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The Microwave Spectrum of Carbonyl Selenide*

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The microwave absorption spectrum of carbonyl selenide, OCSe, is reported. The expected linear structure is confirmed. The spectrum includes absorptions caused by various isotopic forms of the molecule in the zero-point vibrational state and the first excited symmetrical stretching and bending vibrational states. From these data vibration-rotation interaction coefficients, mass differences and approximate interatomic distances have been determined. Values for the nuclear spins of the six stable selenium isotopes are suggested. Observations of the Stark effect lead to a determination of the dipole moment of the molecule in several vibrational states. Intensity measurements are used to determine vibrational frequencies and relative isotopic abundance.

I. INTRODUCTION

WE have previously reported measurement of the microwave absorption spectrum of carbonyl sulfide, OCS[1] (hereinafter referred to as reference 1). An obvious extension of the measurements would be the observation of the absorption spectrum of OCSe and OCTe to complete the chemically available members of the OCX series, where X is a $^3P_2$ atom from the VI_b group of the periodic table. We have observed the spectrum of OCSe, and the results of these measurements are reported in this paper.***

Carbonyl selenide, OCSe, as expected, is a linear molecule. Its preparation and chemical properties have been reported in the literature.[2] No spectroscopic data, neither vibrational nor rotational, were available at the beginning of this work. There are many isotopic forms of the molecule, since, beside the oxygen and carbon isotopes (O^{16}, O^{18}, C^{12}, C^{13}), there are six stable selenium atoms. These selenium atoms have mass numbers 82, 80, 78, 77, 76, and 74. Some packing-fraction data for these atoms are available from the work of Aston,[3] and the nuclear spins of Se^{78} and Se^{80} are tabulated by Herzberg[4] as zero.

II. EXPERIMENTAL

The sample of OCSe was prepared by passing CO over Se at approximately 500°C.[2] In setting up the microwave apparatus for a preliminary search, the $J=2\rightarrow 3$ transition was calculated to be in the 1.25-cm region by using the known O−C resonant bond distance as determined in OCS, and an estimated C−Se resonant bond distance based on published single and double bond radii for selenium.[5]

The sweep spectroscope and frequency standard described in reference 1 were used in measuring the absorption frequencies. The signal generators for the $J=2\rightarrow 3$ were reflex klystrons; for the $J=5\rightarrow 6$ and the $J=6\rightarrow 7$ absorption transitions were measured with the second harmonic power generated in silicon crystals driven by standard klystrons.

III. INTERPRETATION

As in OCS, absorptions occur for each isotopic form of the molecule, in each vibrational state. In the usual notation the absorption frequencies are given as:

$$\nu_{J\rightarrow J+1}=2(J+1)cB_v-4cD_v[(J+1)^3-(J+1)l^2] \text{ cycles/sec.,} \quad (1)$$

where J is the total angular momentum quantum

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** Now at Brookhaven National Laboratory.

[1] M. W. P. Strandberg, T. Wentink, and R. L. Kyhl, RLE Technical Report No. 59, "Rotational absorption spectrum of OCS," May 13, 1948, which appears in Phys. Rev. **75**, 270 (1949).

*** A preliminary report was given at the January, 1948, New York meeting of the American Physcial Society. Phys. Rev. **73**, 1249 (1948).

[2] T. G. Pearson and P. L. Robinson, J. Chem. Soc. (London) 652 (1932); R. H. Purcell and F. D. Zahoorbux, J. Chem. Soc. (London) 1029 (1937).

[3] F. W. Aston, Proc. Roy. Soc. **132**, 487 (1931).

[4] George Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, New York, 1941).

[5] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1939).

TABLE I. Observed absorption frequencies.

Molecule	Transition $J \rightarrow J+1$	Vibrational state v_1	v_2	v_3	Frequency Mc/sec.
	$2 \rightarrow 3$	0	0	0	
$O^{16}C^{12}Se^{82}$					23964.50±.03
Se^{80}					24105.98
Se^{78}					24254.67
Se^{77}					24331.71
Se^{76}					24410.70
Se^{74}					24514.67
$O^{16}C^{13}Se^{80}$					23880.18
Se^{78}					24030.58
	$5 \rightarrow 6$				
$O^{16}C^{12}Se^{80}$					48211.46
Se^{78}					48508.88
	$6 \rightarrow 7$				
$O^{16}C^{12}Se^{82}$					55916.19
Se^{80}					56246.47
Se^{78}					56593.16
	$2 \rightarrow 3$	1	0	0	
$O^{16}C^{12}Se^{82}$					23885.76
Se^{80}					24026.39
Se^{78}					24174.30
Se^{77}					24250.84
	$2 \rightarrow 3$	0	1	0 (*l*-doublet)	
$O^{16}C^{12}Se^{82}$					24014.97 23996.26
Se^{80}					24156.93 24138.05
Se^{78}					24305.95 24286.82
Se^{77}					24383.21 24363.97
Se^{76}					24462.42 24442.98

number, l is the angular momentum quantum number along the molecule figure axis; $|l| \leq J$, D_v is the centrifugal distortion coefficient in cm^{-1}, and B_v is the average reciprocal moment of the molecule in vibrational state v, in cm^{-1}.

