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Microwave Spectrum of Carbonyl Selenide

Yonezo MORINO and Chi MATSUMURA

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo

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The microwave spectra of the OCSe molecule have been measured for the ground and vibrationally excited states of a number of isotopic species under the natural abundance ratio. It was concluded from the results that the r_s-structure is given by $r(\text{O–C})=1.157$ Å and $r_s(\text{C–Se})=1.708$ Å, and that the general quadratic force field is represented by $f_R(\text{CSe})=5.42$, $f_r(\text{CO})=15.38$, $f_{Rr}=0.68$, and $f_\alpha=0.286$ md/Å.

The structure of linear unsymmetric triatomic molecules such as OCSe is given by assigning two bond distances, O-C and C-Se; accordingly, the measurement of the microwave spectrum for a molecular species is insufficient for the determination of the molecular structure, because it provides us with only one observed value, a rotational constant about the axis perpendicular to the molecular axis. It was anticipated that the OCSe molecule would be suitable for exploring the structure in detail, because the natural sample contains many isotopic species in abundance ratios sufficient to detect the microwave spectra of a a number of molecular species in vibrationally excited states. However, as will be described below, we have not succeeded in obtaining the equilibirum structure because of the difficulty of assigning the rotational lines in the ν_3-excited state. Nevertheless, the r_s-structure was derived by the use of the rotational constants in the ground states of the isotopic molecules. At the same time, the measurement of the l-type doubling constants in the spectra for the excited vibrational states made it possible to evaluate the general quadratic force field.

The microwave spectrum of the OCSe molecule has been studied by Strandberg, Wentink and Hill.[1] They reported only the r_0-structure, however.

Experimental

The sample of carbonyl selenide was prepared by passing carbon monoxide gas over melted selenium at

TABLE 1. OBSERVED LINES FOR CARBONYL SELENIDE, $J=4\leftarrow3$ (in Mc/sec)

	^{74}Se	^{76}Se	^{77}Se	^{78}Se	^{80}Se	^{82}Se
Natural abundance	0.87%	9.02%	7.58%	23.52%	49.82%	9.19%
G. S.	32766.14[a]	32547.52[a]	32442.20[a]	32339.47[a]	32141.22[a]	31951.85[a]
$\nu_2(l=1)$	$\begin{cases}32836.1\\32809.7\end{cases}$	32616.49[a] 32590.57[a]	32510.88[a] 32485.22[a]	32407.86[a] 32382.36[a]	32209.24[a] 32184.07[a]	32019.89[a] 31994.94[a]
ν_1	32657.3	32439.52	32040.71[a]	32234.38[a]	32035.12[a]	31847.61[a]
$2\nu_2$ $(l=2)$		32658.8	32552.5	32449.94	32251.02	32061.3
$2\nu_2$ $(l=0)$		32653.1		32444.20	32245.38	32056.3
$\nu_1+\nu_2(l=1)$				$\begin{cases}32304.1\\32277.7\end{cases}$	32106.5 32080.5	31918.4 31891.6
$2\nu_1$				32123.5	31927.15	
$3\nu_2(l=1)$				$\begin{cases}32521.5\\32467.4\end{cases}$	32319.3 32268.1	
$3\nu_1$					31817.5	
^{13}C G. S.		32251.3	32144.8	32040.77[a]	31840.24[a]	31648.2
^{13}C $\nu_2(l=1)$					$\begin{cases}31904.3\\31878.4\end{cases}$	
^{13}C ν_1					31734.0	
^{18}O G. S.				29974.7	28781.5	

a) Calculated from the values observed by Strandberg, Wentink, Jr., and Hill (Ref. 1)

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[1] M. W. P. Strandberg, T. Wentink, Jr., and A. G. Hill, *Phys. Rev.*, **75**, 827 (1949).

about 500°C. The yield of the reaction was low: 0.5 cc of liquid OCSe was obtained in three hours with a CO flow of 4 *l*/hr. The gas thus prepared contained a small amount of SO_2, since the selenium used in the preparation was contaminated with a trace of sulfur.

The spectral lines were measured with a spectrometer of a conventional Stark-modulation type in the temperature range up to 250°C. The sample decomposed so rapidly that slow-sweep recording was not applicable above 150°C. This made it difficult to observe the lines in higher excited states of the vibrational motions. The $J=4\leftarrow3$ transitions were searched for in most cases, since they are the strongest in the frequency region used in the present measurement. The $J=3\leftarrow2$ transitions were also searched in order to confirm the assignment. The observation of the Stark effect gave additional evidence for the assignment, since the lines in the excited state with a finite vibrational angular momentum show a first-order Stark effect.

