the anti form.

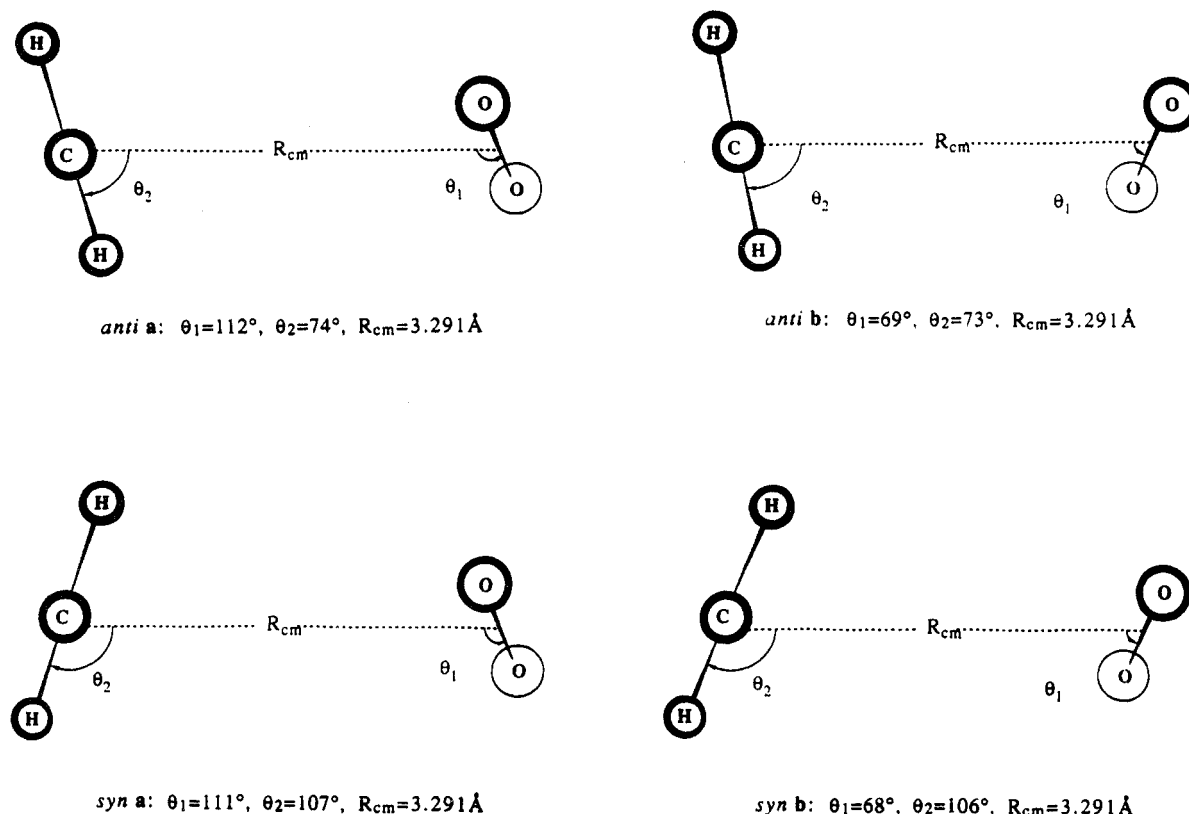
The combination of the ambiguity in the assignment to the syn or anti forms of  $O_3\text{-cis-}CHD=CHD$  and the lack of oxygen-18 isotopic substitution required to distinguish  $\theta_1 = 68^\circ$  from  $\theta_1 = 112^\circ$  leaves four geometries consistent with the observed moment of inertia data. All four fits listed in Table VII determine  $R_{cm}$  to be 3.290 (3) Å. However, the ethylene and ozone planes are tilted  $\pm 16^\circ$  and  $\pm 22^\circ$ , respectively, from the parallel plane  $\theta_1 = \theta_2 = 90^\circ$  structure shown as structure A in Figure 1. These four structures are illustrated in Figure 2.

Chutjian's double substitution equations give the hydrogen coordinates for the observed form of  $O_3\text{-cis-}CHD=CHD$ .<sup>21</sup> Table VIII compares these substitution coordinates with the syn and anti hydrogen coordinates calculated from the fits given in Table VII. Unfortunately, only the *c* hydrogen coordinate differs among the syn and anti forms. Furthermore, supplementary angles for  $\theta_1$  and  $\theta_2$  are obtained in the syn a, anti b and syn b, anti a pairs of fits. As shown in Table VIII, this leads to *c* hydrogen coordinates, which are equal in magnitude but opposite in sign for each of the two pairs of fits. Since Chutjian's substitution method does not give the signs of the atomic coordinates, it is not possible to distinguish the *syn*- and *anti*-( $O_3\text{-cis-}CHD=CHD$ ) isotopic assignment. The magnitudes of the *c* hydrogen coordinates do not differ greatly between the two pairs of fits. However, a little better agreement is found between the magnitude of the *c* hydrogen coordinates determined for the syn b, anti a pair and the substitution value of 0.8504 Å.

**Internal Motions.** The two tunneling states observed for  $O_3-CH_2=CH_2$ ,  $O_3-CD_2=CH_2$ , and  $O_3\text{-trans-}CHD=CHD$

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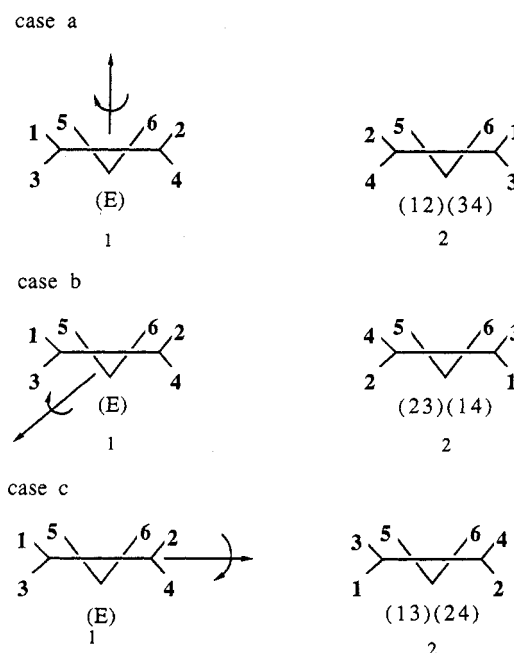


**Figure 2.** Conformations designated anti a, anti b, syn a, and syn b obtained from the least-squares fits of second moments of inertia of ozone-ethylene complex isotopic species.

likely arise from a motion that exchanges equivalent pairs of hydrogen and/or deuterium atoms in ethylene, i.e., internal rotation of ethylene about one of its  $C_2$  symmetry axes. An inversion motion of ozone reverses the direction of the dipole moment of ozone along the  $c$  principal axis of the complex, which gives  $c$ -type rotation-inversion transitions. Since the  $c$ -type transitions fit to within the experimental uncertainty of the frequency measurements to a standard Watson Hamiltonian, there is no evidence that an inversion of ozone is the origin of the tunneling states.

