

# Matrix isolation FTIR spectroscopical study of ethene secondary ozonide

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**Abstract:** A new method is used for the separation of ethene secondary ozonide (SOZ) from the other products of ethene ozonization reaction. The reaction was performed in the neat films of the reactants at 77 K. Ethene SOZ was separated from other products of the reaction by vacuum distillation at 190–210 K and analyzed by means of the matrix isolation IR absorption spectroscopy. Spectroscopic data from photolysis of the matrix isolated ozonide was used as an argument for assignment of the infrared spectral bands either to ethene SOZ or to other products of the reaction. The spectra of ethene SOZ isolated in the Ar matrix were analyzed by combining experimental results with the theoretical calculations performed at the MP2 6-311+G (3df, 3pd) level.

A new assignment of some experimental fundamental bands is proposed taking in to account the Fermi resonance between CH stretch and the five membered ring vibrations. For the first time more than 30 weak infrared absorption bands were observed and assigned to various combination vibrations and overtones. By using new spectral information concerning the overtones and the combination bands it is concluded that the dissociation of unstable ethene SOZ involving breaking of any of the four CO bonds of the five membered ring of ethene SOZ has low probability. Dissociation of the ring starts from breaking of the OO bond.

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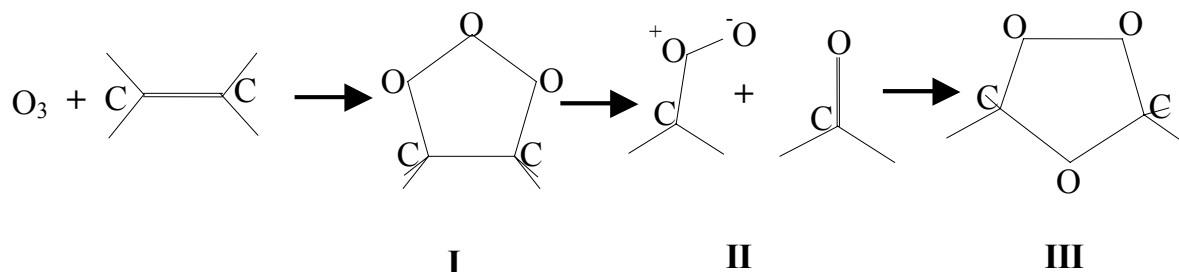
*Keywords:* Ozonization, ethene secondary ozonide, IR spectroscopy, matrix isolation

## 1 Introduction

Ozone together with the hydroxyl radical OH and the nitrate radical NO<sub>3</sub> are the main oxidant species of the unsaturated hydrocarbons in the atmosphere. Ozone reacts with the hydrocarbons breaking down the double bonds and forming the carbonyl compounds.

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Aliphatic alkenes seem to be suitable compounds for the detailed investigation of such ozonization reactions. This is particularly true for ethene - the smallest member in the homologous row of the aliphatic alkenes.



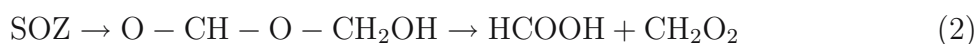
**Fig. 1** Schematic representation of *Criegee* mechanism of ozonization reaction of alkenes.

Starting from 1950's ethene ozonization reaction has been studied intensively. The ozonization is believed to be proceeded under so called *Criegee* three-step mechanism [1] (see Fig. 1). Primary ozonide (POZ) I, carbonyl oxide (COX) II and the secondary ozonide (SOZ) III are formed as transitory products of the reaction.

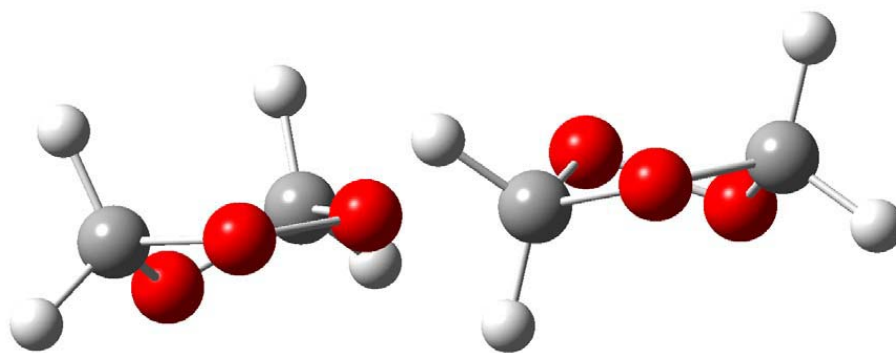
Despite numerous studies of this reaction by different spectroscopic techniques the precise mechanism of the reaction is still unknown [2–10]. This is also true for the dissociation of the secondary ozonide. Two different paths of the ethene SOZ dissociation are theoretically predicted [11]. One path includes the direct formation of dioxymethane and formaldehyde (1). Dioxymethane decomposes unimolecularly, following three different paths - isomerization to formic acid (a), dissociation to carbon dioxide (b), hydrogen and some radical fragmentation (c):



Another possible path (2) is tautomerization, involving the split of the ring O-O bond and H shift from carbon to oxygen, which yields hydromethylformate O-CH-O-CH<sub>2</sub>OH. The hydromethylformate decomposes unimolecularly to formic acid and formaldehyde:



Actually, both paths end up with the same final products - formic acid, formaldehyde, water and carbon dioxide. Therefore, investigation of the final products does not give an answer about the first step of the dissociation of ethene SOZ. Selective excitation of the



**Fig. 2** Conformations of five membered ring of ethene secondary ozonide: a) C-O half-chair conformation; b) O-O half-chair conformation.

normal vibrations of the ozonide by means of tunable infrared laser can give information about breaking of the chemical bonds during the decomposition of the ozonide. Another approach is to analyze the structure of ethene SOZ and its vibrational spectra in order to make predictions concerning the first step of the dissociation.

