= PHOTOCHEMISTRY ===

Infrared Multiphoton Dissociation of Tetramethoxygermane

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Abstract—Infrared multiphoton dissociation of $Ge(OCH_3)_4$ molecules by irradiation with a pulsed TEA CO₂ laser has been studied. The basic characteristics of the process have been experimentally investigated. The spectral characterization of the dissociation has been made. The product composition of the dissociation has been analyzed, and possible dissociation pathways have been proposed.

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INTRODUCTION

Germanium is known to have five stable isotopes: ⁷⁰Ge, 20.3, ⁷²Ge, 27.3; ⁷³Ge, 7.7; ⁷⁴Ge, 36.7; and ⁷⁶Ge, 7.8%. Pure germanium isotopes are used in fundamental physics research. In particular, the isotope ⁷⁶Ge is needed in experiments on searching for neutrinoless double beta-decay (GERDA experiment [1]). The future demand for enriched ⁷⁶Ge for this experiment is about one ton.

Recent years have seen significant progress in improving the IR laser separation of silicon isotopes using multiphoton dissociation (**MPD**) of organometallic compounds. High isotopic selectivity parameters were obtained for the IR MPD of 1,2-dichloroethyltrifluorosilane [2] and 2-chloroethyltrifluorosilane [3]. It seems proper to study the IR MPD processes of organoelemental germanium compounds with the aim to find the compounds that hold promise for laser isotope separation.

Tetramethoxygermane $Ge(OCH_3)_4$ is one of the few volatile organogermanium compounds. At room temperature, its saturated vapor pressure is 3.5 torr. The IR MPD of tetramethoxygermane (**TMOS**) using pulsed CO_2 laser radiation was studied by Okada et al. [4]. The IR spectrum of $Ge(OCH_3)_4$ contains a strong band at 1050 cm⁻¹. It was assumed in [4] that this band is due to stretching vibrations of the Ge–O bond. The isotopic frequency shift for such vibrations is estimated at a value of up to 5 cm⁻¹. Based on these estimates, the cited authors studied the isotopic selectivity of MPD with IR excitation in the region around 1050 cm⁻¹. However, the MPD selectivity in this region turned out to be low.

In this work, we conducted a more extensive investigation of the multiphoton dissociation of Ge(OCH₃)₄. The composition of gaseous products was studied, as well as the elemental composition and structure of nonvolatile products deposited on the walls of the reaction vessel. The assignment of absorption bands in the IR spectrum showed that the attribution of the 1050-cm⁻¹ band to Ge–O vibrations is incorrect. Quantum-chemical calculations of the pathways of monomolecular decay of Ge(OCH₃)₄ were performed.

EXPERIMENTAL

Tetramethoxygermane $\text{Ge}(\text{OCH}_3)_4$ was available from Sigma-Aldrich. IR spectra were recorded on a Bruker Vector 22 FTIR spectrometer with a resolution of 1 cm⁻¹. The spectra were taken in a gas-measurement glass cell with KBr windows. The cell length was 180 mm; the diameter, 30 mm.

All operations with tetramethoxygermane-storage, purification, reaction cell loading, sampling for IR spectroscopy—were carried out in a glass vacuum system. The pressure of the sample during these operations was measured with an MKS Baratron 626A capacitance manometer designed for measurements in the pressure range of 0-75 torr. To simplify the analysis of complex mixtures, a procedure of low-temperature separation of their components was used. The procedure consisted in preliminary freezing of the gas mixture into a thermostated glass "finger" coupled with a 250-cm³ tube to which an MKS Baratron 227A pressure sensor (measuring pressure in the range of 0-1 torr) was connected. Then, the "finger" temperature was slowly (over ~10 min) elevated. The pressure sensor during the elevation fixed the characteristic "steps" corresponding to the evaporation of individual components of the mixture.



Fig. 1. Experimentally obtained IR spectrum of tetramethoxygermane (solid curve); a pressure of 2 torr. The vertical lines refer to the calculated Ge–O stretching vibration lines.