There are three different internal rotations of ethylene. As shown in Figure 3,  $180^\circ$  rotation about each of the  $C_2$  axes in ethylene exchanges two pairs of equivalent hydrogen atoms. Since two tunneling states are observed, only one of these three internal motions are possible. On the basis of a complex having  $C_s$  symmetry, each of the three internal rotations produces two equilibrium frameworks. For each internal rotation, the permutation inversion operation to be applied upon the wave function of framework 1 is given under that framework in Figure 3. The permutation inversion group for each internal rotation of ethylene is isomorphic to the  $C_2$  symmetry group. This means each asymmetric rotor level is split into two components and the symmetry species of these components are  $A_1$  and  $A_2$ . The allowed transitions are  $A_1-A_1$  and  $A_2-A_2$ , which give rise to two sets of lines designated  $A_1$  and  $A_2$ .

Exchange of the two pairs of hydrogens in  $O_3-CH_2=CH_2$  gives nuclear spin statistical weights of  $g = 10$  and  $g = 6$  for the  $A_1$  and  $A_2$  states, respectively. This produces an intensity ratio of  $10/6 = 1.67$  for a given transition pair arising from the  $A_1/A_2$  states, respectively. Since all three possible internal rotations of ethylene exchange two pairs of hydrogens, the  $10/6$  nuclear spin weighting of the  $A_1/A_2$  states is expected for all of these internal motions shown in Figure 3. Relative intensity measurements show the set of lines designated "ground state" in Table I of ref 7 is a factor of 1.6 more intense than the set of lines designated "excited state" in the same reference. The good agreement between the measurements of the relative intensities and the intensities predicted by nuclear spin statistics supports the assignment of the tunneling motion to an internal rotation of ethylene, which ex-



**Figure 3.** Nonsuperimposable frameworks of  $O_3-CH_2=CH_2$  projecting the complex approximately in the  $b,c$  plane. Cases a, b, and c refer to the three different internal rotations of ethylene. Two equilibrium frameworks designated 1 and 2 are possible for each of the three internal rotations, and the permutation inversion operation to be applied upon the basis function of framework 1 is given in parentheses under that framework. 1, 2, 3, and 4 represent hydrogen atoms in ethylene, while 5 and 6 denote oxygen atoms in ozone.

changes the hydrogen pairs. From the observed relative intensities, it is possible to assign the  $A_1$  state to the more intense "ground state" lines and the  $A_2$  state to the less intense "excited state" lines. This tunneling state designation is employed for the spectral constants of  $O_3-CH_2=CH_2$  listed in Table V.

Nuclear spin statistics and measurements of relative intensities of lines from the two tunneling states in  $O_3-CD_2=CH_2$  and  $O_3-trans-CHD=CHD$  can be used to determine the axis of rotation in ethylene that causes the tunneling splitting of the transitions. Since the moments of inertia and electric dipole data show that the complex has  $C_s$  symmetry, only one structural isomer is possible for both  $O_3-CD_2=CH_2$  and  $O_3-trans-CHD=CHD$ . The two tunneling states observed for each of these isotopic species have different nuclear spin statistical weights depending upon which local  $C_2$  axis of rotation is involved in the internal motion. In case a,  $180^\circ$  rotation about the  $C_2$  axis perpendicular to the  $C=C$  axis and lying in the plane of ethylene, i.e., the  $b$  inertial axis of ethylene, does not lead to equivalent frameworks for either  $O_3-CD_2=CH_2$  or  $O_3-trans-CHD=CHD$  (see Figure 3); hence,  $g = 1$  for both of the tunneling states of these two isotopic species. In case b, the internal rotation gives equivalent frameworks for  $O_3-trans-CHD=CHD$  but not for  $O_3-CD_2=CH_2$ . Therefore, nuclear spin weights of  $g = 15$  and  $g = 21$  are required for the  $A_1$  and  $A_2$  states, respectively, of  $O_3-trans-CHD=CHD$ , while  $g = 1$  for both states of  $O_3-CD_2=CH_2$ . A  $180^\circ$  rotation about the  $C=C$  axis of ethylene for case c results in the converse of case b; i.e., nuclear spin weights of  $g = 15$  and  $21$  are expected for the  $A_1$  and  $A_2$  states of  $O_3-CD_2=CH_2$ , while  $g = 1$  for both states of  $O_3-trans-CHD=CHD$ .

Averages of intensity ratio measurements of pairs of a given rotational transition from the two tunneling states give 0.97 and 0.68 for  $O_3-CD_2=CH_2$  and  $O_3-trans-CHD=CHD$ , respectively. These ratios are in good agreement with the values of 1.0 and 0.71 obtained from nuclear spin statistical weights for case b. Therefore, the relative intensity data indicate that the tunneling states arise from internal rotation about the  $C_2$  axis that is perpendicular to the molecular plane of ethylene. The tunneling state designations of the sets of lines for  $O_3-CD_2=CH_2$  and  $O_3-trans-CHD=CHD$  in Tables I and III were obtained from the intensity measurements and nuclear spin statistical weights.