Theoretically, five membered ring of ethene SOZ can possess two different structures - so called C-O half chair conformation and O-O half chair conformation (see Fig. 2). According to Kuckowski's and Bauld-Bailey's theories [12, 13] the five membered ring of the secondary ozonides is in the O-O half-chair configuration (see Fig. 2b). Such configuration was proved experimentally by means of the microwave spectroscopy [12].

Infrared absorption (IR) spectra contain information about potential functions of the normal vibrations. The functions are related to the dissociation reaction coordinates and can be used for estimation of different pathways of the dissociation. For such estimation infrared absorption spectral bands, corresponding to different fundamental vibrations, overtones and combination vibrations, have to be recorded and analyzed. Unfortunately, this is not an easy task due to (I) instability of ethene SOZ and (II) the fact that the ozonide is formed together with the other products of the ozonization reaction.

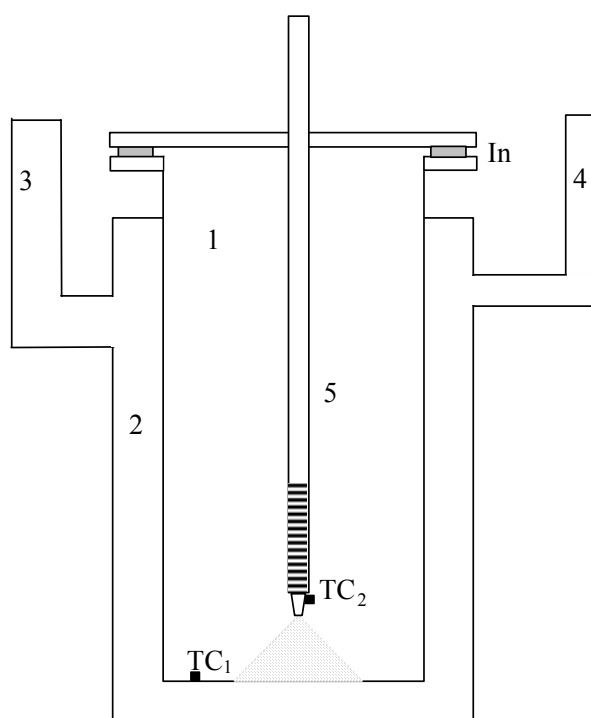
The first comprehensive study of the ethene secondary ozonide by means of infrared spectroscopy was made by Kuhne and Gunthard [14] in 1976. In this paper the infrared absorption spectra of three isotopic modifications of the ethylene SOZ isolated in solid argon were reported. The ozonization reaction took place in methyl chloride solution of the reactants. The authors assigned spectral bands to normal vibration of SOZ by using some empirical parameters and normal coordinate analysis. They also explained appearance of some spectral bands by Fermi resonance between  $\text{CH}_2$  stretching and bending modes. In that time the authors used a grating spectrometer for the measurements and they were not able to observe very weak spectral bands of the overtones and combination vibrations. Another drawback of this work is that the assignment of the spectral band was not supported by high level *ab initio* calculations which were also not possible at that time. In the early 1980's Niki et al [4] investigated gaseous products of ethene ozonization reaction. The reaction occurred in the gas phase and no separation of the products was made. Some kinetic IR absorption studies of the product mixture were used for tentative assign-

ment of the spectral bands to the different products of the reaction. Ethene SOZ was a minor product of the ozonization reaction in the gas phase and its weak spectral bands were not found in the IR absorption spectra of the products. One year later Andrews et al. [5] did the matrix experiment similar to [14] extending matrix isolation technique to the photolysis and pyrolysis. They characterized the SOZ vibrations from  $^{18}\text{O}$ ,  $^{13}\text{C}$  and  $^2\text{H}$  isotopic shifts. The authors assumed that the photolysis and pyrolysis proceeds *via* formation of excited hydroxymethylformate. The experimental results were not supported by the theoretical calculations and no attempts to assign ethene SOZ spectral bands were made. Rather high level *ab initio* calculations of ethene SOZ were done by Samuni and Haas [7]. They presented a detailed description of the normal modes by combining calculations with the available experimental results [5, 14]. Some small modifications of the former assignments based on empirical force field were proposed but no attempts to analyze overtones and combination bands were made. Authors of [15] have studied UV and IR laser induced decomposition of 2-butene secondary ozonide. They found that UV induced decomposition significantly differs from IR laser induced decomposition. Highly energetic photons at 193.3 nm cause simultaneous splitting of CO and OO bonds, while photons at 10.6  $\mu\text{m}$  cause only OO bond splitting.

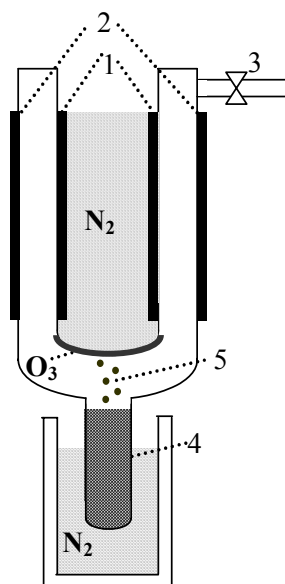
In this work we present the infrared absorption study of pure ethene SOZ isolated in Ar matrix together with the high level *ab initio* calculations of the structure and vibrational spectrum of this compound. Such experimental and theoretical data are used to revise previous assignment of the fundamentals and to make an assignment of new weak spectral bands corresponding to the different combination vibrations and overtones.