The vibrational reciprocal moment is more usually represented as

$$B_v = (h/8\pi^2 c)\langle 1/I \rangle_{\mathrm{Av}} = B_e - \sum \alpha_i [v_i + (d_i/2)], \quad (2)$$

where I is the moment of inertia, B_e is the reciprocal moment of inertia of the molecule with the atoms in the minima of their vibrational potential, and α_i is a coefficient measuring the change of the equilibrium reciprocal moment when the molecule is in the v_ith excited state of the ith vibrational state which has a degeneracy d_i. This expression is useful since one may assume that the equilibrium reciprocal moment B_e depends only upon the vibrational constant potential minima, and the masses of the various atomic isotopes. The α_i depend in a complicated fashion upon an averaging of the vibrational properties, e.g., the vibration amplitudes and motions of the various atomic isotopes, and lead ultimately to a study of the binding potential of the molecule. It should be noticed that even in the ground vibrational state ($v_i = 0$) the ever present half-quantum of vibrational energy enters into the calculation of $\langle 1/I \rangle_{\mathrm{Av}}$, so that even for the ground vibrational state the reciprocal of $\langle 1/I \rangle_{\mathrm{Av}}$ is only approximately equal to I.

The molecule OCSe has three non-degenerate vibrational states. The first is a symmetrical stretching state, v_1. The second, v_2, is a doubly degenerate bending vibration composed of an appropriate phase combination of the modes in which the atoms vibrate transverse to the figure axis in two orthogonal planes. Such a vibration can give rise to angular momentum along the figure axis which is commonly designated by the quantum number l. As in OCS, these two bending modes have different α's because of a difference in the vibration-rotation interaction for the two states. We retain the convention of calling them degenerate l states and listing the average α as α_2. The third vibration is an antisymmetrical stretching vibration v_3. In OCSe at room temperature this last vibration, v_3, has a first excited state above the ground state by about $10kT$ so that the Boltzmann factor allows only a very small population of this level. For this reason we have not observed any absorption due to the molecule in the first excited v_3 vibrational mode.

The observed absorption frequencies for various vibrational states are listed in Table I. These data may be used to deduce the term-value parameters as listed in Table II.

Some approximations must now be made to deduce molecular-structure parameters from their term-value parameters. The internuclear distances must be calculated on a rigid rotor basis since α_3 cannot be determined with the present data, and cannot be calculated since the potential constants of OCSe are not known. The rigid rotor values calculated from the zero-point B_v of $O^{16}C^{12}Se^{78}$, $O^{16}C^{13}Se^{78}$, $O^{16}C^{12}Se^{80}$, and $O^{16}C^{13}Se^{80}$ are listed in Table II. The error listed there indicates merely the consistency of the determination from both sets of data. The lack of greater internal consistency presumably results from using data uncorrected for vibration-rotation interaction. We have used the values $h = 6.6242 \times 10^{-27}$ erg sec., 1 a.m.u. $= 1.66990 \times 10^{-24}$ g and in atomic mass units $C^{12} = 12.00382$, $C^{13} = 13.00758$, $O^{16} = 16.00000$, $Se^{78} = 77.9424$, and

TABLE II. Derived constants for OCSe.

	Term-value parameters				
Molecule	cB_{000} Mc/sec.	$c\alpha_1$ Mc/sec.	$c\alpha_2$ Mc/sec.	cq Mc/sec.	cD_v c/sec.
$O^{16}C^{12}Se^{82}$	3994.009±.005	13.12±.005	−6.86±.005	3.12±.005	875±50
Se^{80}	4017.677	13.27	−6.92	3.15	755±20
Se^{78}	4042.460	13.40	−6.96	3.19	830±50
Se^{77}	4055.300	13.48	−6.98	3.21	
Se^{76}	4068.465		−7.00	3.24	
Se^{74}	4095.793				
$O^{16}C^{13}Se^{80}$	3980.045				
Se^{78}	4005.112				

	Interatomic distances		
	$r_0(C=O)$†	$r_0(C=S)$†	$r_0(C=Se)$†
Covalent radii	1.17A	1.54	1.69*
OCO	1.1632		
OCS	1.1637	1.5586	
OCSe	1.1588±.0001**		1.7090±.0001**

* By extrapolating for the Se triple-bond radius. See text.
** From internal consistency of data. See text.
† Rigid rotor approximation.