With  $C_s$  symmetry, two different structural isomers are possible but were not observed for  $O_3-cis-CHD=CHD$  (see structure section of this paper). Only the internal rotation of ethylene illustrated as case a in Figure 3 leads to equivalent frameworks for  $O_3-cis-CHD=CHD$ . Hence, only this tunneling motion exchanges the deuteriums and hydrogens to give two tunneling states. Note that the internal rotations described by cases b and c cannot give two tunneling states for  $O_3-cis-CHD=CHD$  because the rotations give a different structural isomer. Consequently, the absence of two tunneling states for  $O_3-cis-CHD=CHD$  is consistent with an internal rotation about the  $C_2$  axis that is perpendicular to the molecular plane of ethylene (case b).

For both  $O_3-CD_2=CH_2$  and  $O_3-trans-CHD=CHD$ , the nuclear spin of each deuterium is 1, which leads to a symmetry-state dependence of the deuterium nuclear electric quadrupole interaction.<sup>22</sup> There must be a distinct difference in the quadrupole hyperfine structure of rotational lines arising from the two isotopic species that depends upon the axis of internal rotation in ethylene. Observation of these hyperfine effects can be used to independently determine the axis of rotation and confirm the conclusions obtained from the relative intensity measurements.

For case b in Figure 3, the tunneling motion exchanges the two deuterium nuclei for  $O_3-trans-CHD=CHD$  but not  $O_3-CD_2=CH_2$ , which makes the two deuterium nuclei equivalent in  $O_3-trans-CHD=CHD$ . These two equivalent deuterium nuclei are coupled to each other to give  $I_1 + I_2 = I_D$ , where  $I_D = 0, 1$ , and  $2$ .  $I_D$  couples to the complex rotational framework so that  $J + I_D = F$ . The pairs of equivalent deuterium and hydrogen nuclei have spin 1 and  $1/2$ , respectively, and obey Fermi-Dirac statistics in  $O_3-trans-CHD=CHD$  for the tunneling motion in case b of Figure 3. Thus, the symmetric  $A_1$  state wave function combines with the antisymmetric  $I_D = 1$  spin wave function, while the antisymmetric  $A_2$  state wave function is combined with  $I_D = 0, 2$  symmetric spin wave functions. Because of the tunneling motion,

only one quadrupole coupling constant characterizes the two deuterium nuclei. Furthermore, the hyperfine structure of a given rotational transition for the  $A_1$  state will differ markedly from the  $A_2$  state due to the absence of the  $I_D = 1$  components. This is analogous to the  $^{14}N_2-H_2O$  complex, where analysis of the hyperfine components demonstrated  $\chi(^{14}N)$  is the same in the tunneling states due to the exchange of the two  $^{14}N$  nuclei.<sup>22</sup>

The two deuterium nuclei in  $O_3-CD_2=CH_2$  are not exchanged by the tunneling motion for case b in Figure 3, and all the nuclear spin states ( $I_D = 0, 1, 2$ ) are allowed for each rotational level of the  $A_1$  and  $A_2$  tunneling states. Consequently, the complete set of hyperfine components will be present for each transition. Since the two quadrupole coupling constants are expected to be quite similar for the  $A_1$  and  $A_2$  states, the hyperfine structure will be similar for a given rotational transition arising from the  $A_1$  and  $A_2$  states of  $O_3-CD_2=CH_2$ .

There is not a sufficient number of resolved hyperfine components in the transitions of  $O_3-trans-CHD=CHD$  and  $O_3-CD_2=CH_2$  to obtain the state  $F$  labels and the quadrupole coupling constants. However, the  $1_{10}-0_{00}$  transition clearly shows that the hyperfine structure is almost identical for the  $A_1$  and  $A_2$  states of  $O_3-CD_2=CH_2$ , while the  $A_1$  and  $A_2$  states of  $O_3-trans-CHD=CHD$  have distinctly different hyperfine structure. Figure 4 compares the two  $1_{10}-0_{00}$  transitions arising from the  $A_1$  and  $A_2$  states of  $O_3-CD_2=CH_2$  and  $O_3-trans-CHD=CHD$ . The tunneling motion shown in Figure 3 as case c will lead to the opposite hyperfine structure expected in case b for the two isotopes. This is because the  $180^\circ$  rotation exchanges the deuterium nuclei in  $O_3-CD_2=CH_2$  but not in  $O_3-trans-CHD=CHD$ . Since the tunneling motion in case a does not exchange the deuterium nuclei in either isotopic species, the hyperfine structures of the  $A_1$  and  $A_2$  states will be similar in each isotopic species. Therefore, the observed hyperfine structure for the  $A_1$  and  $A_2$  states of  $O_3-trans-CHD=CHD$  and  $O_3-CD_2=CH_2$  is consistent only for the tunneling motion described in Figure 3 as case b, which supports the conclusion drawn from the relative intensity measurements, i.e., *rotation of ethylene about the axis perpendicular to its plane*.