Results

A. r_s-Structure. In addition to the spectral lines reported by Strandberg *et al.*,[1] many new lines in the ground as well as in the excited states of various vibrational modes were observed for various isotopic species. The frequencies are given in Table 1, in which the lines already measured by Strandberg *et al.* are also inserted. The rotational constants and the moments of inertia for the ground states of various isotopic species are listed in Table 2. The observation of the rotational constants for the ^{18}O species made it possible to calculate the r_s-structures. The r_s-structures were calculated from a number of combinations of the rotational constants of the isotopic species as listed in Table 3, and r_s(C–Se)=1.708 Å and r_s(O–C)=1.157 Å were obtained as their averages.

TABLE 2. ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA IN THE GROUND STATES FOR VARIOUS ISOTOPIC OCSe MOLECULES

Isotopic[a] species	Rotational constants (Mc/sec)	Moments of inertia (amuÅ²)
$OC^{74}Se$	4095.793	123.4269
$OC^{76}Se$	4068.465	124.2560
$OC^{77}Se$	4055.300	124.6593
$OC^{78}Se$	4042.460	125.0553
$OC^{80}Se$	4017.677	125.8267
$OC^{82}Se$	3994.009	126.5723
$O^{13}C^{76}Se$	4031.39	125.3990
$O^{13}C^{77}Se$	4018.08	125.8141
$O^{13}C^{78}Se$	4005.112	126.2214
$O^{13}C^{80}Se$	3980.045	127.0164
$O^{13}C^{82}Se$	3956.00	127.7884
$^{18}OC^{78}Se$	3746.81	134.9222
$^{18}OC^{80}Se$	3722.63	135.7994

a) O and C without specification denote ^{16}O and ^{12}C, respectively.

TABLE 3. r_s-STRUCTURE OF CARBONYL SELENIDE IN Å

Isotopic species	$^{16}O^{12}C^{80}Se$	$^{16}O^{12}C^{78}Se$	$^{16}O^{13}C^{78}Se$
	X_s(Se)[a]		
^{82}Se	0.6161[b]	0.6224	0.6375
^{80}Se	—	0.6252	0.6364
^{78}Se	0.6134	—	—
^{77}Se	0.6153	0.6244	0.6360
^{76}Se	0.6150	0.6241	0.6354
^{74}Se	0.6148	0.6239	—
mean	0.6149	0.6240	0.6363
	X_s(C)		
^{12}C	—	—	−1.0728
^{13}C	−1.0937	−1.0830	—
	X_s(O)		
^{18}O	−2.2509	−2.2393	
r_s(C–Se)	1.709	1.707	1.709
r_s(O–C)	1.157	1.156	—

a) X_s(Se) denotes the coordinate of the Se atom on the molecular axis, referred to the center of gravity of the molecule.

b) X_s(Se)=0.6161 Å was obtained by combining the rotational constant of $^{16}O^{12}C^{82}Se$ with that of the mother molecule $^{16}O^{12}C^{80}Se$. The same for the followings.

B. Force Constants from the *l*-Type Doubling Constants. The OCSe molecule has three normal vibrations, ν_1, ν_2, and ν_3; ν_2 is a doubly-degenerate bending vibration, so that the rotational spectra in the excited states of this vibration reveal the *l*-type doubling. According to the theory of the second-order vibration-rotation interaction, the magnitude of the splitting is given by:[2]

$$\Delta\nu = q_v(v_2+1)(J+1), \qquad (1)$$

The *l*-type doubling constant can be calculated if the harmonic potential field of the molecule is known; inversely, the potential constants can be determined by using the observed value of the q_v constant. As has been described in the preceding paper,[3] the calculation of the force constants should be made by the use of q_e instead of q_v. Considering that the q_e value is not yet known for OCSe because of the lack of observed values of q_v for higher excited states, however, we must be satisfied with using $q(01^10)$ in place of q_e.

The potential function for the linear XYZ-type molecule involves three force constants for the stretching motions:

$$V = \frac{1}{2}f_R(\Delta R)^2 + \frac{1}{2}f_r(\Delta r)^2 + f_{Rr}\Delta R\Delta r + \frac{1}{2}f_\alpha(\mathrm{d}\Delta\alpha)^2, \qquad (2)$$

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[2] H. H. Nielsen, *Rev. Mod. Phys.*, **23**, 90 (1951).