## 2 Experimental

Oxygen (99.999 %) from Aga and ethene (99.95) from Air Liquide were used as received. The ozonization reaction was performed in condensed phase in a stainless steel reactor cooled down by liquid nitrogen to 77 K (Fig. 3). Ethene and ozone were introduced into the reactor in small portions (about 15 torr\*litre), consequently, forming multi-layered film of the reactants at the bottom of the reactor. Temperature of the reaction was measured by means of K-type thermocouple TC1, fixed to the bottom of the reactor. The nozzle in the reactor was heated to 273 K in order to prevent condensation of the reactants in the nozzle. Temperature of the nozzle was measured by K-type thermocouple TC2 attached to the nozzle. After the reaction, the reactor was slowly warmed up and the products after each 10 K temperature rise were pumped out. Continuous pumping of the reactor during the warm up allowed us to separate ethene SOZ from the other products of the reaction. Various products of the reaction started to evaporate actively only at the temperatures close to their temperatures of fusion. For instance, ethene was removed at 104 K, formaldehyde - at 181 K. Only the products, which evaporate from the walls of the reactor at 190 - 210 K temperature interval, were transferred to the vacuum system and used for the preparation of the matrix mixture.



**Fig. 3** A sketch of the stainless steel ozonization reactor. In – indium gasket, 1 - the inner volume, 2 - the outside volume filled with liquid nitrogen, 3 and 4 - tubes for filling and evaporating liquid nitrogen, 5 – the nozzle for inserting the reactants and removing the products.



**Fig. 4** Side view of double wall glass reactor for preparation of ozone: 1, 2 - inner and outer cylindrically shaped electrodes, 3 - the inlet valve, 4 - silica gel, 5 - drops of  $O_3$ .

Ozone was prepared from oxygen by electric discharge in glass reactor, cooled down to 77 K by liquid nitrogen. The sketch of the reactor is presented in Fig. 4. The reactor was filled with 0.8 atm of oxygen, which was condensed on the cold wall of the reactor. At LN temperature remaining in gas phase oxygen pressure was 100 torr. By applying high voltage on the electrodes of the reactor electrical discharge in oxygen gas was created. Ozone, formed from oxygen atoms during the discharge, was condensed on the cold inner walls of the reactor. It takes about one hour to convert nearly all oxygen to ozone. After the discharge was stopped, the rest of oxygen was removed from the reactor by pumping oxygen out for 30 min. Subsequently, ozone was trapped on silica gel by warming inner walls of the reactor and cooling the silica gel at the bottom of the reactor by means of liquid N<sub>2</sub>. Trapping of ozone in to silica gel allowed us to store ozone safely.

The closed cycle Leybold RW2 helium cryostat was used for the matrix experiments. The matrix mixture (ratio ethene SOZ/Ar ÷ 1/300) was deposited on CsI optical window cooled down to 8.3 K. During the deposition the mixture was kept at room temperature. Conventional high pressure Hg arc lamp was used for photolysis of the matrix with UV light. A Hg arc lamp delivers UV radiation from 170 nm to 400 nm. Spectra were recorded on BRUKER Vertex 70 Fourier transform spectrometer by using 0.5 cm<sup>-1</sup> spectral resolution.

The gas spectra were obtained at infrared beam line BL73 at Swedish National laboratory of Synchrotron radiation – MAX-lab. Reaction products evaporated at 190 - 210 K temperature interval were transferred to the coolable infrared gas cell equipped with White optics [16, 17]. The spectra were recorded on BRUKER IFS 120 HR spectrometer. The resolution of 4 cm<sup>-1</sup> was used for the low resolution spectrum and 0.003 cm<sup>-1</sup> for the high resolution spectrum.