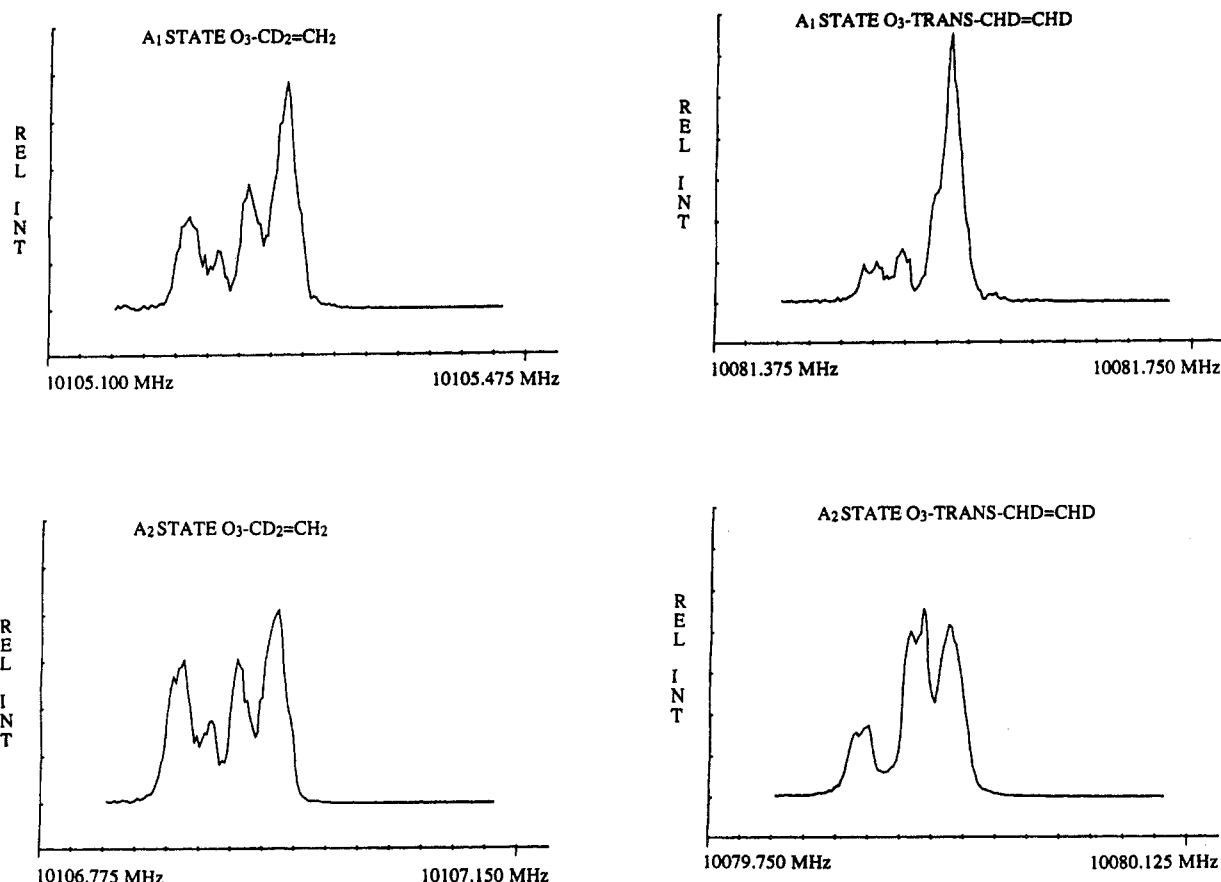
Only the  $A$  rotational constant and  $\Delta_K$  differ significantly between the tunneling states in  $O_3-CH_2=CH_2$ ,  $O_3-CD_2=CH_2$ , and  $O_3-trans-CHD=CHD$ . The internal rotation axis of ethylene perpendicular to its molecular plane falls almost along the  $a$  inertial axis of the complex. This can be seen qualitatively in Figure 2 for the syn  $a$  form, where the  $a$  axis of the complex is located approximately along  $R_{cm}$  and  $\theta_2 = 106^\circ$  places the internal rotation axis at approximately a  $16^\circ$  angle with respect to the  $a$  inertial axis. This means that the  $b$  and  $c$  coordinates of the complex and consequently the  $A$  rotational constant will be primarily affected by the tunneling motion. Although  $\Delta_K$  does not have a simple interpretation in terms of the principal axes coordinates, it is closely related to the  $A$  rotational constant.

It is important to note that the tunneling motion may also involve ozone and still be consistent with the observed spin weights and nuclear quadrupole hyperfine structure as long as the ozone motion does not involve an inversion of the dipole moment along the  $a$  and  $c$  inertial axes. For example, a gearlike internal rotation of ozone coupled to the internal rotation of ethylene also exchanges the equivalent terminal oxygen atoms of ozone. Since the nuclear spin of oxygen nuclei is zero and oxygen has no nuclear electric quadrupole moment, this gearlike motion will lead to two tunneling states with the same nuclear spin weights and nuclear quadrupole structure expected for a tunneling motion that only involves internal rotation of ethylene. The tunneling splitting should be less sensitive to deuteration of ethylene for a concerted gearlike motion involving both ethylene and ozone due to the larger, reduced mass associated with the motion. Although deuteration of ethylene in  $O_3-C_2H_4$  does generally reduce the tunneling splitting by a factor of 2–3 (for example, compare the tunneling splitting for  $O_3-trans-CHD=CHD$  in Table III with  $O_3-CH_2=CH_2$  in Table I of ref 7), it does not exclude some contribution from ozone to the tunneling motion.

**Theoretical Results.** Various levels of theory ranging from Hartree-Fock (HF) to fourth-order Møller-Plesset (MP) per-

(22) Leung, H. O.; Marshall, M. D.; Suenram, R. D.; Lovas, F. J. *J. Chem. Phys.* **1989**, *90*, 700.





**Figure 4.**  $1_{10}-0_{00}$   $c$ -type transitions of the two tunneling states of  $\text{O}_3\text{-CD}_2=\text{CH}_2$  and  $\text{O}_3\text{-trans-CHD=CHD}$  illustrating the deuterium quadrupole hyperfine components. The frequency markers are at 25-kHz intervals. Beam expansion conditions were chosen such that Doppler splitting was eliminated.

turbation theory with single (S), double (D), triple (T), and quadruple (Q) excitations [MP4(SDTQ)]<sup>23</sup> have been used to investigate the  $\text{O}_3\text{-C}_2\text{H}_4$  complex, computationally. Three different basis sets have been tested, namely, the 6-31G(d,p), 6-311G(d,p), and 6-31G(2d,p) basis sets,<sup>24</sup> which are of DZ + P, TZ + P, and DZ + 2P quality in the valence shell. It is known that a reliable description of weakly bound van der Waals complexes requires basis sets of TZ + P quality and a method that covers correlation effects to a large extent. In this research, it was not feasible to use the two larger basis sets at the highest level of theory. However, the overall description of the complex at the MP4/6-31G(d,p) level of theory is rather useful when combined with the results of the microwave investigation.

In the first step, the energies of the four forms shown in Figure 2 have been calculated. Utilizing the parameters  $R_{\text{cm}}$ ,  $\theta_1$ , and  $\theta_2$  given in Figure 2 allows the energies summarized in Table IX to be obtained. At all levels of theory, the syn a form turns out to be most stable. According to MP4(SDTQ) calculations, the anti a form is 0.4 kcal/mol less stable, while the anti b and syn b forms are 1.0 and 1.2 kcal/mol higher in energy than the syn a form (Table IX).

