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Infrared Spectrum of Matrix Isolated Selenoformaldehyde, CH_2Se, and CD_2Se

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Thermolysis of highly diluted $(CH_2Se)_3$ or $(CD_2Se)_3$ in a flow of argon with subsequent quenching of the products in an matrix at 15 K yields monomeric CH_2Se and CD_2Se, respectively. Six fundamental vibrations $\upsilon_1 = 2972.5$, $\upsilon_2 = 1413.3$, $\upsilon_3 = 854.2$, $\upsilon_4 = 916.4$, $\upsilon_5 = 3052.9$, and $\upsilon_6 = 913.2$ cm^{-1} and two combination bands have been observed for CH_2Se as well as three fundamentals of CD_2Se. The vibrational wavenumbers are compared with those of CH_2O and CH_2S. Matrix isolated selenoformaldehyde decomposes slowly by UV photolysis to yield the CSe molecule.

Introduction

The series of formaldehyde analogues CH_2X, X = O, S, Se, Te are of wide interest from a spectroscopic and chemical point of view. With increasing molar mass, they become more and more transient, prone to polymerization. Monomeric selenoformaldehyde, CH_2Se, is unstable in the condensed phase and hence insufficiently spectroscopically characterized. However, monomeric derivatives of selenoaldehyde can be stabilized by sterically bulky substituents or strong electron releasing aromatic groups.[1–3] In this manner, the spectral data of the –CH(Se) moiety has been investigated in detail.[2,3] Recently, its geometric parameters were determined in the crystal structure of 2-tert-butylindolizine-3-selenoaldehyde by X-ray diffraction.[4]

CH_2Se was first produced by pyrolysis of dimethyl selenide and detected in the gas phase in the 825–700 nm region.[5] More efficient is its formation by pyrolysis of oligomeric $(CH_2Se)_x$[6] which was subsequently used to record the photoelectron spectrum.[7] Microwave studies have been performed on a number of isotopomers of CH_2Se yielding a ground-state substitution structure.[8,9] Laser fluorescence-excitation studies of rotationally resolved vibronic bands in the very weak $^1A_2$–X^1A_1 transition at 735 nm of the visible band system of CH_2Se and CD_2Se yielded excited-state parameters.[10,11] Chemiluminescence spectra of CH_2Se, obtained by the reaction of fluorine with methylated selenium compounds,[12,13] revealed four ground-state frequencies $\nu_2 = 1460 \pm 20$, $\nu_3 = 860 \pm 10$, $\nu_4 = 906 \pm 10$, and $\nu_6 = 914 \pm 20$ cm^{-1} which were later confirmed by ab initio calculations.[14]

In this paper, we report a deeper insight of the thermolysis of $(CH_2Se)_3$ and the first direct measurement of the complete vibrational spectrum of matrix isolated CH_2Se and CD_2Se.

Experimental Section

Chemicals. Oligomeric $(CH_2Se)_x$ was obtained by reacting Na_2Se with CH_2Cl_2 according to the described procedure.[6] For the synthesis of the deuterated compound, CD_2Cl_2 (EURISO-TOP GmbH) was used in place of CH_2Cl_2. Parts of the crude products

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Table 1. IR Band Positions (cm^{-1}) and Absorbances of Matrix Isolated Pyrolysis Products of (CH$_2$Se)$_3$ and (CD$_2$Se)$_3$ before and after UV Photolysis

	absorbance			
band position[a]	before	after photol	deuterated species	assignment
4447.8	0.008	0.005		CH$_2$Se $\nu_5 + \nu_2$
3776.3	0.065	0.058		H$_2$O
3756.3	0.143	0.209		H$_2$O
3726.9	0.000	0.009		H$_2$O
3706.5	0.027	0.014		
3555.4	0.019	0.006		
3052.9	0.007	0.004		CH$_2$Se ν_5
2995.3	0.009	0.002		CH$_2$Se$_2$
2985.9	0.000	0.005		
2975.3	0.031	0.015		
2972.5	0.073	0.043		CH$_2$Se ν_1
2887.9	0.001	0.002		
2348.7	0.000	0.126		CO$_2$
2344.9	0.206	0.258		CO$_2$
2338.9	0.077	0.089		CO$_2$
2279.4	0.002	0.004		
2233.9	0.000	0.002 (br)		
2138.7	0.025	0.040 (br)		CO
1839.6	0.014	0.008	1436.9	CH$_2$Se ν_4
1661.4	0.015	0.018		CSe$_2$
1623.9	0.120	0.173		
1594.5	0.016	0.002		
1572.9	0.032	0.022		
1413.2	0.012	0.006	1092.3	CH$_2$Se ν_2
1378.4	0.009	0.000		CH$_2$Se$_2$
1298.7	0.007	0.671		CSe$_2$
1251.8	0.000	0.006		^{13}CSe$_2$
1190.9	0.004	0.000		
1029.7	0.000	0.031		CSe
981.8	0.007	0.000		CH$_2$Se$_2$
929.1	0.010	0.000		
916.4	0.229	0.175	718.8	CH$_2$Se ν_4
913.2	0.051	0.030	690.1	CH$_2$Se ν_6
857.7	0.023	0.000		CH$_2$Se$_2$
854.2	0.005	0.003		CH$_2$^{80}Se ν_3
779.7	0.000	0.004		
662.0	0.025	0.035		CO$_2$