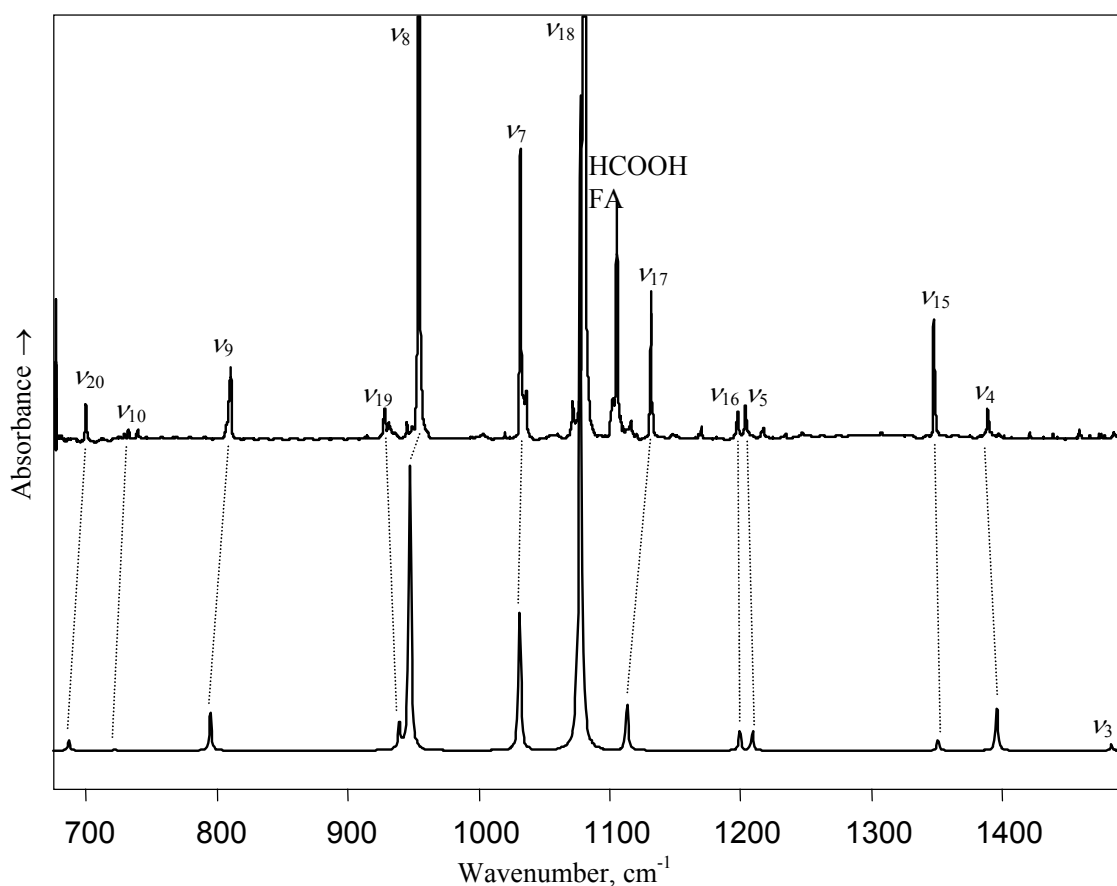
### 3 Results

The five membered ring of ethene SOZ has O-O half-chair configuration (see Fig. 2a) corresponding to C<sub>2</sub> point symmetry group. Normal frequencies of ethene SOZ should be classified as A type (11 vibrations) and B type (10 vibrations). According to the character table of C<sub>2</sub> symmetry group, the vibrations of both types are active in the infrared absorption spectra. However, many more spectral bands were observed in the investigated spectrum of the ethene SOZ isolated in Ar matrix, which makes the assignment rather complicated. There are two main reasons that result a high number of spectral bands: (I) – the presence of a small amount of other products of the ozonization reaction in the sample; (II) - some combination vibrations and overtones can also be active in the infrared spectra of such a strained and unstable molecule. The instability of the ethene SOZ can be used to distinguish the spectral bands belonging to the impurities. The ethene SOZ photolyzed by UV radiation easily breaks apart while such impurities like formaldehyde, formic acid, ethene are less sensitive to UV radiation. High level theoretical calculations should be used in order to assign the spectral bands to the normal vibrations, combination vibrations or overtones. The fundamental spectral bands and the bands caused by

anharmonicity of the potentials of normal vibrations will be discussed separately in this paper.

### 3.1 Spectral bands of the fundamental vibrations

The infrared absorption spectrum of the ethene SOZ in argon matrix was observed in the conventional region of the normal vibrations from 500 to 4000  $\text{cm}^{-1}$ . The *ab initio* calculations at MP2/6-311+G(3df,3pd) theory level were carried out for the assignment of the spectral bands. The low frequency part of the experimental spectrum together with the calculated spectrum, generated from the results of our *ab initio* calculations, is presented in Fig. 5. Each experimental spectral band has a counterpart in the calculated spectrum, which makes the assignment of the experimental spectral bands straightforward. The numbering of the fundamentals is made according to the *ab initio* calculations by taking in to account  $C_2$  symmetry of the ozonide. An assignment of experimental bands in this spectral region is similar to the assignment made by Kuhne and Gunthard [14] and later by Haas et al. [7].



**Fig. 5** Experimental (top) and *ab initio* at MP2/6-311+G(3df,3pd) level calculated (bottom) infrared absorption spectrum of ethene SOZ. Numbering of the fundamental bands is based on the calculations.

High frequency region of the spectrum is more complicated (see Fig. 6a). According to the *ab initio* calculations in this region there should be only 4 fundamentals: 2 A type spectral bands (CH<sub>2</sub> symmetric and asymmetric “in phase” stretching) and 2 bands of B type (CH<sub>2</sub> symmetric and asymmetric “out of phase” stretching) (Table 1). The A-type CH stretching bands should be very weak, which allows us to expect only two strong spectral bands in this spectral region. Contrary to the predictions, in the CH stretching region of the experimental spectrum, at least 11 spectral bands were observed and 5 of them at 2800, 2867, 2895, 2978 and 2990 cm<sup>-1</sup> demonstrate medium or high intensity. Some of these bands can be attributed to the CH vibrations of the impurities while some to combination vibrations and overtones. Spectral bands of the impurities can be identified from photolysis experiments. Only those spectral bands which disappear after photolysis of the sample can be attributed to the ethene SOZ. The photolysis experiments carried out using UV light enabled us to conclude, that spectral bands at 2800 and 2867 cm<sup>-1</sup> can be attributed to formaldehyde [5], the band at 2953 cm<sup>-1</sup> to formic acid, and the band at 2995 cm<sup>-1</sup> to some unidentified impurity. However, the accounting of these impurities has not been enough to explain all peculiarities of the spectrum since in this spectral region three strong spectral bands at 2895, 2967 and 2990 cm<sup>-1</sup> have been observed, instead of two bands predicted by the theoretical calculations.

It was assumed that the Fermi resonance could be a possible reason for this discrepancy. It is well known that in the case of coincidence of the frequency of normal vibration with the frequency of some overtone or combination band of the same symmetry, Fermi resonance between these two vibrations can occur. In the studied system there can be two consequences of Fermi resonance: (I) coinciding spectral bands move away from each other by 20-100 cm<sup>-1</sup> and (II) the weaker overtone or combination band “borrows” some intensity from fundamental band, which makes these two Fermi resonance spectral bands look like a doublet in the spectrum. It is not possible to evaluate quantitatively probability of the Fermi resonance for the vibrations of the particular molecule, but empirically it is known, that this probability is higher, when interacting vibrations involve atoms, which actively participate in both vibrations. Taking into account the above mentioned arguments in the analysis of fundamentals (Table 1), overtones and combination bands it has been found that in ethene SOZ Fermi resonance can occur between  $\nu_{12}$  and  $\nu_{18}+2\nu_8$ .

