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Infrared Spectrum and Fourier Transform Spectroscopy of the $2\nu_1$ Band of OCSe: Synthesized by Using a Heat Pipe Reactor

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In order to observe the infrared spectrum of OCSe, a sufficient amount was readily synthesized by using a heat pipe reactor. Thirteen vibrational bands were observed in the region of $400 \sim 4000\ \mathrm{cm}^{-1}$, seven of which have never been reported. The high-resolution FTIR spectrum of the $2\nu_1$ band of OCSe was recorded with a resolution of $0.005\ \mathrm{cm}^{-1}$. Analysis provided molecular constants for the $2\nu_1$ band of $^{16}O^{12}C^{80}Se$ and $^{16}O^{12}C^{78}Se$ in natural abundance.

1. INTRODUCTION

So far, only a limited number of papers reported on the infrared spectrum of carbonyl selenide (OCSe). Wentink (*1*) was the first to report the frequencies of the three fundamental vibrations. Bavia *et al.* (*2*) have reported the frequencies of six bands. Maki *et al.* (*3*) have observed high-resolution spectra of the ν_1 band, its hot bands, and the $\nu_1 + \nu_3$ band for various isotopically substituted OCSe. This is, however, the extent of information available on the infrared spectrum of OCSe. Even a recorder trace of the overall spectrum has not appeared in the literature.

In order to synthesize OCSe by using CO and Se powder, i.e., $CO + Se \rightleftharpoons OCSe$, a flask is usually used as a reaction vessel, which is heated to ca. 780°C (*4*). Although this synthesis is well established, the operation of the reaction vessel at 780°C is troublesome. A large amount of Se dust is carried downstream of the vessel and is deposited on the inner wall of the apparatus. Moreover, the yield of OCSe is quite low, usually less than 10%.

In the present study, a new method of synthesis using a heat pipe reactor has been developed. A substantial amount of OCSe in purity higher than 90% is readily obtained. The ease with which OCSe is synthesized by the present method permits the observation of an abundant infrared spectrum. The low-resolution infrared spectrum in the region of $400 \sim 4000\ \mathrm{cm}^{-1}$ shows 13 bands. The Fourier transform spectrum of the $2\nu_1$ band with a resolution of $0.005\ \mathrm{cm}^{-1}$ is also reported in this paper.

2. HEAT PIPE REACTOR

A heat pipe reactor for the preparation of the OCSe used in this study is a variant of a heat pipe oven developed for the spectroscopy of BaO by Hessel *et al.* (*5*) and BiO by Sakurai and Broida (*6*). Figure 1 shows the schematic diagram of the present

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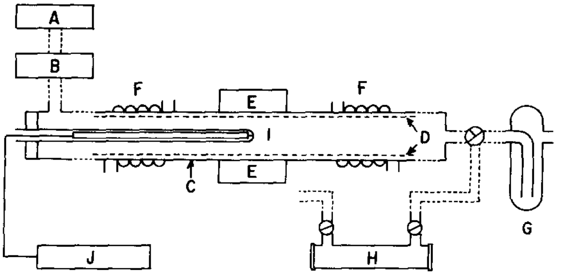

FIG. 1. A schematic diagram of a heat pipe reactor. (A) CO cylinder; (B) gas flow meter; (C) stainless-steel pipe; (D) wick; (E) electric furnace; (F) water cooling system; (G) cold trap; (H) infrared gas cell; (I) thermocouple (CA); and (J) thermometer.

heat pipe reactor. The stainless-steel pipe has a length of 700 mm and a diameter of 13 mm. The inner wall of the pipe is lined with a stainless-steel mesh wick. The center zone of the pipe, 10 cm in length, is heated with an electric furnace. Water cooling systems are mounted on both ends of the pipe.

Selenium powder (7 g, 99.999% pure) was placed in the reactor. When the center zone is heated, liquid Se wets the wick and becomes a working fluid. The working fluid evaporates from the wick at the center zone, and the resultant vapor moves toward the ends of the pipe, i.e., to the cooled parts. Then, the vapor condenses on the wick and the condensate returns to the center by capillary action.

One end of the pipe was connected to a carbon monoxide cylinder through a gas flow meter and the other end to a cold trap as shown in Fig. 1. The temperature was measured with a thermocouple (Chromel-Alumel) sealed within a quartz tube and inserted into the pipe. Carbon monoxide was admitted continuously with a flow rate of 4 l/hr. The reaction zone was heated to a temperature of 600°C. Since the yield of OCSe was very low, the reaction products were continuously trapped in a cold trap kept at ca. −154°C.