[a] Only bands are mentioned which changed in absorbance during photolysis.

were sublimed in vacuo yielding mainly the most volatile trimer. The observed Raman bands of (CH$_2$Se)$_3$, 2974(s), 2910(vs), 1374(w), 1363(w), 1352(w), 1119(w), 1111(w), 644(m), 634(m), 554(s), 278(m), 210(m), 188(m), 154(w), and 145(w), are in good agreement with the reported bands.[15] Raman bands of the deuterated products are at 2238(s), 2142(vs), 1016(w), 1004(w), 799(w), 591(m), 525(vs), 280(w), 236(s), 175(s). IR bands of (CH$_2$Se)$_3$ isolated in Ar matrix are at 611(m), 748(s), 763(s), 786(w), 837(w), 1019(m), 1034(s), 1042(m), 1136(s), 1266(m), 1373(w), and 2941(s) cm^{-1}.

CH$_3$SeSeCH$_3$ (ACROS Organics) and F$_2$ (Solvay) were used as received.

Preparation of the Matrices. A few milligrams of (CH$_2$Se)$_3$, (CD$_2$Se)$_3$, or CH$_3$SeSeCH$_3$ were placed in a small U-trap, connected to the heated spray on nozzle in front of the matrix support. A stream of Ar (2 mmol/h) was directed over the sample held at 80 °C or −60 °C for (CH$_2$Se)$_3$ and CH$_3$SeSeCH$_3$, respectively, and the resulting gas mixture was quenched on the matrix support held at 15 K. For the thermolysis experiments, the heated nozzle (i.d. 1.6 mm, length 20 mm corundum tube, Ta wire) was adjusted to ca. 1000 °C. Photolysis of the matrices was undertaken with full light of a high pressure mercury lamp (TQ 150, Heraeus) directed through a water-cooled quartz lens optic. Details of the matrix apparatus are given elsewhere.[16]

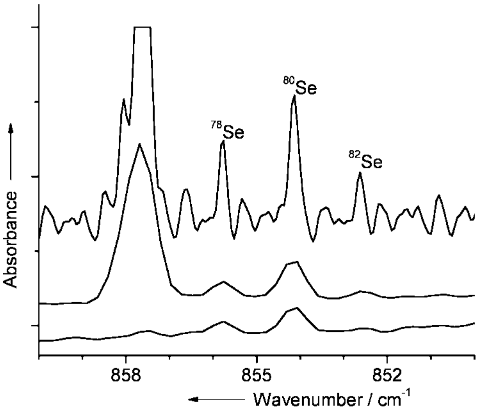

Figure 1. Se-isotopic pattern of the CSe stretching fundamental of CH$_2$Se isolated in Ar matrix. (upper and middle trace) IR spectra of the pyrolysis products of (CH$_2$Se)$_3$ with resolutions of 0.15 and 0.5 cm^{-1}, respectively. (lower trace) IR spectrum after 3 min of UV photolysis, resolution 0.5 cm^{-1}. The strong band at 857.7 cm^{-1} is presumably to photosensitive CH$_2$Se$_2$.

Table 2. Band Position (cm^{-1}) and Absorbance of the Fundamentals of CH$_2$Se$_2$

	CH$_2$Se$_2$				
Ar matrix	int[a]	calc[b]	A[b]	assignment	
2995.3	30	3077	2.9	ν_1	a$_1$
1378.4	27	1407	5.8	ν_2	a$_1$
		688	0.7	ν_3	a$_1$
		293	0.6	ν_4	a$_1$
		886	0	ν_5	a$_2$
		3190	0.2	ν_6	b$_1$
857.3	100	859	6.1	ν_7	b$_1$
981.8	28	1008	0.4	ν_8	b$_2$
		472	7.4	ν_9	b$_2$

[a] Integrated relative absorbance. [b] MP2/TZVP. A is in km/mol; wavenumbers are scaled with a factor of 0.967.