Analysis of the calculated wave functions reveals that, in the syn a form, electrostatic attraction between the positively charged H atoms of ethylene and the negatively charged terminal O atoms of ozone is more pronounced than in any of the other three forms. In particular, the exo positioned H atoms are closer to the terminal O atoms in the syn a form than in syn b or the anti forms. This leads to an induced dipole moment for ethylene that contributes to the stability of the  $\pi$  complex by dipole-induced dipole at-

**Table IX.** Calculated Energies of the Anti and Syn Forms (See Figure 2) as Obtained at Various Levels of Theory by Employing the 6-31G(d,p) Basis Set<sup>a</sup>

method	syn a	anti a	syn b	anti b
HF	-302.285 64	0.45	0.40	0.50
MP2	-303.207 30	0.40	1.75	1.50
MP3	-303.185 68	0.40	1.24	1.09
MP4(SDQ)	-303.208 98	0.42	0.95	0.83
MP4(SDTQ)	-303.261 40	0.41	1.23	1.04

<sup>a</sup> For the syn a form, absolute energies are given in hartrees; for the other forms, relative energies are given in kilocalories per mole relative to the energy of the syn a form.

traction. If  $\pi\text{-}\pi$  overlap was the most important factor in the stability of the complex, then the molecular planes of ozone and ethylene would be parallel ( $\theta_1 = \theta_2 = 90^\circ$ ). In the syn a and the anti b forms, the  $\pi$  orbitals deviate from parallel alignment by about  $40^\circ$ , while the deviation is just  $5^\circ$  in the case of the anti a and syn b forms. However, in the latter forms, the lateral displacement between the  $\pi$  orbitals at the C and the terminal O atoms is almost 1 Å and, therefore,  $\pi$  overlap is not a significant factor in any of the four forms considered here. This is in line with the fact that  $\pi$  overlap between C and O at a distance of 3.3 Å is less than 0.01 Å. Hence, factors that increase electrostatic attraction between ozone and ethylene dominate the stability of the complex.

After the preferred conformation of the  $\text{O}_3\text{-C}_2\text{H}_4$  complex is established, its geometry has been calculated directly at the HF, MP2, MP4(SDQ), and MP4(SDTQ) levels of theory with recently developed analytical gradients for MP4.<sup>25</sup> Results of these calculations are listed in Table X. The HF/6-31G(d,p) and

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Table X. Comparison of Calculated and Experimental Geometries of  $O_3-C_2H_4^a$ 

parameter	HF 6-31G(2d,p)	MP2 <sup>b</sup> 6-31G(d,p)	MP4(SDQ) 6-31G(d,p)	MP4(SDTQ) 6-31G(d,p)	exptl <sup>c</sup> $r_0$	$r_e^d$ ( $O_3$ , $C_2H_4$ )
$R(OO)$	1.196	1.324	1.269	1.306	(1.276)	1.276
$R(CC)$	1.316	1.347	1.336	1.339	(1.339)	1.330
$R(C-H_{endo})$	1.076	1.080	1.081	1.082	(1.086)	1.076
$R(C-H_{exo})$	1.076	1.079	1.080	1.082	(1.086)	1.076
$\theta(O-O-O)$	118.9	114.1	117.4	117.2	(117.0)	116.8
$\theta(C-C-H_{endo})$	121.7	121.5	121.7	121.7	(121.1)	121.7
$\theta(C-C-H_{exo})$	121.7	121.3	121.7	121.7	(121.1)	121.7
$R$	3.523	2.425	3.048	2.984	3.216	
$\alpha_1$	85.5	113.2	105.9	112.7	107.6	
$\alpha_2$	108.0	94.0	102.7	108.9	110.7	
$\alpha_3$	72.0	90.6	77.5	71.1	69.3	

<sup>a</sup> Distances  $R$  are given in Angstroms, angles  $\alpha$  in degrees. <sup>b</sup> Reference 26a. <sup>c</sup> Assumed  $r_0$  values taken from the experimental geometry of either ethylene or ozone (see Table VII) are indicated by parentheses. <sup>d</sup> Experimental  $r_e$  geometries:  $O_3$ , Tanaka, T.; Morino, Y. *J. Mol. Spectrosc.* **1970**, *33*, 538;  $C_2H_4$ , Kuchitsu, K. *J. Chem. Phys.* **1966**, *44*, 906.

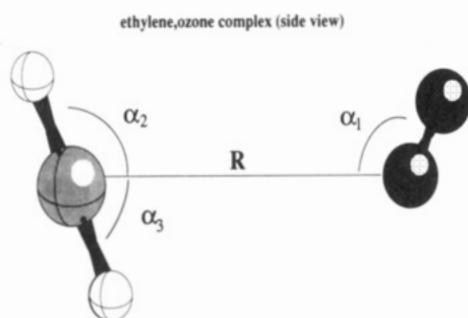


Figure 5. Definitions of the structural parameters  $R$ ,  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  used in the ab initio calculations. A side view of ethylene (left) and ozone (right) is shown.  $R$  is the distance between the center of the  $C=C$  bond and the midpoint between the terminal O atoms of ozone.  $\alpha_1$  is defined as the angle between the distance  $R$  and the  $C_2$  axis of ozone.  $\alpha_2$  and  $\alpha_3$  are the angles between  $R$  and the local  $C_2$  axes of the two  $HC=CH$  entities of ethylene. Note that the two  $HC=CH$  entities are no longer in one plane if interactions with ozone lead to a pyramidalization at the C atoms.

MP2/6-31G(d,p) results have been published before by McKee and Rohlfing.<sup>26</sup>

The parameters  $R$ ,  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  rather than  $R_{cm}$ ,  $\theta_1$ , and  $\theta_2$  have been used to describe the conformation of the complex. The distance  $R$  is the distance between the midpoint of the  $C-C$  bond and the midpoint between a line connecting the terminal O atoms. The angles  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  are defined with respect to this line as is shown in Figure 5. HF and MP2 values of  $R$  differ considerably from the experimental value also given in Table X. HF overestimates the intermolecular distance  $R$  by 0.3 Å, while MP2 underestimates  $R$  by 0.8 Å.