The one-trip yield of OCSe was 1.2 vol%, estimated from the amount of trapped OCSe and the total amount of CO which flowed through the reaction tube. Brauer (*4*) and Pearson and Robinson (*7*) reported yields of 9.8 and 3.6 vol%, respectively, for the reaction of $CO + Se \rightleftharpoons OCSe$. The present yield is lower than theirs. However, it should be noted that a large amount of OCSe was readily obtained by the present heat pipe reactor method. Se dust was not a problem during the operation. Gaseous OCSe (0.32 liters) with a purity of 93 vol% was obtained during a 6-hr operation at a CO flow rate of 4.0 l/hr.

3. INFRARED BANDS AND THE FOURIER TRANSFORM SPECTRUM OF $2\nu_1$ BAND

A recorder trace of the infrared spectrum of OCSe from 400 to 4000 cm^{-1} is shown in Fig. 2. The total pressure of the sample gas was 400 Torr in a 10-cm gas cell. A rough idea of the purity (93 vol% of OCSe) of the sample gas can be obtained from the figure. Thirteen vibrational bands of OCSe are identified. Seven of the thirteen bands have never been previously reported. The band at 463 cm^{-1} is the band, ν_2, a perpendicular band. The other 11 bands, except the band at 2483 cm^{-1}, are parallel

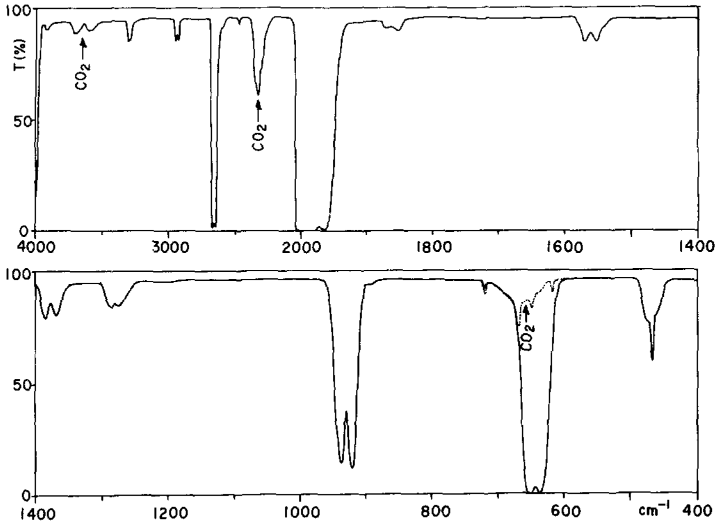

FIG. 2. The infrared spectrum of OCSe in the wavenumber region between 400 and 4000 cm^{-1}.

bands. Assignments and the band center values for the observed bands are listed in Table I.

The spectrum in Fig. 2 can only provide approximate band center values because of overlapping of spectral lines due to several isotopic species and hot bands. In order

TABLE I

Vibrational Frequencies for OCSe

frequencies (cm^{-1})		intensity[a]	assignment
this work	other source[b]		
4023	4020.2	S	$2\nu_1$
3303		W	$\nu_1 + 2\nu_3$
2940		W	$\nu_1 + 2\nu_2$
2666	2664.0	S	$\nu_1 + \nu_3$
2483		VW	$\nu_1 + \nu_2$
2023	2022.3	VS	ν_1
1861		W	$4\nu_2$
1563		W	$\nu_3 + 2\nu_2$
1379		W	$\nu_1 - \nu_3$
1283		W	$2\nu_3$
928	927.1	S	$2\nu_2$
644	643.0	S	ν_3
463	466.5	M	ν_2

a. VS=Very Strong; S=Strong; M=Medium; W=Weak; and VW=Very Weak.

b. Reference 2.

to obtain the values of harmonic frequencies (ω_s) and anharmonicity constants ($x_{ss'}$ and x_{ll}), we have to analyze the high-resolution spectra of the various bands in Table I and determine band center values separately for each isotopic species.