The *ab initio* calculations indicate for vibration  $\nu_{12}$  the value of 3068 cm<sup>-1</sup>. Unfortunately, this value cannot be used directly for estimation of the experimental value of  $\nu_{12}$ . It is known, that *ab initio* calculations usually give 2-3 % elevated value of CH stretch frequency. This overestimation should be similar for different CH stretch vibrations of the same CH<sub>2</sub> group. Comparing calculated (2977 cm<sup>-1</sup>) and experimental (2895 cm<sup>-1</sup>) frequency of the well assigned  $\nu_{13}$  fundamental it has been estimated that the calculated CH<sub>2</sub> stretch frequencies are ca. 2.7 % higher than experimental ones. Therefore, the  $\nu_{12}$  experimental band can be expected at 2984 cm<sup>-1</sup>. On the other hand, if the wavenumbers of the different overtones and combination vibrations involving movement of C and H atoms of the same CH<sub>2</sub> chemical group of ethene SOZ, is taken into account, it is possible to conclude that the combination band  $\nu_{18}+2\nu_8$  should appear at ca. 2978 cm<sup>-1</sup>



**Table 1** Calculated and experimental infrared absorption bands of fundamental vibrations of ethene SOZ.

Mode	Exp.		This work		Assignment	[14]	[7]	
	in Ar matrix		Calculated			Exp.	Exp.	Calculated
	Freq., cm <sup>-1</sup>	Int., a.u.	Freq., cm <sup>-1</sup>	Int., km mole <sup>-1</sup>		in Ar matrix	in Ar matrix	MP2/6- 311+G*
A modes								
$\nu_1$	2978	m	3069	0.1	-CH sym. stretch	2973	2973	3046
$\nu_2$	2900	w, sh	2979	0.3	-CH asym. stretch	2894* 2889*	2900	2952
$\nu_3$	-	-	1494	0	-CH <sub>2</sub> scissoring	-	-	1500
$\nu_4$	1387	m	1397	12.4	-CH <sub>2</sub> wagging	1387	1387	1396
$\nu_5$	1202	m	1210	5.1	-CH <sub>2</sub> twisting	1196	1202	1203
$\nu_6$	1146	vw	1117	0.1	-CH <sub>2</sub> rocking	1129	1143	1122
$\nu_7$	1030	s	1032	40	CO <sub>p</sub> stretch	1078	1029	1033
$\nu_8$	952	vs	948	73.7	COC sym. stretch	952	952	951
$\nu_9$	809	s	796	10.7	OO stretch	808	808	806
$\nu_{10}$	738	vw	723	0.4	Ring def. (i.p.)	737	737	726
$\nu_{11}$	-	-	381	8.2	Ring pucker	352	352	384
B modes								
$\nu_{12}$	2990* 2967**	s s	3068	30.2	-CH asym. stretch	2967	2967	3046
$\nu_{13}$	2895	vs	2977	110.4	-CH sym. stretch	2900	2894	2951
$\nu_{14}$	1483	vw	1484	1.7	-CH <sub>2</sub> scissoring	1483	1483	1489
$\nu_{15}$	1346	m	1351	2.8	-CH <sub>2</sub> wagging	1346	1346	1343
$\nu_{16}$	1196	m	1200	5.3	-CH <sub>2</sub> twisting	1202	1196	1195
$\nu_{17}$	1130	s	1115	12.4	-CH <sub>2</sub> rocking	1143	1129	1117
$\nu_{18}$	1079	vs	1078	191.5	COC asym. stretch	1029	1078	1078
$\nu_{19}$	927	w	940	7.3	CO <sub>p</sub> stretch	926	926	940
$\nu_{20}$	698	m	687	2.7	Ring def. (o.p.)	698	698	688
$\nu_{21}$	-	-	193	20.8	Ring bend	193	193	170

\* Fermi resonance between  $\nu_2$  and  $2\nu_3$  ( $\nu_2$  and  $\nu_3$  experimental wavenumbers from [9]),

\*\*Fermi resonance between  $\nu_{12}$  and  $2\nu_8+\nu_{18}$  ( $\nu_{12}$ ,  $\nu_8$  and  $\nu_{18}$  experimental wavenumbers from this work), o.p.–out of plane, i.p.–in plane.

in the experimental spectrum. The vibrations  $\nu_{12}$  and  $\nu_{18} + 2\nu_8$  coincide in frequency, have the B-type symmetry and involve movement of the same atoms. Two bands of similar intensity separated from each other by 23 cm<sup>-1</sup> at 2990 and 2967 cm<sup>-1</sup> appear in the spectrum as a consequence of the Fermi resonance between these vibrations. Such assignment is supported by gas phase IR spectroscopy measurements. The shape of fully (or even partly) resolved vibro-rotational infrared spectral bands gives information about