This is one of the few cases where the MP2 result is worse than that obtained at the HF level. Test calculations with the 6-311G(d,p) and the 6-31G(2d,p) basis sets show that the value of  $R$  is due to deficiencies of MP2 and, therefore,  $R$  does not improve with larger basis sets. The reason for this failure at the MP2 level can be seen by comparing the calculated dipole moment ( $\mu$ ) of ozone: (HF/6-31G(d,p), 0.83; MP2/6-31G(d,p), 0.16; MP4(SDQ)/6-31G(d,p), 0.56; and MP4(SDTQ)/6-31G(d,p), 0.44 D) with the experimental one (0.53 D, see Table VI). The HF value of  $\mu$  is too large by 60%, which is due to the fact that HF overestimates the polarity of the O-O bond in ozone. As a consequence, electrostatic interactions between ozone and ethylene come out too large at the HF level, thus leading to a large value of the intermolecular distance  $R$ .

The reverse is true at the MP2 level: MP2 mixes too much biradical character into the ozone wave function, which underestimates the charges at the O atoms and predicts a  $\mu$  value 70% too small. Hence, at the MP2 level,  $O_3$  and  $C_2H_4$  have to come rather close together in order to form a stable complex. Ac-

cordingly, the geometries of the two interacting molecules change much more at the MP2 level than at the HF level. This is evident from the calculated small pyramidalization at the C atoms reflected by  $\alpha_2 + \alpha_3 = 184.6$  at the MP2 level in Table X.

Reliable predictions of the complex geometry are only possible at the MP4 level of theory, where in view of the calculated values of the ozone dipole moment, MP4(SDQ) seems to be better than MP4(SDTQ). This is confirmed by the results given in Table X, which show that MP4(SDQ) provides a somewhat better description of both the monomers and the complex. The calculated MP4(SDQ) value of  $R$  is 0.17 Å too short, and the angles  $\alpha_1$  and  $\alpha_2$  are 2° and 8° too small. On the other hand, MP4(SDTQ) leads to a little better agreement with experimental  $\alpha$  values but predicts  $R$  0.23 Å too short. Test calculations with the 6-31G(2d,p) and 6-311G(d,p) basis sets indicate that these deviations are due to basis set rather than method deficiencies.

The geometry obtained at the MP4 level confirms that the syn form is the most stable conformation of the  $O_3-C_2H_4$  complex. Furthermore, the calculated MP4 energy provides an estimate of the stability of the complex. At MP4(SDTQ)/6-31G(d,p), the complex is more stable by 2.1 kcal/mol than the separated molecules ozone and ethylene. Since the employed basis set is rather small, corrections for the basis set superposition error (BSSE) are important. Utilizing the counterpoise method<sup>27</sup> for ozone and ethylene allows the stability of the  $O_3-C_2H_4$  complex to be found to be 0.74 kcal/mol.

Since the internal motion that gives rise to the tunneling splitting in the rotational spectrum of  $O_3-C_2H_4$  likely involves internal rotation of ethylene, we have investigated the barriers and transition-state geometries for the three different internal rotation pathways shown in Figure 3. Assuming rigid rotation, i.e., fixing the geometry of ozone and ethylene at the experimental values listed in Table VII, barriers of 8.31, 0.37, and 2.92 kcal/mol are calculated at the MP4(SDTQ)/6-31G(d,p) level for cases a, b, and c, respectively. Optimization of  $R$  and the  $\alpha$  angles for the transition states reveals that the two monomers separate in case a for a rotation about the  $C_2$  axis located in the plane of ethylene perpendicular to the  $C=C$  axis, while ethylene swings into the plane of ozone ( $\alpha_1 = 180^\circ$ ) for rotation about the  $C=C$  axis of ethylene (case c). A true transition state for internal rotation is obtained only for case b. This is in agreement with the observed spin weights and nuclear hyperfine splitting, which indicates that the internal rotation is about the  $C_2$  axis perpendicular to the molecular plane of ethylene.

## Discussion

**Structure and Internal Dynamics.** The ab initio calculations have found that, of the four forms in Figure 2 consistent with the microwave spectral data, the syn a structure is the most stable. Since  $\theta_1 = 112^\circ$  and  $\theta_2 = 106^\circ$ , the two monomer planes are not parallel for the syn a form and the  $C-O_{terminal}$  distances equal 3.24 Å. The best ab initio result obtained in this research predicts the stability of the complex to be 0.74 kcal/mol.

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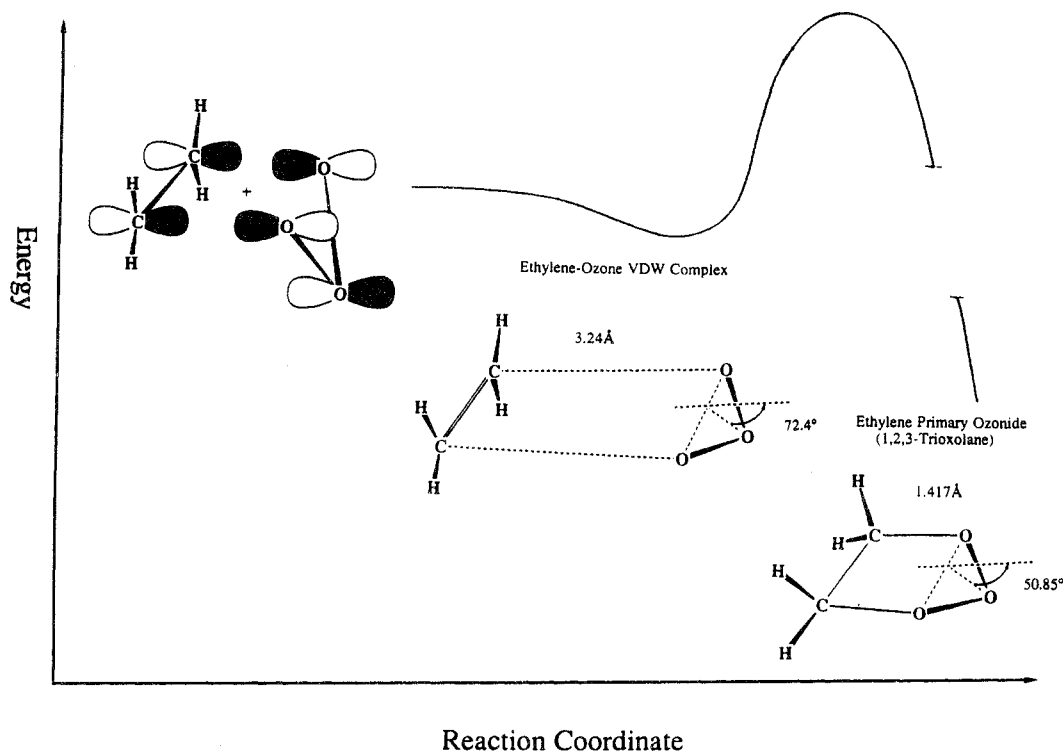


Figure 6. One-dimensional reaction potential surface of ozone plus ethylene defined by 1,3-dipolar cycloaddition theory.