There has been only one infrared high-resolution study of OCSe (*3*), and it described only the ν_1 and $\nu_1 + \nu_3$ bands. Therefore, we have recorded the high-resolution spectra, by using the following FTIR spectrometers: Bomem DA3.002 and Bruker IFS113v. All of the above-mentioned 13 bands of OCSe have been recorded using only the natural isotopic abundance. In the case of the strongest band, ν_1, the assignment of the spectrum recorded at a resolution of 0.005 cm^{-1}, using Loomis–Wood type diagrams, has successfully revealed series of the spectral lines for the following isotopes: $^{16}O^{12}C^{82}Se$, $^{16}O^{12}C^{80}Se$, $^{16}O^{12}C^{78}Se$, $^{16}O^{12}C^{77}Se$, $^{16}O^{12}C^{76}Se$, $^{16}O^{12}C^{74}Se$, $^{16}O^{13}C^{82}Se$, $^{16}O^{13}C^{80}Se$, $^{16}O^{13}C^{78}Se$, $^{16}O^{13}C^{77}Se$, $^{16}O^{13}C^{76}Se$, and $^{18}O^{12}C^{80}Se$. These spectra and the results of their analyses are reported in separate papers (*8, 9*). In this paper, we confine our attention to the high-resolution spectrum of the $2\nu_1$ band.

The high-resolution spectrum of the $2\nu_1$ band was observed with a resolution of 0.005 cm^{-1} by using a Bomem DA3.002. Using a 20-cm cell at a sample pressure of 4 Torr, 100 scans were coadded over the bandpass of 3950–4050 cm^{-1}. We used, without further calibrations, the outputted values of the spectrometer for the line positions. The instrumental calibration values of the spectrometer for the absolute and relative accuracies, ±0.001 and ±0.0002 cm^{-1}, respectively, at 2000 cm^{-1} were confirmed by observing the spectrum of NH_3 (*10*). In Fig. 3, a part of the recorder trace of the $2\nu_1$ band is shown.

4. ANALYSIS, RESULTS, AND DISCUSSION

The energy of a rotational–vibrational level may be written as

$$E_{v,J} = G_v + B_v[J(J+1) - l^2] - D_v[J(J+1) - l^2]^2. \qquad (1)$$

The symbol v represents the quantum numbers $v_1v_2^lv_3$. For a Σ–Σ band, we obtain the usual expression

$$\nu_m = \nu_0 + (2B'' + \Delta B)m + (\Delta B - \Delta D)m^2 - 2(2D'' + \Delta D)m^3 - \Delta Dm^4, \qquad (2)$$

where, $\nu_0 = G_{v'} - G_{v''}$, $\Delta B = B' - B''$, and $\Delta D = D' - D''$.

Spectral lines of the 20^00–00^00 transitions (Σ–Σ band) of ^{80}Se and ^{78}Se isotopic species were assigned by the Loomis–Wood diagrammatic method and were fitted to

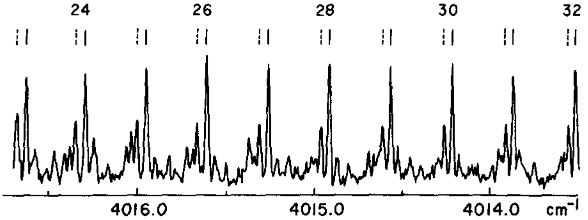

FIG. 3. A part of the P-branch region of the $2\nu_1$ band of OCSe. Numbers correspond to J values for the $J - 1 \leftarrow J\,(20^00$–$00^00)$ transitions. Solid lines: $^{16}O^{12}C^{80}Se$. Broken lines: $^{16}O^{12}C^{78}Se$.

TABLE II

Observed Line Positions (in cm^{-1}) in the 20^00–00^00 Transitions for OCSe[a]