Instrumentation. The matrix infrared spectra were recorded on a Bruker IFS 66v FTIR instrument in reflectance mode using a transfer optic. An MCT detector and a KBr/Ge beam splitter were used in the 5000–600 cm^{-1} region. Twenty and one hundred scans were added for the spectra using apodized resolutions of 0.5 and 0.15 cm^{-1}, respectively. Raman spectra of the precursors were recorded in the 4000–100 cm^{-1} range using a spectral resolution of 2 cm^{-1} on a Bruker FRA 106 Raman spectrometer and the 1064 nm excitation line of a Nd:YAG laser (120 mW).

Results and Discussion

The strongest IR band of CH$_2$Se was predicted by ab initio calculations to be in the vicinity of 920 cm^{-1}.[14] This band guided us in the search of the desired product in matrix isolation experiments. Three different routes to CH$_2$Se were attempted: (i) heating a mixture of CH$_3$SeSeCH$_3$/Ar and F$_2$/Ar during its deposition as a matrix, (ii) pyrolysis of CH$_3$SeSeCH$_3$/Ar with subsequent quenching of the products in Ar matrix, and (iii) matrix isolation of (CH$_2$Se)$_3$/Ar pyrolysis products. While method i and ii yielded only traces of CH$_2$Se, in method iii, a high concentration of CH$_2$Se was obtained, when the (CH$_2$Se)$_3$/Ar mixture was heated so high

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Table 3. Band Position (cm^{-1}) and Absorbance of the Fundamentals of CH_2Se and CD_2Se

CH_2Se					CD_2Se			
Ar matrix	int[a]	gas phase[b]	calc[c]	A[c]	Ar matrix[d]	calc[c]	assignment	
2972.5	30		3030	16	(2148)	2165	ν_1	a_1
1413.3	4	1460 ± 30	1436	4	1092.3	1091	ν_2	a_1
854.2[e]	3	860 ± 10	878	0.4	(785)	797	ν_3	a_1
916.4	100	914 ± 20	931	63	718.8	723	ν_4	b_1
3052.9	4		3134	2	(2276)	2310	ν_5	b_2
913.2	17	906 ± 10	923	9	690.1	688	ν_6	b_2

[a] Integrated relative absorbance. [b] Reference 13. [c] MP2/TZVP. A is in km/mol, and wavenumbers is scaled with a factor of 0.967.[14] [d] Values in parenthesis are estimated by force field calculations. [e] Band position for $CH_2{}^{80}Se$; $CH_2{}^{78}Se$ is at 855.8, and $CH_2{}^{82}Se$ is at 852.6 cm^{-1}.

that the precursor was nearly dissociated (heat power 28 W). In the resulting IR matrix spectra, many bands were observed and they could be attributed to at least three new species by UV photolysis experiments. One group of bands belongs to UV-stable products, Universitducts (CO_2, H_2O, bands of unknown species at the following wavenumbers: 947.4(w), 1033.7(vs), 154.0(m), 1055.8(m), 1077.3(w), 1201.0(m), 1215.2(m), 1330.2(s), 1361.4(m), 2797.5(w), 2847.6(w) cm^{-1}). A second group of bands decreases slowly, and a third group of bands decreases quickly in intensity during UV photolysis. These bands together with those bands of the photoproducts are listed in Table 1. By comparison with the predicted band positions and band intensity of CH_2Se[14] and their photochemical behavior (slow decomposition) all fundamental vibrations and two combinations of selenoformaldehyde have been assigned. The selenium isotopic pattern was resolved only for the CSe stretching mode ν_3 as depicted in Figure 1. The bands of ^{78}Se, ^{80}Se, and ^{82}Se isotopomers are clearly visible but the weak bands of ^{76}Se and ^{77}Se are covered by a band of a more photosensitive byproduct. After 3 min of UV photolysis, this band nearly vanished and the full isotopic pattern of ν_3 appeared (^{76}Se:^{77}Se:^{78}Se:^{80}Se:^{82}Se = 18:15:47:100:19).

