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Fourier Transform Spectroscopy on the ν_1 Band of OCSe

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The ν_1 fundamental band of OCSe in natural abundance was observed near 2000 cm^{-1} with a resolution of 0.005 cm^{-1}. Results of the analysis are given for $^{16}O^{12}C^{80}Se$ and $^{16}O^{12}C^{78}Se$.

So far, only one paper by Maki et al.[1] has been reported on the high-resolution infrared spectrum of carbon oxide selenide (OCSe). They observed, with a resolution of 0.025 cm^{-1}, the ν_1 band and its hot bands for $^{16}O^{12}C^{80}Se$, $^{18}O^{12}C^{80}Se$ and $^{16}O^{13}C^{80}Se$ near 2000 cm^{-1} and also the $\nu_1+\nu_3$ band for $^{16}O^{13}C^{80}Se$ near 2600 cm^{-1}. We synthesized OCSe using a heat pipe reactor and observed thirteen infrared bands between 400 and 4000 cm^{-1} for OCSe in natural abundance.[2] High-resolution spectra for all of the thirteen bands were recorded by FTIR spectrometers, BOMEM DA3.002 and BRUKER IFS 113v. The strongest band, ν_1 band, was recorded by BOMEM DA3.002 with a resolution of 0.005 cm^{-1}.

The spectrum of the ν_1 band shows the most complex features due to the hot bands in addition to the Se isotopes. However, the present high-resolution has led to the successful assignment of the spectral lines for each isotope species and the accurate determination of the molecular constants. In this letter, we report the high-resolution infrared spectra and the analysis of the ν_1 band confining our attention to the two most abundant species, $^{16}O^{12}C^{80}Se$ and $^{16}O^{12}C^{78}Se$.

A part of the recorder trace of the ν_1 band is shown in Fig. 1. Spectral lines assigned to the 10^00-00^00 transitions (Σ-Σ band) for $^{16}O^{12}C^{80}Se$ and $^{16}O^{12}C^{78}Se$ are indicated by solid and broken lines, respectively. Some of the lines overlap and their intensities apparently increase. Figure 2 illustrates the intensities and positions for the spectral lines assigned to $^{16}O^{12}C^{80}Se$. The locally-perturbed intensity distribution is clearly seen, which is due to the overlapping of the lines. Figure 2 also illustrates the values of obs-calc for each transition wavenumber.

The spectral lines assigned to the 10^00-00^00 transitions for $^{16}O^{12}C^{80}Se$ and $^{16}O^{12}C^{78}Se$ were analysed with a program system SALS[3] in least-squares fitting to energy levels given by[1]

$$E=G_v+B_vJ(J+1)-D_v[J(J+1)]^2 \qquad \text{and} \qquad \nu_0=G_v'-G_v''.$$

In the final fits, severely overlapped lines were excluded. The values of the observed transitions and obs-calc are listed in Table 1. The observed values listed are just the output values of the DA3.002 spectrometer. The absolute and the relative uncertainties in the observed values are ±0.001 cm^{-1} and ±0.0002 cm^{-1}, respectively. The spectral lines excluded from the final fits are marked by *.

Molecular parameters ν_0, B", B', D", and ΔD(=D'-D") were accurately determined by the present fits. They are listed in Tables 2 and 3. Rotational constants for OCSe have extensively been given by microwave spectroscopy[4] for various states of a number of isotopic species. Rotational and distortion constants in the present study are in good agreement with the microwave values.[4,5] The present rotation-