Tetramethoxysilane samples were irradiated with a pulsed IR laser in a glass cell of a 300 mm length and a 22 mm diameter with NaCl windows glued at the ends. The laser used for irradiation was a pulsed TEA CO_2 laser. The homogeneous part of the laser beam was isolated with an aperture of 1 cm in diameter. The laser beam was not focused. The initial Ge(OCH₃)₄ pressure in the experiments was 250–420 mtorr.

The chemical composition of the photolysis products was determined using an SRSRGA 300 quadrupole mass spectrometer. The mass spectrometer recorded ion current with a Faraday cup. The mass spectrometer was connected directly to the reaction cell through a 10- μ m hole. Quantum-chemical calculations were performed using the software package Gaussian 98.

IR SPECTRUM OF TETRAMETHOXYGERMANE

The molecular structure of $Ge(OCH_3)_4$ was studied in [5]. The central atom is surrounded by four oxygen atoms, which occupy the vertices of a slightly distorted tetrahedron. The tetrahedron is compressed by 1.2% in the direction of one of the S₄ axes. The C–O bonds form an angle of 122.7° with the Ge–O bonds and turned by 72° relative to the O–Ge–O plane.

Although the tetramethoxygermane molecule no longer has tetrahedral symmetry, its IR spectrum is very simple and has the features typical of the spectra of highly symmetric molecules. Figure 1 shows the most intense IR absorption bands. The wave numbers of C-H stretching vibrations are in the range of the $2800-3100 \text{ cm}^{-1}$. Bands at 670 and 1052 cm⁻¹ are of the greatest interest for laser excitation. Osada et al. [4] attributed the 1052-cm⁻¹ band to stretching vibrations of the Ge-O bond. However, quantum-chemical calculations show that this oscillation is mainly localized in the CO groups. The results of these calculations on the C–O and Ge–O stretching vibrations are given in the table. Rows 22–25 refer to the stretching vibrations of the C–O groups. In the case of tetrahedral symmetry, one inactive symmetric mode (line 25) in the IR region and triply degenerated vibration of T₂ symmetry would be expected. Due to the distortion of the tetrahedral symmetry, the triple degeneracy is partially lifted: the vibration frequency of 1056.1861 cm⁻¹ (line 22) is slightly less than 1060.8165 cm^{-1} (line 23) and $1060.8194 \text{ cm}^{-1}$ (line 24). The vibrations (lines 22–24) in the experimentally measured IR spectrum have a frequency of 8 cm^{-1} below the calculated values. The bandwidth of the experimental spectrum is $\sim 22 \text{ cm}^{-1}$, so that the 5-cm⁻¹ splitting predicted by calculations is not observed in the spectrum.

A similar pattern is observed for the Ge–O stretching vibrations at 650 cm⁻¹. There are one inactive symmetric mode (line 18) and three active modes (lines

Sequential number	Frequency, cm^{-1}	IR intensity	Experiment
18	570.8020	0.0000	
19	628.8789	70.0224	669 cm^{-1}
20	642.6053	107.5045	
21	642.6072	107.5056	
22	1056.1861	299.3204	1052 cm^{-1}
23	1060.8165	321.1414	
24	1060.8194	321.1443	
25	1082.8805	0.0000	

Calculated vibration frequencies of the ${}^{76}\text{Ge}(\text{OCH}_3)_4$ molecule in the range of 500–1100 cm⁻¹. DFT B3lyb method with the 6-311++g(d, p) basis set



Fig. 2. Plot of the dissociation probability versus laser radiation fluence. Pressure, 35 mtorr; the 9P18 line.

19–21). The triple degeneracy is partially removed by distortion of the tetrahedral symmetry.

The assignment of these bands is confirmed by calculating the isotopic shifts for germanium isotopes. The isotopic shift due to the $^{76}\text{Ge}-^{72}\text{Ge}$ replacement is 0.77–0.83 cm⁻¹ for vibrations at 1052 cm⁻¹ (lines 22– 24), but it is 5.9 cm⁻¹ for vibrations at 669 cm⁻¹ (lines 19–21).