[3] Y. Morino and C. Matsumura, This Bulletin, **40,** 1095 (1967).

where $\varDelta R$ denotes the displacement of the C–Se distance, and $\varDelta r$, that of the O–C distance. The last term in Eq. (2) represents the contribution of the bending motion, the factor $d=(Rr)^{1/2}$ being introduced in order to keep the dimension of f_α the same as that for other force constants. The f_α constant is determined to be 0.286 md/Å from the frequency $\nu_2=466\ \text{cm}^{-1}$. The three other force constants cannot be determined from the vibrational frequencies alone, since the molecule has only two stretching vibrations. The l-type doubling constant gives additional information on the force constants. It has been shown that:(3,4)

$$q_\mathrm{v} = \frac{2B_e^2}{\boldsymbol{h}\nu_2}\left[1 + 4(\zeta_{12}^{(\mathrm{X})})^2\frac{\nu_2^2}{\nu_1^2-\nu_2^2} + (\zeta_{23}^{(\mathrm{X})})^2\frac{\nu_2^2}{\nu_3^2-\nu_2^2}\right], \tag{3}$$

where:

$$\begin{aligned}\zeta_{12}^{(\mathrm{X})} &= \alpha L_{33} + \beta L_{13},\\ \zeta_{23}^{(\mathrm{X})} &= \alpha L_{31} + \beta L_{11},\end{aligned} \tag{4}$$

and:

$$\begin{aligned}\alpha &= \frac{m_\mathrm{O}(m_\mathrm{C}+m_\mathrm{Se})R+m_\mathrm{O}m_\mathrm{Se}r}{(m_\mathrm{O}+m_\mathrm{C}+m_\mathrm{Se})(I_e)^{1/2}},\\ \beta &= \frac{m_\mathrm{O}m_\mathrm{Se}R+m_\mathrm{Se}(m_\mathrm{O}+m_\mathrm{C})r}{(m_\mathrm{O}+m_\mathrm{C}+m_\mathrm{Se})(I_e)^{1/2}},\end{aligned} \tag{5}$$

B_e denotes the equilibrium rotational constant; I_e, the equilibrium moment of inertia; m, the mass of the atom, and L_{ij}, the element of the $\boldsymbol{L}$ matrix (the 1 and 3 suffixes correspond to the C–Se stretching and O–C stretching vibrations respectively). Thus the force constants of OCSe are calculated by using the following values: $B_e \cong B_0 = 4017.68$ Mc/sec, $q_v=3.15$ (obtained for $^{16}\mathrm{O}^{12}\mathrm{C}^{80}\mathrm{Se}$), $\nu_1=642.1\ \text{cm}^{-1}$, and $\nu_3=2021.2\ \text{cm}^{-1}$,(5) the atomic mass of Se=79.016, C=12.015, O=16.004, r(C–Se)= 1.708 Å, and r(O–C)=1.157 Å. Since the vibrational frequencies have not been observed separately for each of the isotopic species, the masses averaged for the isotopes are adopted for the calculation.

From Eqs. (3) and (4), $(\zeta_{12}^{(\mathrm{X})})^2$ and $(\zeta_{23}^{(\mathrm{X})})^2$ are obtained as 0.03199 and 0.96802 respectively; from these values, Eqs. (4) and the normalizing relation,

$$\boldsymbol{L}\,\boldsymbol{L}' = \boldsymbol{G} \tag{6}$$

lead to the following $\boldsymbol{L}$ matrix elements:

$$\begin{aligned}L_{11} &= 0.19835, \quad & L_{13} &= -0.12378\\ L_{31} &= 0.03596, \quad & L_{33} &= 0.38003\end{aligned} \tag{7}$$

TABLE 4. VIBRATION-ROTATION INTERACTION CONSTANTS

Isotopic species	l-Type doubling q_v constant (Mc/sec)	Vibration-rotation α_v constant (Mc/sec)
	ν_2 state	
$\mathrm{OC^{74}Se}$	3.17	−7.10
$\mathrm{OC^{76}Se}$	3.24	−7.00
$\mathrm{OC^{77}Se}$	3.21	−6.98
$\mathrm{OC^{78}Se}$	3.19	−6.96
$\mathrm{OC^{80}Se}$	3.15	−6.93
$\mathrm{OC^{82}Se}$	3.12	−6.94
$\mathrm{O^{13}C^{80}Se}$	3.24	−6.40
	$\nu_1+\nu_2$ state	
$\mathrm{OC^{78}Se}$	3.30	6.08
$\mathrm{OC^{80}Se}$	3.25	5.96
$\mathrm{OC^{82}Se}$	3.35	5.86
	$3\nu_2$ state	
$\mathrm{OC^{78}Se}$	3.38	−19.38
$\mathrm{OC^{80}Se}$	3.20	−19.06