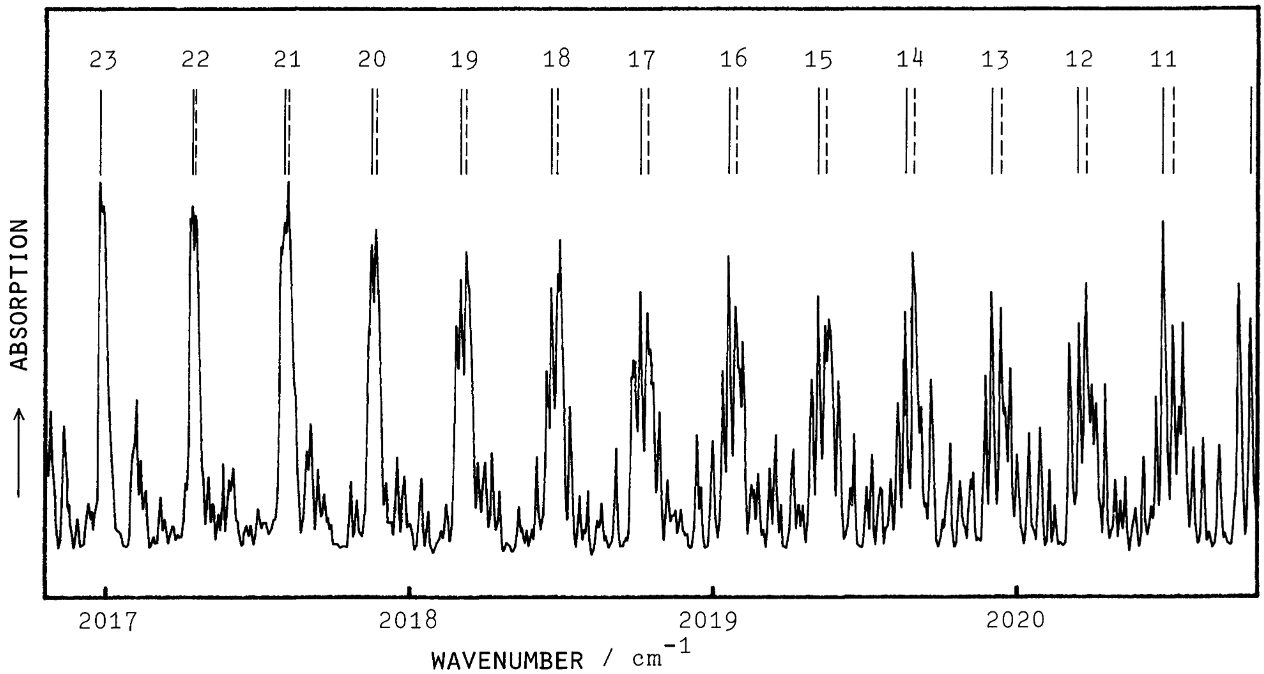

Fig. 1. Part of the high-resolution spectrum of OCSe near 2019 cm^{-1}. Numbers correspond to J values for the J-1←J (10^00-00^00) transitions. Solid lines: $^{16}O^{12}C^{80}Se$. Broken lines: $^{16}O^{12}C^{78}Se$.

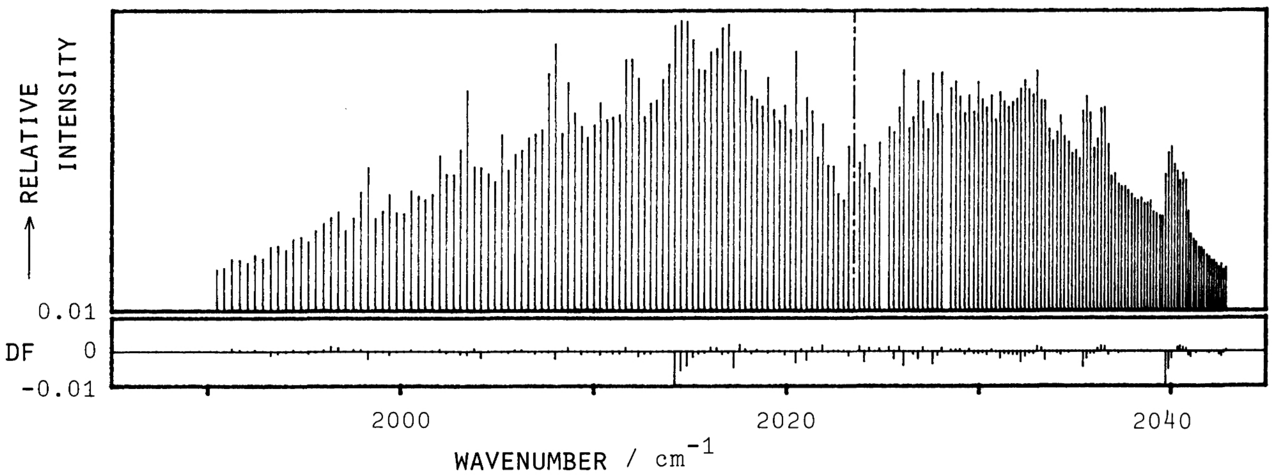

Fig. 2. Observed intensities and the values of (obsd-calcd) for the transition wavenumbers for $^{16}O^{12}C^{80}Se$. DF and ——·——·——indicate the values of (obsd-calcd) in cm^{-1} and the position of the band center, respectively.