The small isotopic shifts for C–O vibrations (1052 cm^{-1}) suggest that no dissociation selectivity for germanium isotopes can be achieved with the use of a CO₂ laser. The germanium isotope-selective IR MPD requires a radiation source in the frequency range of $650-680 \text{ cm}^{-1}$. In this work, we studied the general IR MPD characteristics and dissociation products of Ge(OCH₃)₄ for the case of excitation of C–O vibrations (1052 cm⁻¹) in the lasing range of the CO₂ laser.

FEATURES OF MULTIPHOTON DISSOCIATION OF Ge(OCH₃)₄

We measured absorbed energy as a function of laser radiation fluence Φ at a frequency of 1050 cm⁻¹. The measurements were made in the range of $\Phi = 0$ – 0.32 J/cm^2 . The measurement results are described well by the formula

$$\langle n \rangle = 11.1\Phi(1+12\Phi)/(\Phi+0.039)$$

where $\langle n \rangle$ is the number of absorbed photons per molecule. The average number of absorbed photons $\langle n \rangle$ reaches 50 under the given conditions. The formula describes the dependence close to the linear relationship $\langle n \rangle = 133\Phi$ [J/cm²], except for a small initial portion, where $\langle n \rangle = 280\Phi$ [J/cm²]. The linear nature of the multiphoton absorption allows us to introduce an effective absorption cross section defined as the ratio



Fig. 3. Spectrum of multiphoton dissociation of tetramethoxygermane. Fluence, 200 mJ/cm^2 . The solid curve refers to the linear absorption spectrum of tetramethoxygermane.

of the number of absorbed photons to the photon fluence. Conversion of the factor of 134 cm²/J gives the value of $\sigma_{eff} = 2.7 \times 10^{-18}$ cm². The cross section of the linear absorption spectrum (Fig. 1) at this frequency is $\sigma_{lin}(1048.7) = 5 \times 10^{-18}$ cm², that is, only twice as high. This means that the process of multiphoton excitation pertaining to C–O vibrations of the methoxy group is very efficient and is characterized by an absorption cross section comparable with the cross section in the linear spectrum.

Figure 2 shows the dissociation probability for $Ge(OCH_3)_4$ molecules as a function of fluence. At low energy densities of $\Phi < 0.35 \text{ J/cm}^2$, the experimental data points fit well the exponential relation $\beta = 0.00098 \exp(7.26\Phi)$. A low dissociation yield is associated with a large number of vibrational degrees of freedom of the molecule. Indeed, although the average number of absorbed photons is a few tens, there is less than one absorbed quantum per each of the 57 vibration modes.

These results are consistent with the measurements by Laptev et al. [6] at an energy density of 0.38 J/cm^2 . Note that a sharp increase, most likely due to thermal effects, in the yield of tetramethoxygermane dissociation with an increase in pressure above 0.5 torr was observed in [6].

The dependence of the tetramethoxygermane dissociation probability on the laser frequency (multiphoton dissociation spectrum) is shown in Fig. 3. The maximum of the dissociation spectrum is shifted by \sim 7 cm⁻¹ relative to the maximum in the linear spectrum.



Fig. 4. Dependence of the concentration of the dissociation products on the 9R24 line of CO_2 laser upon the initial reactant concentration. The initial pressure of the reactant is 388 mtorr.

STUDY OF THE GASEOUS PRODUCTS

The composition of the gaseous products of tetramethoxygermane MPD was found to be complex. To

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simplify the analysis of the mixture, a procedure of the low-temperature separation of the components was used. The dissociation products were frozen into the thermostated "finger", whose temperature was slowly increased. The corresponding pressure—temperature plot exhibited separate steps due to the evaporation of different fractions of the mixture.

In a typical experiment in which 300 mtorr $Ge(OCH_3)_4$ was irradiated with 230 laser pulses, the products were separated into the following fractions. The first fraction having a pressure of about 30 mtorr included components that are not frozen at the liquid nitrogen temperature. Mass spectrometric analysis showed that the fraction is composed of hydrogen H₂ with admixtures of CO and CH₄. The next fraction evaporated at a temperature of $-110^{\circ}C$. This was mainly formaldehyde H₂CO with an admixture of acetylene C₂H₂. At a temperature of $-55^{\circ}C$, methanol CH₃OH with a small amount of propane evaporated. The last fraction of the mixture evaporated at about 0°C, which was represented by the unreacted tetramethoxygermane.