$^{16}O^{12}C^{80}Se$			$^{16}O^{12}C^{78}Se$		
J	P(J)	R(J)	J	P(J)	R(J)
3	4022.70939 (-467)*	4024.57200 (213)	3	4022.80501 (-388)	
4	4022.41834 (-1895)*	4024.82629 (296)	4		
5	4022.15835 (73)	4025.07286 (-100)	5		4025.17872 (-463)
6	4021.86915 (-587)*	4025.32277 (128)	6		
7	4021.58566 (-386)*	4025.56395 (-223)	7	4021.67512 (-231)	
8	4021.30244 (132)	4025.80779 (-18)	8		
9	4021.00941 (-37)	4026.04689 (5)	9	4021.09718 (303)	4026.16339 (95)
10	4020.70926 (-629)*	4026.28513 (234)	10		4026.40336 (348)
11	4020.41623 (-218)	4026.51837 (255)	11	4020.49991 (75)	4026.62761 (-675)*
12	4020.12021 (184)	4026.74468 (-123)	12	4020.19647 (-79)	4026.86598 (5)
13	4019.81722 (180)	4026.97481 (170)	13	4019.89727 (480)	
14	4019.50732 (-222)	4027.19884 (147)	14	4019.58803 (329)	4027.32361 (338)
15	4019.20179 (101)	4027.41910 (38)	15	4019.27653 (245)	4027.54577 (280)
16	4018.88721 (-188)	4027.63573 (-140)	16		4027.76311 (34)
17	4018.57691 (239)	4027.85210 (-52)	17	4018.63976 (-423)	4027.97825 (-137)
18	4018.25512 (-190)	4028.06482 (-37)	18		4028.18700 (-653)*
19	4017.93383 (-280)	4028.27515 (30)	19	4017.99603 (-619)*	4028.40405 (-45)
20	4017.61351 (17)	4028.47781 (-376)*	20	4017.67093 (-602)*	4028.61200 (-53)
21	4017.28118 (-595)*	4028.68495 (-41)	21	4017.34908 (32)	4028.81919 (157)
22	4016.95929 (125)	4028.88630 (6)	22	4017.01316 (-447)	4029.01665 (-309)
23	4016.62514 (-88)	4029.08241 (-177)	23	4016.67540 (-819)*	4029.21902 (8)
24	4016.28966 (-145)	4029.27870 (-50)	24	4016.34351 (-312)	4029.41651 (134)
25	4015.95247 (-83)	4029.47125 (-4)	25	4016.00074 (-600)*	4029.60619 (-225)
26	4015.61198 (-60)	4029.65930 (-115)	26	4015.66228 (-165)	
27	4015.26831 (-66)	4029.84743 (74)	27	4015.31862 (41)	4029.98624 (7)
28	4014.92457 (211)	4030.02704 (-294)	28	4014.96361 (-594)*	4030.17022 (-37)
29	4014.57278 (-26)	4030.21032 (-3)	29		4030.35154 (-52)
30	4014.22004 (-68)	4030.38647 (-132)	30	4014.26592 (244)	4030.52963 (-94)
31	4013.86501 (-50)	4030.56162 (-68)	31	4013.90521 (-83)	4030.70363 (-250)
32	4013.50560 (-179)	4030.73277 (-111)	32	4013.54562 (-8)	
33	4013.14602 (-36)	4030.90136 (-116)	33	4013.17749 (-493)*	4031.05077 (239)
34	4012.78396 (148)		34	4012.81498 (-125)	4031.22055 (550)*
35	4012.41562 (-4)	4031.23146 (44)	35	4012.44875 (163)	4031.38059 (182)
36	4012.04392 (-204)	4031.38059 (-1026)*	36	4012.07510 (3)	4031.54093 (141)
37	4011.67653 (316)	4031.54093 (-683)*	37	4011.69272 (-738)*	4031.69701 (-28)
38	4011.29777 (-9)	4031.69701 (-472)*	38	4011.32139 (-81)	
39	4010.91982 (34)	4031.85203 (-73)	39	4010.94317 (178)	
40	4010.53904 (85)	4032.00186 (99)	40		
41	4010.15566 (166)	4032.14631 (28)	41	4010.17207 (109)	
42		4032.28731 (-93)	42		
43	4009.37960 (265)	4032.43016 (263)	43		
44	4008.98290 (-118)	4032.56586 (199)	44		
45	4008.58822 (-10)	4032.69843 (115)	45		4032.84888 (-374)
46	4008.19161 (194)	4032.82745 (-28)	46		4032.98471 (105)
47	4007.78788 (-24)	4032.95548 (22)	47		
48	4007.38522 (153)	4033.07909 (-73)	48		
49	4006.97434 (-201)	4033.19799 (-347)*	49		
50	4006.56172 (-441)*	4033.32034 (18)	50		
51	4006.14629 (-673)*	4033.43656 (66)	51	4006.14629 (305)	
52	4005.72956 (-746)*	4033.54841 (-29)	52	4005.72956 (521)*	4033.70697 (-17)
53	4005.30961 (-852)*	4033.65945 (89)	53	4005.30961 (708)*	4033.81856 (128)
54	4004.88392 (-1243)*	4033.76351 (-195)	54	4004.88392 (615)*	
55	4004.45921 (-1247)*	4033.87022 (79)	55		
56	4004.04263 (-149)	4033.96340 (-704)*	56		
57	4003.61515 (147)	4034.07274 (423)*	57	4003.58612 (22)	
58		4034.16420 (57)	58		
59	4002.74353 (-58)		59	4002.70380 (-617)*	4034.42353 (843)*
60			60	4002.26521 (-239)	
61		4034.42353 (-774)*	61	4001.82171 (-59)	
62	4001.41855 (43)	4034.51361 (-98)	62		
63		4034.59484 (-11)	63	4000.92078 (-208)	
64		4034.67669 (432)*	64		
65		4034.75477 (795)*	65		
67			67	3999.08843 (-27)	
68			68	3998.62507 (226)	
69	3998.22280 (-31)		69		
70	3997.75496 (-18)		70		