Table 1. Observed line positions (in cm^{-1}) in the 10^00-00^00 transitions for $^{16}O^{12}C^{80}Se$ and $^{16}O^{12}C^{78}Se$

$^{16}O^{12}C^{80}Se$			$^{16}O^{12}C^{78}Se$		
J	P(J)	R(J)	J	P(J)	R(J)
0		2023.79360 (186)*	0		2023.84373 (87)
1	2023.25568 (-146)*	2024.05348 (-338)*	1	2023.29943 (-552)*	2024.10662 (-299)*
2	2022.98816 (51)	2024.32188 (135)*	2	2023.01808 (-1573)*	2024.37545 (55)
3	2022.71717 (45)	2024.58293 (19)	3	2022.76167 (47)	2024.63859 (-14)
4	2022.44477 (44)	2024.84463 (114)*	4	2022.48632 (-81)	2024.90079 (-30)
5	2022.17042 (-7)		5	2022.21433 (274)*	2025.15752 (-446)*
6	2021.89744 (224)*	2025.36233 (170)*	6	2021.93392 (-68)	2025.42274 (134)*
7	2021.61858 (13)	2025.61460 (-241)*	7	2021.65827 (213)*	2025.68150 (214)*
8	2021.34170 (144)*	2025.87350 (156)*	8	2021.37801 (178)*	2025.93581 (-4)
9	2021.05791 (-271)*	2026.12058 (-482)*	9	2021.09479 (-6)	2026.19104 (17)
10	2020.78035 (82)	2026.37768 (27)	10	2020.81035 (-167)*	2026.44228 (-214)*
11	2020.49328 (-371)*	2026.62732 (-64)	11	2020.52489 (-284)*	2026.69610 (-41)
12	2020.21320 (20)	2026.87463 (-242)*	12	2020.23926 (-272)*	2026.94676 (-36)
13	2019.92669 (-88)	2027.12649 (182)*	13	2019.95516 (38)	2027.18823 (-803)*
14	2019.64103 (35)	2027.37094 (10)	14	2019.66849 (238)*	2027.44368 (-25)
15	2019.35267 (31)	2027.61157 (-397)*	15	2019.37621 (21)	2027.69010 (-3)
16	2019.06241 (-17)	2027.85767 (-112)*	16	2019.08581 (139)*	2027.93472 (-14)
17	2018.77147 (10)	2028.10175 (118)*	17	2018.79284 (144)*	2028.17900 (88)
18	2018.47923 (53)		18	2018.49919 (227)*	2028.42027 (37)
19	2018.18424 (-36)	2028.58040 (66)	19	2018.20376 (278)*	2028.65899 (-122)*
20	2017.88977 (72)	2028.81789 (76)	20	2017.90510 (151)*	2028.89956 (51)
21	2017.59458 (252)*	2029.05387 (81)	21	2017.60708 (232)*	2029.13419 (-222)*
22	2017.28829 (-534)*	2029.28698 (-54)	22	2017.30770 (323)*	2029.37252 (22)
23	2016.99355 (-21)	2029.52145 (93)	23	2016.99355 (-918)*	2029.60642 (-30)
24	2016.69175 (-69)	2029.75159 (-46)	24	2016.69175 (-779)*	2029.83975 (9)
25	2016.39085 (116)*	2029.98165 (-47)	25	2016.39085 (-405)*	2030.07050 (-62)
26	2016.08693 (143)*	2030.21044 (-28)	26	2016.08693 (-188)*	2030.30074 (-37)
27	2015.77972 (-15)	2030.43701 (-85)	27	2015.77972 (-155)*	2030.53047 (85)
28	2015.47229 (-51)	2030.66417 (64)	28	2015.47229 (0)	2030.75634 (-31)
29	2015.16245 (-185)*	2030.88771 (-2)	29	2015.16245 (59)	2030.98117 (-104)*
30	2014.84956 (-480)*	2031.10837 (-209)*	30	2014.84956 (-43)	2031.20835 (206)*
31	2014.53651 (-648)*	2031.33135 (-38)	31	2014.53651 (-16)	2031.42809 (-81)
32	2014.21875 (-1143)*	2031.55096 (-57)	32	2014.21875 (-315)*	2031.64976 (-26)
33	2013.91632 (39)	2031.76887 (-99)*	33	2013.89818 (-752)*	2031.86763 (-204)*
34	2013.60073 (47)	2031.98593 (-79)	34	2013.58218 (-587)*	2032.08703 (-81)
35	2013.28331 (16)	2032.19874 (-337)*	35	2013.26556 (-340)*	2032.30486 (33)
36	2012.96415 (-45)	2032.41460 (-144)*	36	2012.94316 (-526)*	2032.52235 (261)*
37	2012.64417 (-46)	2032.62827 (-22)	37	2012.60914 (-1731)*	2032.73581 (234)*
38	2012.32166 (-157)*	2032.83896 (-52)	38	2012.28583 (-1721)*	2032.94606 (34)
39	2012.00062 (22)	2033.05099 (200)*	39	2011.97974 (156)*	2033.15500 (-149)*
40	2011.67754 (140)*	2033.25828 (125)*	40	2011.65132 (-57)	
41	2011.35000 (-45)	2033.46090 (-271)*	41	2011.32405 (-12)	2033.56639 (-719)*
42	2011.02282 (-52)	2033.66875 (4)	42	2010.99522 (22)	2033.78030 (39)
43	2010.69475 (-4)	2033.87242 (8)	43	2010.66215 (-225)*	2033.98454 (-21)
44	2010.36382 (-100)*	2034.07431 (-18)	44	2010.33235 (-2)	2034.18777 (-35)
45	2010.03335 (-8)	2034.27440 (-78)	45	2009.99943 (53)	2034.38983 (-17)
46	2009.70043 (-19)	2034.47434 (-5)	46	2009.66262 (-137)*	2034.59034 (-6)