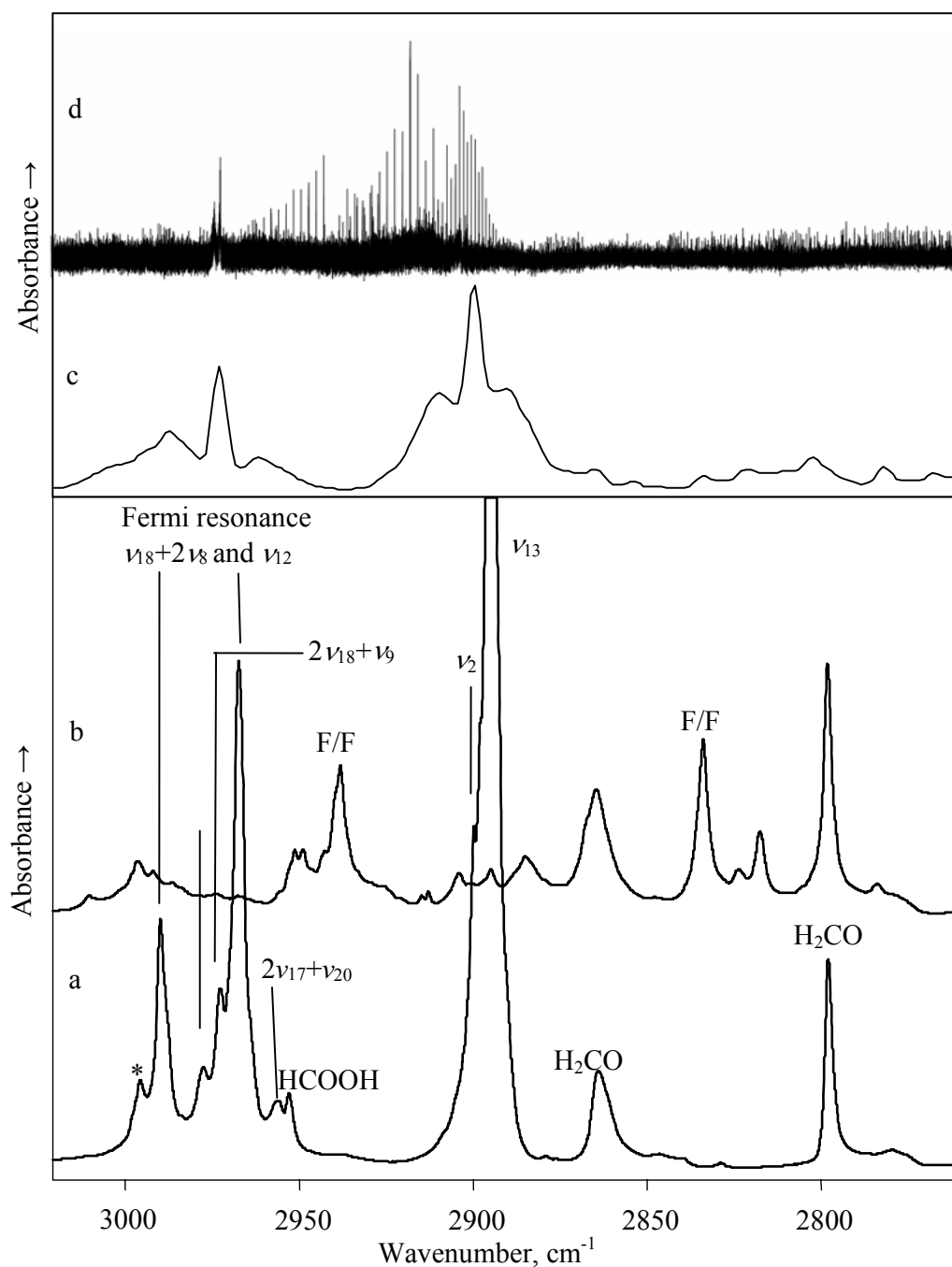
orientation of transition dipole moment vectors of corresponding vibration. Parallelity of the transition moment vectors of the vibrations of the same symmetry and frequency is important for the occurrence of Fermi resonance between these vibrations. According to the theoretical calculations the spectral vibro-rotational band of  $\nu_{12}$  vibration is a,c-hybrid band and the band of  $\nu_{18}+2\nu_8$  vibration should appear as a,b,c-hybrid band. Low and high resolution infrared spectral band of gaseous ethene SOZ at  $2974\text{ cm}^{-1}$  ( $\nu_{12}$ ) is a,c-type, while the spectral band at  $2900\text{ cm}^{-1}$  is a,b,c-hybrid band (see Fig. 6c). The detailed high resolution vibro-rotational infrared absorption spectrum of ethene SOZ is published separately in [17].

Infrared spectra of gaseous ethene SOZ support our assignment of the band pair at  $2990$  and  $2967\text{ cm}^{-1}$  to Fermi resonance between  $\nu_{12}$  and  $\nu_{18}+2\nu_8$ . Such Fermi resonance explains appearance of three strong bands instead of two bands in CH stretching vibration region of the infrared absorption spectrum of matrix isolated ethene SOZ. Taking this into account, there are good candidates for  $\nu_1$  and  $\nu_2$  fundamentals in this spectral region, the remaining two weak spectral bands at  $2978$  and  $2900\text{ cm}^{-1}$ . Such assignment differs from that in [14]. First of all authors of [14] have assigned the band at  $2900\text{ cm}^{-1}$  to  $\nu_{13}$  and the band at  $2895\text{ cm}^{-1}$  to  $\nu_2$  (our assignment is  $2900\text{ cm}^{-1}$  to  $\nu_2$  and  $2895\text{ cm}^{-1}$  to  $\nu_{13}$ ). The authors of [14] were able to use only empirical normal coordinate analysis for the assignment, which is not sufficient for assignment of so closely located spectral bands. Our *ab initio* calculations predict  $\nu_{13}$  spectral band to be much stronger than  $\nu_2$  band and shifted downwards in frequency. This argument was used for the assignment done in the paper.

The remaining two bands at  $2894\text{ cm}^{-1}$  and  $2989\text{ cm}^{-1}$  have been assigned to Fermi resonance between  $\nu_2$  ( $\nu_{13}$  in our assignment) and  $2\nu_3$  by the authors of [14]. Unfortunately, the  $\nu_3$  spectral band due to its weakness is not observable in the spectrum and its experimental frequency is unknown. Also, it is very unlikely that an overtone of such extremely weak vibration can be important in Fermi resonance. The frequency differences between *ab initio* calculated and experimental  $\nu_{13}$  and the assigned  $\nu_1$  is another argument, that  $\nu_{13}$  fundamental ( $\nu_2$  in [14]) is not involved in Fermi resonance. The *ab initio* calculations carried out in this work predict this difference to be ca.  $89\text{ cm}^{-1}$  and experimental difference is found to be  $83\text{ cm}^{-1}$ . In the case that the  $\nu_2$  is involved in Fermi resonance, its frequency will be shifted substantially from the calculated one.