Thus, the main gaseous products are formaldehyde and methanol. There are also H₂, C₂H₂, CH₄, CO, and C_3H_8 , which are present in small quantities. After determining the qualitative product composition, a procedure for the mass spectroscopic analysis of the gas mixture without fractionation was developed. A mass spectrum was recorded during the irradiation of the sample, using continuous sampling of the reaction cell. The amount of $Ge(OCH_3)_4$ was determined from the intensity of the group of lines at m/e 105, and the C₃H₈ and CH₃OH contents were found by referring to the lines at m/e 44 and 32, respectively. The H₂CO concentration was determined according to the line at m/e 30 after subtracting the contribution of CH₃OH. The CO concentration was determined from the line intensity at m/e 28 after subtracting the contributions of CH_3OH , H_2CO , and C_3H_8 . The concentration of C_2H_2 was determined according to the line at m/e 25.

Figure 4 shows the rate curves for $Ge(OCH_3)_4$ consumption and the buildup of the main gaseous products (left) and minor products (right). By the time t =350 s, when about 20% $Ge(OCH_3)_4$ is consumed, the amounts of CH_2O and CH_3OH are about 2.5 and 5%, respectively. The amount of the other products CH_4 , CO, C_2H_2 , H_2 , and C_3H_8 is less than 1%. No germanium-containing products were found in the gas phase. During the dissociation of methoxygermane, a film is formed on the walls of the reaction cell. Gas chromatographic–mass spectrometric analysis of a wipe sample of this deposit washed off with various hydrocarbon solvents gave no results.

POSSIBLE FORMATION PATHWAYS OF IR MPD PRODUCTS

The composition of the gaseous products of tetramethoxygermane MPD is similar to that observed in the MPD of the analogous silicon compound $Si(OCH_3)_4$ [6]. The primary process of $Si(OCH_3)_4$ dissociation is believed to be the elimination of the methanol molecule. Similarly, we suggest that the elimination of methanol is the primary process of tetramethoxygermane MPD.

$$\operatorname{Ge}(\operatorname{OCH}_3)_4 + nhv \to \operatorname{Ge}(\operatorname{OCH}_3)_4^*,$$

$$\operatorname{Ge}(\operatorname{OCH}_3)_4^* \rightarrow \operatorname{Ge}(\operatorname{OCH}_3)_2\operatorname{OCH}_2 + \operatorname{CH}_3\operatorname{OH};$$

 $\Delta H = 55 \text{ kcal/mol.}$

The heat of the reaction was found by quantumchemical calculations using the DFT B3lyb 6-311++g(d, p) method. Calculations in terms of the RRKM theory showed that a sufficiently rapid degradation of Ge(OCH₃)₄ molecules is impossible unless the energy is 1.5–2 times above the activation barrier. This means that the dissociation products remain excited and can degrade as well. The decomposition of Ge(OCH₃)₂OCH₂ yields a formaldehyde molecule:

$$Ge(OCH_3)_2OCH_2 \rightarrow Ge(OCH_3)_2 + H_2CO;$$

$$\Delta H = -25.5 \text{ kcal/mol.}$$

This sequence explains the formation of the main products.

CONCLUSIONS

The isotopic shift of germanium isotopes for Ge– O stretching vibrations is on the order of 6 cm⁻¹, which may be sufficient for isotope-selective multiphoton dissociation. However, the Ge–O stretching vibration band lies in the region of 15 μ m. The tuning range of the CO_2 laser covers the vibration bands of the CO group, for which the isotope shift is negligible.

The Ge(OCH₃)₄ molecule very efficiently absorbs IR laser light. The absorption cross section in quasicontinuum in the case of pumping with a CO₂ laser is greater than 2×10^{-18} cm². This feature makes the twofrequency scheme promising for selective processes. In this case, the selective stage of vibrational excitation will be at 15 µm and the subsequent excitation with the CO₂ laser will be at 9.6 µm. Germanium-containing dissociation products are deposited as a nonvolatile residue on the walls of the reaction vessel. The composition of the nonvolatile products calls for further investigation.

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