47	2009.36555 (-83)	2034.67190 (-23)	47	2009.32716 (-50)	2034.78940 (8)
48	2009.03075 (4)	2034.86850 (10)	48	2008.99069 (80)	2034.98637 (-38)
49	2008.69499 (136)*	2035.06344 (24)	49	2008.64792 (-277)*	2035.18254 (-16)
50	2008.35527 (14)	2035.25666 (14)	50	2008.31164 (157)*	2035.37712 (-5)
51	2008.01272 (-248)*	2035.44326 (-511)*	51	2007.96823 (22)	2035.57066 (51)
52	2007.67382 (-4)	2035.63633 (-241)*	52	2007.62438 (-14)	2035.76120 (-45)
53	2007.33094 (-16)	2035.82714 (-51)	53	2007.27917 (-44)	2035.95171 (4)
54	2006.98635 (-57)	2036.01470 (-37)	54	2006.93232 (-95)	2036.14042 (22)
55	2006.64129 (-3)	2036.20220 (117)*	55	2006.58580 (30)	2036.32672 (-53)
56	2006.29490 (59)	2036.38766 (215)*	56	2006.23612 (-19)	2036.51270 (-11)
57	2005.94630 (41)	2036.57048 (197)*	57	2005.88571 (1)	2036.69692 (3)
58	2005.59567 (-38)	2036.74926 (-78)	58	2005.53430 (64)	2036.87947 (-2)
59	2005.24480 (1)	2036.93032 (23)	59	2005.17991 (-29)	2037.06045 (-15)
60	2004.89212 (-1)	2037.10904 (37)	60	2004.82567 (35)	2037.24086 (64)
61	2004.53827 (22)	2037.28563 (-15)	61	2004.46537 (-365)*	2037.41779 (-57)
62	2004.18057 (-200)*	2037.46139 (-1)	62	2004.10781 (-348)*	2037.59522 (21)
63	2003.82653 (86)	2037.63566 (11)	63	2003.75351 (136)*	2037.77033 (16)
64	2003.46627 (-109)*	2037.80832 (9)	64	2003.39231 (72)	2037.94405 (20)
65	2003.10699 (-66)	2037.97963 (20)	65	2003.02973 (11)	2038.11604 (-1)
66	2002.74678 (25)	2038.14922 (7)	66	2002.66601 (-22)	2038.28702 (27)
67	2002.38372 (-29)	2038.31755 (15)	67	2002.30150 (8)	2038.45603 (5)
68	2002.02074 (66)	2038.48445 (27)	68	2001.93513 (-7)	2038.62374 (3)
69	2001.65491 (17)	2038.64947 (0)	69	2001.56737 (-20)	2038.78988 (-8)
70	2001.28802 (1)	2038.81376 (47)	70	2001.19825 (-28)	2038.95487 (14)
71	2000.91974 (-13)	2038.97563 (0)	71	2000.82823 (16)	2039.11862 (62)
72	2000.55078 (45)	2039.13670 (21)	72	2000.45459 (-161)*	2039.27992 (14)
73	2000.17943 (4)	2039.29605 (17)	73	2000.08360 (67)	2039.43223 (-785)*
74	1999.80693 (-12)	2039.45416 (37)	74	1999.70870 (46)	2039.59381 (-509)*
75	1999.43220 (-111)*	2039.61048 (25)	75	1999.33251 (36)	2039.75398 (-225)*
76	1999.05798 (-20)	2039.75398 (-1120)*	76	1998.95411 (-55)	2039.91288 (81)
77	1998.68147 (-18)	2039.91288 (-578)*	77	1998.57715 (139)*	2040.06846 (205)*
78	1998.30115 (-257)*	2040.06846 (-220)*	78	1998.19448 (-97)	2040.22126 (198)*
79	1997.92485 (45)	2040.22126 (8)	79	1997.81320 (-54)	2040.37166 (100)
80	1997.54405 (37)	2040.37166 (143)*	80	1997.42855 (-208)*	2040.51966 (-88)
81	1997.16145 (-13)	2040.51966 (186)*	81	1997.04495 (-116)*	2040.66530 (-365)*
82	1996.77934 (126)*	2040.66530 (141)*	82	1996.66060 (40)	2040.80944 (-642)*
83	1996.39462 (163)*	2040.80944 (93)	83	1996.27275 (-14)	2040.95051 (-1078)*
84	1996.00723 (31)	2040.95051 (-113)*	84	1995.88288 (-130)*	2041.10533 (11)
85	1995.61905 (-20)	2041.09152 (-178)*	85	1995.49424 (17)	2041.24762 (-6)
86	1995.22950 (-70)	2041.23363 (15)	86	1995.10215 (-42)	2041.38868 (4)
87	1994.83963 (-13)	2041.37198 (-20)	87	1994.70917 (-50)	2041.52799 (-12)
88	1994.44837 (43)	2041.50956 (15)	88	1994.31578 (40)	2041.66627 (18)
89	1994.05436 (-37)	2041.64515 (-1)	89	1993.91500 (-469)*	2041.80214 (-45)
90	1993.65934 (-80)	2041.77953 (10)	90	1993.52230 (-32)	2041.93736 (-25)
91	1993.26270 (-147)*	2041.91203 (-19)	91	1993.12259 (-156)*	2042.07072 (-41)
92	1992.86664 (-18)	2042.04320 (-33)	92	1992.72496 (67)	2042.17344 (-2972)*
93	1992.46843 (34)	2042.17344 (7)	93	1992.32312 (7)	
94	1992.06773 (-25)	2042.30163 (-10)	94	1991.92023 (-19)	
95	1991.66689 (40)	2042.42853 (-8)	95	1991.51637 (-3)	
96	1991.26444 (81)	2042.55308 (-94)	96		
97	1990.85928 (-11)	2042.67639 (-155)*	97	1990.70448 (27)	
98	1990.45348 (-29)	2042.80002 (-37)			
99		2042.92188 (52)			