### 3.2 Spectral bands of combination vibrations and overtones

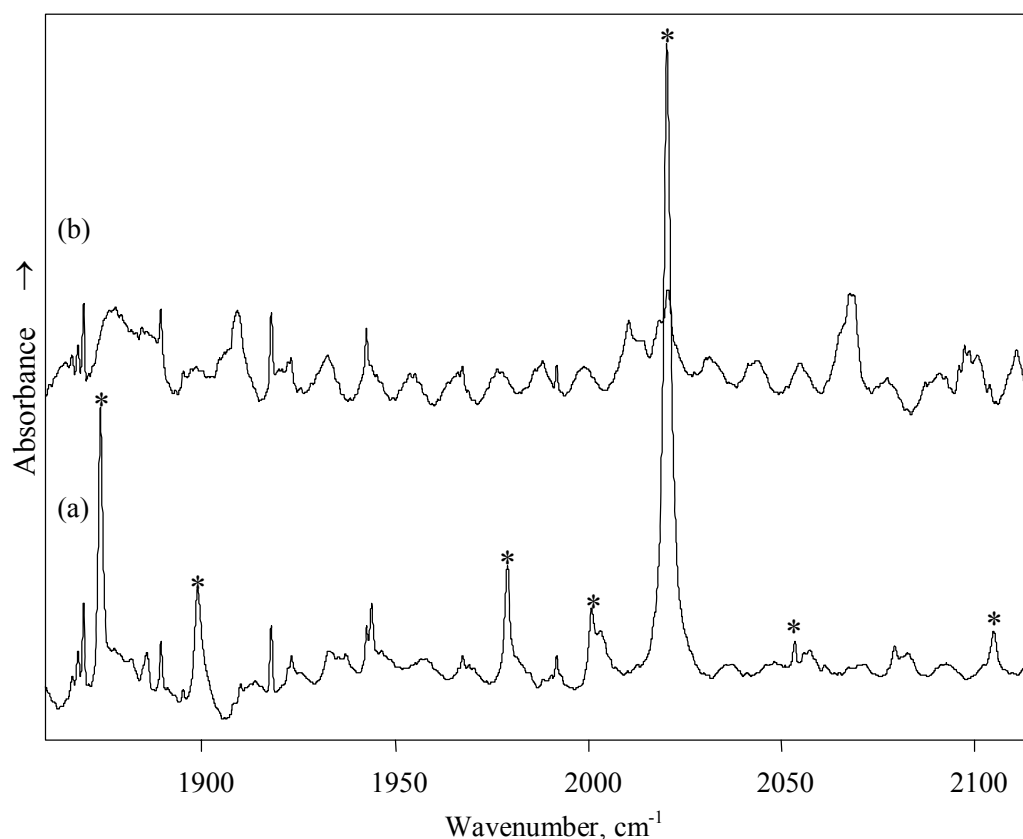
In the infrared absorption spectrum of ethene SOZ isolated in Ar matrix many new weak spectral bands not assigned to the fundamental vibrations were observed. In order to check assignment of these bands to ethene SOZ or impurities, the matrix was photolyzed by using UV radiation. By comparing infrared absorption spectra of the matrix before and after photolysis, the bands belonging to ethene SOZ were identified. It is well known that UV radiation easily breaks ethene SOZ. Therefore, ethene SOZ infrared absorption spectral bands were not observable in the spectrum after the photolysis of the matrix.



**Fig. 6** IR absorption spectra of (a) ethene SOZ isolated in Ar matrix; (b) the sample after photolysis with UV radiation; (c) gaseous ethene SOZ (resolution  $4\text{ cm}^{-1}$ ); (d) gaseous ethene SOZ (resolution  $0.003\text{ cm}^{-1}$ ) in the wavenumber range of the CH stretch vibrations. F/F- formic acid-formaldehyde dimer [5], \* - not identified product.

The selected spectral region of the overtones and combination vibrations in the spectrum of the matrix isolated ethene SOZ before and after photolysis is presented in Fig. 7. The spectral bands disappearing after photolysis were assigned to the ethene SOZ overtones and combination bands. In such a way more than 30 new combination and overtone

spectral bands were found. These spectral bands with their assignment are listed in Table 2. Due to the low symmetry of ethene SOZ, symmetry arguments did not help in the assignment of overtones and combination vibrations. Therefore only the intensity values and fitting of all possible combinations of wavenumbers of the normal vibrations were used.



**Fig. 7** (a) Selected region of infrared absorption spectrum of ethene SOZ isolated Ar matrix with combination bands and overtones. (b) the spectrum of the same sample after UV irradiation. \* - denotes the combination bands or overtones of ethene secondary ozonide.

### 3.3 Reaction coordinates of ethene SOZ dissociation

Infrared spectral bands contain information about potential functions of normal vibrations. Since the potential functions are related to the dissociation reaction coordinates this peculiarity can be used for determination of different pathways of the dissociation. However, the IR spectral bands, corresponding to different fundamental vibrations, overtones and combination vibrations, should be recorded and analyzed. The vibrational term of anharmonic potential, taking into account only the first order anharmonicity  $\tilde{\nu}_e x_e$ , can

be expressed as [18, 19]:

$$E(v) = \hbar\tilde{\nu}_e(v + \frac{1}{2}) - \hbar\tilde{\nu}_e x_e(v + \frac{1}{2})^2 + \dots \quad (1)$$

And the dissociation energy  $D_0$  is related with  $\tilde{\nu}_e$  and  $\tilde{\nu}_e x_e$  by:

$$D_0 \approx \frac{1}{4} \frac{\tilde{\nu}_e^2}{\tilde{\nu}_e x_e}. \quad (2)$$

Therefore, if in the spectrum one can observe spectral bands corresponding to transitions  $v=0 \rightarrow v=1$  and  $v=0 \rightarrow v=2$ , two equations can be set:

$$\begin{cases} \nu_{0 \rightarrow 1} = \tilde{\nu}_e - 2\tilde{\nu}_e x_e \\ \nu_{0 \rightarrow 2} = 2\tilde{\nu}_e - 6\tilde{\nu}_e x_e \end{cases} \quad (3)$$

and  $D_0$  from (2) calculated.