$Se^{80}=79.9435$. For the reasons given in reference 1, the internuclear distances may be high by 0.5 percent.

We include values from Table II of reference 1 for comparison. Since Se has no pure triple-bond structure, we have estimated a triple-bond radius by extrapolating from the Se single- and double-bond distances, being guided by the variation of the bond lengths in O and S. This triple-bond length 1.63A was used to calculate the expected CSe resonant bond length. It is interesting to note that, though the OC distance is fitted well with a resonant bond structure, the CSe distance is best approximated with a pure double-bond length, 1.72A.

Since there is an uncertainty in the selenium packing fractions, we have investigated the problem of determining the mass of the selenium isotopes from spectroscopic data. The solution of the problem is rather simple theoretically. If the equilibrium reciprocal moments for, say, $O^{16}C^{12}Se^{80}$, $O^{16}C^{13}Se^{80}$, and $O^{18}C^{12}Se^{80}$ are known, the selenium mass and the two internuclear distances may be determined from the three absorption equations. If the reciprocal moments are known to two parts in 10^6, the selenium packing fraction may be determined to 10 percent. It should be noted that the equilibrium reciprocal moments must be used, so all three α_i for the three isotopic molecules must be determined. This would be difficult to do directly from measurements unless concentrated isotopic molecules were used. The excited vibrational states are only slightly populated at room temperature, and with a rare isotope like C^{13}, present naturally in only one percent abundance, the absorption signal is reduced by another factor of 100. One could, knowing the α_i for one isotopic form, say $O^{16}C^{12}Se^{80}$, calculate the α_i for the other isotopes with a mass perturbation calculation so that the equilibrium reciprocal moment could be determined to within the generous error limits, ±2 parts in 10^6, listed above.

Mass differences, however, may be determined to fair accuracy in the following way. As we have shown in reference 1, the equilibrium interatomic distances of a linear triatomic molecule may be expressed as

$$r_{12}=\frac{[m_3{}^0/(m_1{}^0+m_2{}^0)]\delta_e-\delta_c}{m_1{}^0[[m_3{}^0/(m_1{}^0+m_2{}^0)]-1]},$$

$$r_{23}=(\delta_e-\delta_c)/\Sigma m^0,$$

$$\delta_e{}^2=\Sigma m^0\Sigma m^e(I_e{}^0-I_e{}^e)/(m_3{}^0-m_3{}^e),$$

$$\delta_c{}^2=\Sigma m^0\Sigma m^c(I_e{}^0-I_e{}^c)/(m_2{}^0-m_2{}^c).$$

In this notation I_e and m refer to an equilibrium moment of inertia and mass; the superscript refers to the isotopic molecule, i.e., the original molecule, (0), or the one with the end atom, number 3, isotopically substituted, (e), or the one with the central atom changed, (c). Since we assume that the vibration potential is not changed by isotopic substitutions, we may say that the equilibrium distances, i.e., the potential minima, will remain unvaried by isotopic substitutions. It can be seen, therefore, that if a series of isotopes (1, 2, 3, 4···) are substituted for an end or a central atom, all must have the same δ's or

$$\delta_c{}^{(1)}=\delta_c{}^{(2)}=\delta_c{}^{(3)}=\cdots \tag{3a}$$

$$\delta_e{}^{(1)}=\delta_e{}^{(2)}=\delta_e{}^{(3)}=\cdots. \tag{3b}$$

Townes[6] has used the relation expressed in (3b) to interpolate for the S^{33} mass from that of S^{32} and S^{34}, since it follows from (3b) that

$$\Sigma m^{(1)}(I_e{}^0-I_e{}^{(1)e})/\Sigma m^{(2)}(I_e{}^0-I_e{}^{(2)e}) = (m_3{}^0-m_3{}^{(1)e})/(m_3{}^0-m_3{}^{(2)e}). \tag{4}$$

It should be noted, as Townes has indicated, that the equilibrium moment of inertia must be

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[6] C. H. Townes, Phys. Rev. 72, 513 (1947).

TABLE III. Se mass differences.

Atomic number	Mass a.m.u.	Δm a.m.u.
74	73.9550	1.9903
76	75.9453	0.9974
77	76.9427	0.9997
78	77.9424*	2.0011
80	79.9435*	1.9975
82	81.9410	

* Assumed from packing-fraction data.

used. The equilibrium values are not available at present, but the zero-point vibrational values may be used with some caution. In reference 1 we have shown that a ratio of vibrational moments of inertia is exact to zero order, and experience with OCS has shown that, in fact, such a ratio is good to better than 0.1 percent. For the present we can say no more until the change of α_3 with selenium mass is determined. Because it is interesting in any case, mass differences have been calculated by using ground vibrational data and by assuming the mass values given above for Se^{76} and Se^{82}. The results given in Table III indicate a smooth variation of selenium mass with mass number.