a. The values of obs-calc × 10^5 are given in parentheses. Lines marked with an asterisk were not fitted.

Eq. (2) by a least-squares method. Molecular parameters ν_0, B'', ΔB, D'', and ΔD were determined. Inclusion of the higher term $H_v[J(J+1)]^3$ gave no improvement in the fit, thus, the H_v term was not included in the present least-squares fit. The values of the observed transitions and obs − calc are listed in Table II.

Spectral lines due to the different Se isotopic species and hot bands overlap each other. Therefore, in order to obtain accurate molecular constants it was essential to exclude from the fit heavily perturbed spectral lines. The lines excluded from the final fits are marked by *. Molecular parameters for $^{16}O^{12}C^{80}Se$ and $^{16}O^{12}C^{78}Se$ determined by the fits are listed in Table III. The present values of the molecular constants for the ground state are in good agreement with microwave values (*11–13*), which are included in Table III. The accuracy of the (effective) values of B' and D' which can be obtained from Table III therefore, are also guaranteed within the experimental errors.

In the present analysis, we have determined the values of ν_0, B'', ΔB, D'', and ΔD by polynomial fitting. To get the best possible values of the rotational constants for N_2O, Amiot (*14*) determined first the ground state constants from the combination differences. Then, he calculated ν_0 and the upper state constants, using the observed transition wavenumbers, by fixing the ground state constants at the values previously obtained. We have also followed this method. However, in the present case of OCSe, the number of the experimental values for $\Delta_2F''(J)$ is limited because of the severe overlapping of the lines. Thus, the determination of the constants B'' and D'' from the combination differences was rather difficult.

The ν_0 values for the ν_1 band were determined previously (*3, 8*) as 2023.52516 and 2023.57464 cm^{-1} for $^{16}O^{12}C^{80}Se$ and $^{16}O^{12}C^{78}Se$, respectively. Using these values for the ν_1 band and the present results for the $2\nu_1$ band we obtain the vibrational constants $x_{11} = -11.762$ cm^{-1} for both $OC^{80}Se$ and $OC^{78}Se$ and $\omega_1^0 = 2035.287$ and 2035.336 cm^{-1} for $OC^{80}Se$ and $OC^{78}Se$, respectively.

The present analysis of the Fourier transform spectrum of the $2\nu_1$ band has successfully determinated the molecular constants for the two most abundant isotopic species. The good agreement of the ground state constants between the present study and the microwave values suggests that the present molecular constants are accurate

TABLE III

Molecular Parameters of OCSe for the $2\nu_1$ Band

parameters (cm^{-1})	$^{16}O^{12}C^{80}Se$		$^{16}O^{12}C^{78}Se$	
	this work	microwave[a]	this work	microwave[a]
ν_0	4023.52690(90)[b]		4023.6267(16)	
B''	0.134015(14)	0.1340153	0.134845(26)	0.1348420
$10^3\Delta B$	-1.4570(13)		-1.4647(26)	
$10^8D''$	2.19(27)	2.233	2.24(66)	2.259
$10^9\Delta D$	0.11(32)		0.97(75)	

a. References 11-13.

b. The uncertainties are three times the standard deviation.

within the experimental uncertainties. Results of the analysis for Fourier transform spectra of the other vibrational bands will be reported elsewhere.

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