The underlying thermal and photochemistry in this study seems to be quite complicated and is only partially understood. Many bands of the thermolysis products of $(CH_2Se)_3$ and the species formed by UV photolysis are yet not assigned. Even the precursor $(CH_2Se)_3$ seems to be not homogeneous. CO_2 and CO are products of the high temperature hydrolysis during deposition in the corundum tube, which seems to contain traces of water at the surface. The only detected new species formed by the UV photolysis of CH_2Se is CSe showing a quite strong band at 1029.7 cm^{-1} (gas phase 1025 cm^{-1}).[17] The assignment of this band is confirmed by its observed Se-isotopic pattern with $\Delta\nu^{78/80}Se$ = 1.6 cm^{-1} (calculated 1.7 cm^{-1}). Another prominent photolysis product is CSe_2, which can be formed only from a precursor which contains two Se atoms and carbon. A possible candidate would be 1,2-diselenirane, CH_2Se_2, which is yet unknown. However, its properties are expected to be similar to those of dithiirane, CH_2S_2, which, if matrix isolated, isomerizes and finally decomposes into $CS_2 + H_2$ by photolysis.[18] The band positions and intensities of the most photosensitive species observed in the matrix isolated product mixture and listed in Table 2 are compared with predicted values of CH_2Se_2 from quantum chemical calculations.[19] Because there is a good agreement between the observed and calculated IR spectrum, the carrier of these bands is most likely CH_2Se_2. It may be formed by the pyrolysis of $(CH_2Se)_n$, but more probably by the thermolysis of cyclic diselenides with Se−Se units, e.g. 1,2,4-triselenolane, $C_2H_4Se_3$, which may be present in the precursor mixture. However, to assign all observed bands, further work is needed.

Pyrolysis of the deuterated precursor yielded CD_2Se, but only three of the six fundamentals have been unambiguously assigned. The three missing fundamentals are predicted to be very weak and/or obscured by bands of impurities. The symmetrical CH stretch of CD_2Se is expected to be very similar to that of CD_2S (2155 cm^{-1}, Ar matrix).[20] The very weak asymmetrical CH stretch, also not observed for CD_2S, is probably obscured by strong absorptions of CO_2. The missing fundamental vibrations have been estimated by a force field calculation. For this purpose, the general valence force field of CH_2S[21] was adjusted to that of CH_2Se using the experimental vibrational data of CH_2Se, listed in Table 3. The obtained force field reproduced the band positions of CH_2Se exactly and those of CD_2Se within the expected anharmonicity differences of both isotopomers. The estimated wavenumbers for the three missing fundamentals of CD_2Se are given in Table 3 together with band positions and band intensities obtained from ab initio calculations. Their uncertainty is probably less than 1%.

In Figure 2, the trend of the fundamental wavenumbers in the series CH_2X, X = O,[9] S,[9] and Se, is visualized. First

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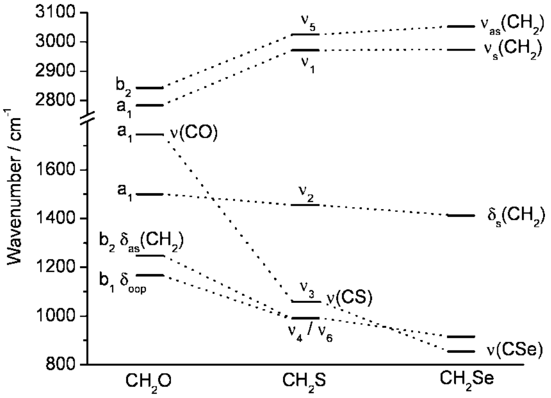

Figure 2. Trends of the fundamental vibrations in the series CH_2X, X = O, S, Se.

of all, the increase of the CH stretches with increasing molar mass of CH_2X is interesting to note. This is in accordance with the decrease of the C−H bond lengths (110.8 for CH_2O, 109.3 for CH_2S, and 109.0 pm for CH_2Se).[9] In terms of a simple molecular orbital model, this observation may be explained by the decrease of hyperconjugation between the filled in plane p-orbital of X with the σ*-orbitals of the C−H bonds with increasing molar mass of X. Such an interaction is not possible in the free CH_2 molecule that exhibits the highest C−H stretching wavenumbers $\nu_1 = 2950$, $\nu_3 = 3080$ cm^{-1}).[22] All further bands reveal more or less dependence on the mass of X, and ν(CX) decreases most with increasing mass. This causes a crossover of ν(CX)/δ(CH) from CH_2O to CH_2S and from CH_2S to CH_2Se. For CH_2S and CH_2Se, three fundamentals appear close to 1100 and 900 cm^{-1}, respectively. They will be difficult to analyze in the high resolution gas phase spectrum as recently demonstrated for CH_2S.[23]

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