Table XI. Van der Waals Stretching Frequencies ( $\omega_s$ ), Force Constants ( $k_s$ ), Radii Sums, and Experimental Bond Lengths

complex	$\omega_s$ ( $\text{cm}^{-1}$ )	$k_s$ ( $\text{mdyn}/\text{\AA}$ )	bond	van der Waals radii ( $\text{\AA}$ ) <sup>a</sup>	exptl dist ( $\text{\AA}$ )
$\text{O}_3\text{-C}_2\text{H}_4$	55.2	0.0318	C-O	3.17	3.24
$\text{O}_3\text{-C}_2\text{H}_2$ <sup>b</sup>	59.7	0.0354	C-O	3.17	3.22
$\text{O}_3\text{-H}_2\text{O}$ <sup>c</sup>	81.0	0.0506	O-O	3.00	3.17

<sup>a</sup> Assumed van der Waals radii of 1.5  $\text{\AA}$  for oxygen and 1.67  $\text{\AA}$  for carbon. <sup>b</sup> Reference 8. <sup>c</sup> Reference 29.

A recent *ab initio* and microwave spectral study of  $\text{O}_3\text{-C}_2\text{H}_2$ <sup>8</sup> finds that this related complex has a geometry remarkably similar to that of  $\text{O}_3\text{-C}_2\text{H}_4$ . The conformation is the same with the *a,c* symmetry plane bisecting the O-O-O angle of ozone and the C-C bond of acetylene. Ozone is tilted in the same sense with respect to the center of mass separation  $R_{\text{cm}}$  with a value of  $\theta_1 = 112^\circ$ . Also,  $R_{\text{cm}} = 3.25 \text{ \AA}$  in  $\text{O}_3\text{-C}_2\text{H}_2$ , which is only 0.04  $\text{\AA}$  shorter than  $R_{\text{cm}}$  in  $\text{O}_3\text{-C}_2\text{H}_4$ .

An investigation of the  $\text{SO}_2\text{-C}_2\text{H}_4$  complex has determined the conformation to be similar to that of  $\text{O}_3\text{-C}_2\text{H}_4$  with an *a,c* symmetry plane, which bisects the O-S-O angle and the C=C bond in ethylene.<sup>20</sup> However, the  $\text{SO}_2$  tilt is in the opposite sense with respect to  $R_{\text{cm}}$  than is that of ozone since  $\theta_1 = 79.8^\circ$  in  $\text{SO}_2\text{-C}_2\text{H}_4$ <sup>20</sup> and  $\theta_1 = 112^\circ$  in  $\text{O}_3\text{-C}_2\text{H}_4$ . This has the effect of placing the sulfur atom in  $\text{SO}_2$  closest to the C=C bond in ethylene, while the two terminal oxygens of ozone are closest to the carbon atoms of ethylene. Unlike  $\text{O}_3\text{-C}_2\text{H}_4$ , the ethylene plane is parallel to the  $\text{SO}_2$  plane since  $\theta_2 = 110^\circ$  for  $\text{SO}_2\text{-C}_2\text{H}_4$ .<sup>20</sup>

Only a few weakly bound ozone-containing bimolecular complexes are known. Table XI compares the van der Waals bond stretching force constant ( $k_s$ ) and vibrational frequency ( $\omega_s$ ) for  $\text{O}_3\text{-C}_2\text{H}_4$ ,  $\text{O}_3\text{-C}_2\text{H}_2$ , and  $\text{O}_3\text{-H}_2\text{O}$ . These constants were estimated from the experimental values of the quartic centrifugal distortion constant ( $\Delta_J$ ) by means of the nonplanar asymmetric top equations developed by Millen.<sup>28</sup> The force constant and vibrational frequency for  $\text{O}_3\text{-C}_2\text{H}_4$  are smaller than those for  $\text{O}_3\text{-H}_2\text{O}$ <sup>29</sup> and about equal to those for  $\text{O}_3\text{-C}_2\text{H}_2$ .<sup>8</sup> Qualitatively, this suggests

that the van der Waals interaction is strongest for  $\text{O}_3\text{-H}_2\text{O}$  and about the same for  $\text{O}_3\text{-C}_2\text{H}_4$  and  $\text{O}_3\text{-C}_2\text{H}_2$ . Comparison of the sum of van der Waals radii with the experimental bond distances appears to support a stronger van der Waals bond in  $\text{O}_3\text{-H}_2\text{O}$ . The sums of the van der Waals radii for oxygen and carbon (assuming 1.5  $\text{\AA}$  for oxygen and 1.67 for carbon) are smaller than the experimental C-O distances in  $\text{O}_3\text{-C}_2\text{H}_4$  and  $\text{O}_3\text{-C}_2\text{H}_2$ , while the experimental O-O distance for  $\text{O}_3\text{-H}_2\text{O}$ <sup>29</sup> is almost the same as the sum of two oxygen van der Waals radii (see Table XI).

Two tunneling states have been observed for the three known bimolecular complexes containing ozone. In  $\text{O}_3\text{-C}_2\text{H}_4$  and  $\text{O}_3\text{-C}_2\text{H}_2$ ,<sup>8</sup> the tunneling splitting is small and the two states fit independently quite well to an asymmetric top Watson Hamiltonian. It appears that the internal motion involves rotation of ethylene or acetylene about a  $C_2$  axis that is perpendicular to the molecular plane of ethylene or the molecular axis of acetylene. The *ab initio* calculation reported here estimates a barrier of 0.4 kcal/mol for the rotation of ethylene described above in  $\text{O}_3\text{-C}_2\text{H}_4$ . For  $\text{O}_3\text{-H}_2\text{O}$ ,<sup>29</sup> the tunneling splitting is large and only one tunneling state fits to an asymmetric top Watson Hamiltonian, which suggests the barrier is quite low. In this case, water may undergo nearly free internal rotation.