vibration constants for $^{16}O^{12}C^{80}Se$ are also in good agreement with those given by Maki et al. However, the accuracy of the present result is higher than that of the former infrared study due to the higher resolution of the spectrometer.

In conclusion, spectroscopy of the ν_1 band of OCSe in natural abundance with a resolution of 0.005 cm^{-1} successfully yielded accurate molecular constants for each Se isotopic species. Thus, accurate parameters would be obtained for each Se isotopic species for almost all of the thirteen bands.

Table 2. Molecular constants for the ν_1 band of $^{16}O^{12}C^{80}Se$

	This work	Maki et al.[1]	Microwave
ν_0 (cm^{-1})	2023.52516 (15)[a]	2023.5270 (6)	
B" (cm^{-1})	0.13401487 (153)	0.13401438[b]	0.13401528[4]
B' (cm^{-1})	0.13328785 (152)	0.13328749 (83)	
10^8D" (cm^{-1})	2.2326 (108)	2.233[b]	2.233[5]
$10^9\Delta$D (cm^{-1})	-0.250 (114)	-0.22 (22)	

a) Values in the parentheses correspond to 2σ in the last quoted digit.
b) Fixed values.

Table 3. Molecular constants for the ν_1 band of $^{16}O^{12}C^{78}Se$

	This work	Microwave[4]
ν_0 (cm^{-1})	2023.57464 (17)[a]	
B" (cm^{-1})	0.13484179 (174)	0.13484195
B' (cm^{-1})	0.13410987 (176)	
10^8D" (cm^{-1})	2.2646 (139)	
$10^9\Delta$D (cm^{-1})	-0.251 (149)	

a) Values in the parentheses correspond to 2σ in the last quoted digit.

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