It is already experimentally established that the activation energy for ethene SOZ decomposition is 134–159 kJ/mol [20], but it is still unclear which potential is responsible for the dissociation of the ozonide. Analysis of our *ab initio* calculated normal vibrations of ethene SOZ shows that in the dissociation process of the five membered ring of ethene SOZ only potentials of  $\nu_7$ ,  $\nu_8$ ,  $\nu_9$  and  $\nu_{18}$  might be important. All these fundamentals are observed at 1030, 952, 809 and 1079  $\text{cm}^{-1}$ . Overtones of  $\nu_7$ ,  $\nu_8$  and  $\nu_{18}$  are observed at 2053, 1899 and 2138  $\text{cm}^{-1}$  (see Fig. 7). Dissociation energy calculated from (2) and (3) for  $\nu_7$  ( $\text{CO}_p$  stretch) is 919 kJ/mol, for  $\nu_8$  (COC sym. stretch) is 1096 kJ/mol and for  $\nu_{18}$  (COC asym. stretch) – 364 kJ/mol. These values are much higher than 134–159 kJ/mol (activation energy for ethene SOZ decomposition [20]) and therefore are too high for these potentials to be a reaction coordinate of dissociation of ethene SOZ.

Theoretically calculated barrier for ethene SOZ dissociation to dioxymethane (dioxirane) and formaldehyde is 204 kJ/mole, while dissociation to hydroxymethylformate is 136.5 kJ/mol [11]. Our experimental results support these theoretical predictions. The obtained results show that at conventional temperatures neither CO nor  $\text{CO}_p$  chemical bonds of the five membered ring can be thermally broken. The ring of ethene SOZ consists only of CO, OO and two  $\text{CO}_p$  chemical bonds and if the ring thermally dissociates, the dissociation should involve the splitting of the ring O-O bond. Therefore, the composition pathway involving the splitting of the ring O-O bond and H shift from carbon to oxygen, which yields hydromethylformate O-CH-O-CH<sub>2</sub>OH should be more realistic than splitting of two CO bonds of the five membered ring leading to formation of dioxymethane (dioxirane) and formaldehyde. Unfortunately, an overtone of  $\nu_9$  (O-O stretch) is not observable in the infrared spectrum of ethene SOZ and dissociation energy can not be estimated directly from experimental frequency of this overtone.

**Table 2** The experimental combination and overtone spectral bands of ethene secondary ozonide and their assignment.

Nr	$\nu$ , $\text{cm}^{-1}$	Rel. int.	This work		$\nu$ , $\text{cm}^{-1}$	Assignment [14]
			Assignment	Calculated $\nu$ , according to the assignment		
1	2957	w	$\nu_{20}+2\nu_{17}$	$698+2260=2958$	-	
2	2839	vw	$3\nu_8$	$952\times 3=2856$	-	
3	2739	vw	$\nu_{17}+2\nu_9$	$1130+2\times 809=2748$	-	
4	2717	m	$\nu_4+\nu_{15}$	$1387+1346=2733$	2716	$\nu_4+\nu_{15}$
5	2692	vw	$2\nu_{15}$	$1346\times 2=2692$	-	
6	2576	vw	$\nu_4+\nu_{16}$	$1387+1196=2583$	-	
7	2541	vw	$\nu_{15}+\nu_{16}$	$1346+1196=2542$	-	
8	2512	vw	$\nu_4+\nu_{17}$	$1387+1130=2517$	-	
9	2392	vw	$2\nu_{16}$	$1196\times 2=2392$	-	
10	2294	vw	$\nu_8+\nu_{15}$	$952+1346=2298$	-	
11	2259	vvw	$2\nu_{17}$	$1130\times 2=2260$	-	
12	2207	vw	$\nu_{17}+\nu_{18}$	$1130+1079=2209$	-	
13	2138	vw	$2\nu_{18}$	$1079\times 2=2158$	-	
14	2105	vw	$\nu_7+\nu_{18}$	$1030+1079=2109$	-	
15	2079	vw	$\nu_8+\nu_{17}$ :	$952+1130=2082$	-	
16	2053	vw	$2\nu_7$	$1030\times 2=2060$	-	
17	2020	w	$\nu_1-\nu_8$	$2973-952=2021$	2020	$\nu_7+\nu_8$
18	2003	vw	$\nu_5+\nu_9$ :	$1202+809=2011$	-	
19	2001	vw	$\nu_9+\nu_{16}$	$809+1196=2005$	-	
20	1979	vw	$\nu_7+\nu_8$	$1030+952=1982$	-	
21	1944	vw	$\nu_{13}-\nu_8$	$2895-952=1943$	-	
22	1937	vw	$\nu_9+\nu_{17}$	$809+1130=1939$	-	
23	1899	vw	$2\nu_8$	$952\times 2=1904$	-	
24	1886	vw	$\nu_9+\nu_{18}$	$809+1079=1888$	-	
25	1874	vw	$\nu_8+\nu_{19}$	$952+929=1881$	-	
26	1834	vw	$\nu_7+\nu_9$	$1030+809=1839$	-	
27	1827	vw	$\nu_{17}+\nu_{20}$	$1130+698=1828$	-	
28	1648	w	$\nu_8+\nu_{20}$	$952+698=1650$	-	
29	1608	w	$2\nu_9$	$809\times 2=1618$	-	
30	1103	m	Formic acid		1103	$\nu_{19}+\nu_{21}$
31	1002	vw	$\nu_9+\nu_{21}$	$809+193=1002$	1001	$\nu_9+\nu_{21}$
32	959	vw	$\nu_{15}-2\nu_{21}$	$1346-2\times 193=960$	-	

## 4 Conclusions

Combining the experimental results with the *ab initio* calculations (MP2 6-311 + G(3df, 3pd)), the previous assignment of normal vibrations of ethene SOZ [7, 14] was revised. More than 30 new spectral bands of combination vibrations and overtones were observed and assigned. Dissociation energy for potentials of three anharmonic vibrations  $\nu_7$ ,  $\nu_8$  and  $\nu_{18}$  of ethene SOZ was calculated to be of 919, 1096 and 364 kJ/mol respectively. The calculated energies are too high for these potentials to be a reaction coordinate of dissociation of ethene SOZ. Therefore, it can be concluded that the instability of the five membered ring is related to the weakness of the O-O bond of the ring. Unfortunately, this

cannot be directly proved by IR spectroscopy due to the inactivity of the  $2\nu_9$  vibration (O-O stretch overtone) in the IR absorption spectrum.

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