Isotopic species	$\varDelta\nu_\mathrm{F}$ Fermi doubling	Vibration-rotation α_v constant[a]
	$2\nu_2$ state	
$\mathrm{OC^{76}Se}$	0.71	−13.92
$\mathrm{OC^{77}Se}$	—	−13.80
$\mathrm{OC^{78}Se}$	0.718	−13.81
$\mathrm{OC^{80}Se}$	0.705	−13.73
$\mathrm{OC^{82}Se}$	0.63	−13.68

Isotopic species	α_v $3\nu_1$ state	α_v $2\nu_1$ state	α_v ν_1 state
$\mathrm{OC^{74}Se}$	13.60		
$\mathrm{OC^{76}Se}$	13.50		
$\mathrm{OC^{77}Se}$	12.69		
$\mathrm{OC^{78}Se}$	13.14	27.00	
$\mathrm{OC^{80}Se}$	13.27	26.78	40.46
$\mathrm{OC^{82}Se}$	13.03		
$\mathrm{O^{13}C^{80}Se}$	13.28		

a) The α_v listed below designates the value for the (02^20) state.

The $\boldsymbol{L}$ matrix elements are not determined uniquely by Eqs. (3) and (4) because $\zeta_{12}^{(\mathrm{X})}$ and $\zeta_{23}^{(\mathrm{X})}$ are involved in squared forms in Eq. (3). Unreasonable sets of $\boldsymbol{L}$ matrix elements were eliminated by the calculation of the $\boldsymbol{F}$ matrix, because the unreasonable set led to unreasonable values of the $\boldsymbol{F}$ matrix elements, which were calculated by the relation:

$$\boldsymbol{F} = (L^{-1})'\varLambda L^{-1}, \tag{8}$$

Thus, the final values of the force constants are as follows:

$$\begin{aligned}f_R &= 5.42\ \text{md/Å}\\ f_r &= 15.38\ \text{md/Å}\\ f_{Rr} &= 0.68\ \text{md/Å}\\ f_\alpha &= 0.286\ \text{md/Å}\end{aligned}$$

These values are in fairly good agreement with the $f_R=5.46_3$, $f_r=16.16_7$, and $f_{Rr}=0.92_3$ values which were calculated from the frequency shift of ν_3 by the substitution of ^{13}C.(5)

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4) Y. Morino and E. Hirota, This Bulletin, **31**, 423 (1958).

5) T. Wentink, Jr., *J. Chem. Phys.*, **30**, 105 (1959).

Discussion

The original aim of this study was to determine the equilibirum structure by combining the equilibrium rotational constants of two or more isotopic species. Unfortunately, the equilibrium rotational constant has not been determined, because the rotational lines in the ν_3-excited state have not been identified for any of the isotopic molecules. It seems likely that the failure to observe the line was due either to the overlapping of the line with stronger lines or to the weakness of the intensity of the line.

As the frequency of the ν_3 vibration is 2021 cm^{-1}, the Boltzmann factor, $\exp(-\boldsymbol{h}\nu_3/\boldsymbol{k}T)$, reduces the intensity at 25°C by 4×10^{-5} compared with the ground-state line. In order to increase the intensity, the line should be searched for at a higher temperature; for instance, the factor increases to 8×10^{-4} at 150°C, and to 3×10^{-3} at 250°C. However, the gas is apt to decompose at a high temperature, which makes the measurement very difficult. Really the search for this line was repeated by having the sample gas flow through the waveguide, but the deposit of selenium by decomposition seems to accelerate further decomposition of the sample.

The Fermi resonance between ν_1 and $2\nu_2$ states was analyzed by Low, who determined the interaction energy to be 45 cm^{-1} from the separation of the $l=0$ and $l=2$ components of the $v_2=2$ state.[6] The interaction energy of this resonance was recalculated to be 48.12 cm^{-1} from the values observed in this study. This value, however, may not be reliable since the analysis ignored the resonance between ν_3 and $2\nu_2$, the effect of which has been found to be serious for the OCS molecule.[7] The treatment cannot, however, be carried out until the spectrum in the ν_3-excited state is really observed.

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[6] W. Low, *Phys. Rev.*, **97**, 1664 (1955).

[7] Y. Morino and T. Nakagawa, to be published.