For all three of these complexes, there is little information related to the motion of ozone and whether or not it is also involved in the tunneling splitting. An inversion of ozone that reverses the *c* dipole component of the complex can be ruled out since "rigid rotor" *c*-type transitions have been observed in the complexes. This is in contrast to  $\text{Ar-O}_3$ , where the *c*-type transitions are rotation-inversion and ozone inverts at a frequency of 460 MHz through a barrier of 50  $\text{cm}^{-1}$ .<sup>30</sup>

A gearlike motion, which involves a concerted internal rotation of both ozone and the second monomer subunit, is possible for the three ozone-containing molecular complexes. The van der Waals complex  $\text{SO}_2\text{-C}_2\text{H}_4$  exhibits two tunneling states, which are thought to arise from internal rotation of ethylene about the  $C_2$  axis perpendicular to the molecular plane of ethylene.<sup>20</sup> Although this is similar to that of  $\text{O}_3\text{-C}_2\text{H}_4$ , there is oxygen-18 and

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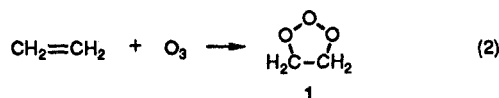
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sulfur-34 data reported for  $\text{SO}_2\text{-C}_2\text{H}_4$  that relates to the involvement of sulfur dioxide in the tunneling motion. The differences in the  $A$  rotational constants of the two tunneling states of  $\text{S}^{18}\text{O}_2\text{-C}_2\text{H}_4$ ,  $\text{S}^{18}\text{O}^{16}\text{O-C}_2\text{H}_4$ , and  $^{34}\text{S}^{16}\text{O}_2\text{-C}_2\text{H}_4$  decrease significantly in comparison to those of the normal isotopic species. It is possible that the reduction in the tunneling splitting observed for oxygen-18 and sulfur-34 isotopic substitution in sulfur dioxide may be due to a concerted gearlike motion, which exchanges the pair of equivalent oxygens as well as the two pairs of equivalent hydrogen nuclei. However, a motion that exchanges the oxygens and two pairs of hydrogens will give four tunneling states in  $\text{S}^{18}\text{O}^{16}\text{O-C}_2\text{H}_4$ , and only two states have been reported.<sup>20</sup> Unfortunately, the study of oxygen-18-substituted ozone complexes does not appear to be feasible.

**Reaction Potential Surface.** Ozone reacts with ethylene in the gas phase and in condensed media. The observation of a van der Waals complex between ethylene and ozone provides experimental structural data for a species located at large reactant distances along the reaction potential surface. The ab initio calculations and spectral data show that this complex is weakly bound and falls in a shallow minimum at large distances on the reaction surface. Scanning the potential energy surface (PES) of  $\text{O}_3\text{-C}_2\text{H}_4$  by ab initio techniques reveals that the  $\pi$  complex (syn a form) is the most stable van der Waals complex between ozone and ethylene.<sup>26b</sup> Furthermore, the  $\pi$  complex is close to the transition state of the cycloaddition reaction between the two molecules and is located at the entrance to the cycloaddition reaction channel. This suggests that it is a precursor to the actual cycloaddition product, which means the stereochemical properties of reaction including product formation will be influenced by the stereochemistry in the  $\pi$  complex. Therefore, it is interesting to relate the geometry of the  $\text{O}_3\text{-C}_2\text{H}_4$   $\pi$  complex as obtained in this work to the geometry of the transition state and the product of the cycloaddition reaction.

Ozone adds to ethylene in a concerted fashion to give primary ozonide **1** as shown in eq 2. The addition is thermally allowed within the context of Woodward-Hoffman symmetry rules.<sup>31-33</sup> Maximal overlap between the  $\pi$  HOMO orbital of ethylene and the  $\pi^*$  LUMO orbital of ozone is achieved by a parallel plane approach to the two molecules.<sup>31-33</sup> As shown in Figure 6, this



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parallel plane orientation of the reacting ethylene and ozone maintains a symmetry plane along the reaction coordinate. It requires an oxygen envelope conformation with  $C_s$  symmetry for the transition state and the primary product **1** (see Figure 6).

Ab initio calculations find the transition-state geometry to correspond to an oxygen envelope conformation with  $C_s$  symmetry.<sup>26,34</sup> Since the C-O distances in the transition state are calculated to be  $\sim 2.3\text{-}2.0$  Å, the complex observed in the present work with C-O distances of 3.24 Å must fall on the reaction coordinate prior to the transition state. Recently we observed the primary product **1** in a low-temperature microwave absorption cell and found that the lowest energy gas-phase conformation is the oxygen envelope form with  $C_s$  symmetry.<sup>13</sup> Earlier ab initio calculations employing large augmented basis sets including polarization functions and complete geometry optimization predicted the oxygen envelope as the lowest energy conformation of **1** in accord with the gas-phase microwave results.<sup>35</sup>

The present results show that the  $\text{O}_3\text{-CH}_2=\text{CH}_2$  complex also has the oxygen envelope conformation with  $C_s$  symmetry. Therefore, a combination of work supports the concerted addition of ozone to ethylene along the reaction coordinate predicted by 1,3-dipolar cycloaddition theory. The present work does not determine what role the observed complex plays in the reaction. It seems unlikely that the species exists in gas-phase ozone plus ethylene reactions at room temperature because the complex binding energy of 0.74 kcal/mol is too low. Detailed chemical dynamical studies that take advantage of the reactant orientation in the  $\text{O}_3\text{-CH}_2=\text{CH}_2$  complex are needed to provide more critical tests of the concerted addition and symmetry requirements of 1,3-dipolar cycloaddition theory. Studies are underway in related cycloadditions that also use substituents to investigate van der Waals complexes and their possible roles in the observed regioselectivity of product formation.

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