We have noted no anomalies in the absorption due to the isotopic forms of OCSe, either in position or intensity or line breadth. We must, therefore, conclude that the quadrupole interaction energy, i.e., eqQ in the usual notation,[7] is less than 0.5 Mc/sec. Since the selenium atom is an end atom and has a very large nucleus, one would expect the interaction energy to be considerably greater than 0.5 Mc/sec. unless the selenium 77 nuclear spin is equal to $\frac{1}{2}$, and the selenium 74, 76, 78, 80, and 82 atoms have nuclear spins of zero. For this reason we suggest a nuclear spin of $\frac{1}{2}$ for Se^{77}, and zero for $\text{Se}^{74,76,78,80,82}$. This confirms the previous assignment of zero spin to Se^{78} and Se^{80}.

IV. STARK EFFECT

We have observed the Stark effect for the $J=2\rightarrow3$ transition in OCSe in the ground vibrational state and in the first excited symmetrical stretching (v_1) and first excited bending (v_2) vibrations. The latter vibrational state has an anomalous Stark effect since there are matrix elements between the two l-split terms.

The Stark effect for the l-doublet is easily calculated, since we may assume that in the bending vibration the linear molecule is nearly a symmetric top. The Stark effect for a nearly symmetric top has been treated by Penny,[8] and his formulation may be used by the simple notation change $K\rightarrow l$.

The observed l-doublet Stark pattern is shown in Fig. 1. This is an excellent example of perturbation. When the perturbation energy of an electric dipole μ in an electric field of strength E is small compared with the level splitting, the molecule is a good asymmetric top and the Stark effect is second order as in asymmetric tops. When the perturbation energy is greater, however, than the term level splitting, then on this scale the molecule looks like a good symmetric top with degenerate K levels and the Stark effect is a first-order effect. Both conditions are readily obtained in the laboratory.

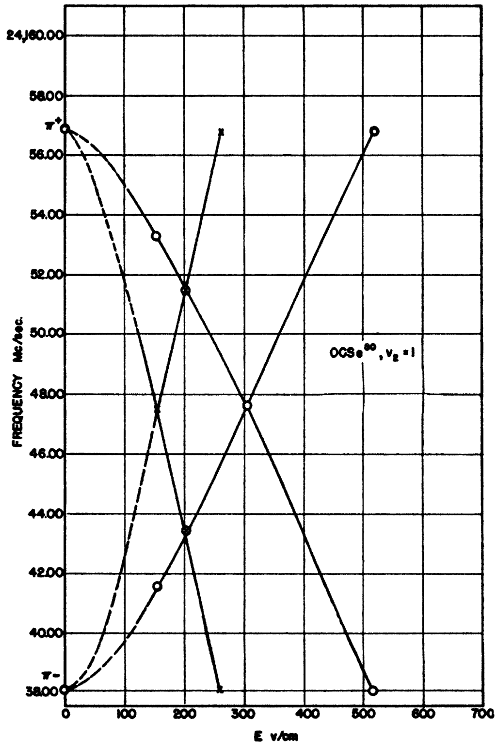

FIG. 1. Observed l-doublet Stark pattern for OCSe^{80}.

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[7] See, for instance, B. T. Feld, Phys. Rev. **72**, 1116 (1947).

[8] W. G. Penney, Phil. Mag. **11**, 602 (1931).

TABLE IV. Observed electric dipole moments, OCSe.

Vibrational state v_1 v_2 v_3	Dipole moment (e.s.u.-cm $\times 10^{18}$)
0 0 0	0.754
1 0 0	0.728
0 1 0	0.730

One may show that if the components of the two l lines having the same magnetic quantum number, M, are made to coincide in absorption frequency in the presence of an electric field E, then in a $J \rightarrow J+1$ transition

$$\mu = J(J+1)(J+2)(J+3)\Delta\nu' h/4ME, \quad (5)$$

where $\Delta\nu'$ = absorption frequency difference of unperturbed l-doublet and h = Planck's constant.

The observed Stark shift for the ground and excited symmetrical stretching vibrations for $O^{16}C^{12}Se^{80}$ are shown in Fig. 2. As we have shown in reference 1, these data also may be used to determine the static dipole moment. These derived data are given in Table IV. Measurements on $O^{16}C^{12}Se^{78}$ yield the same dipole moment as for $O^{16}C^{12}Se^{80}$ to 0.1 percent. This lack of isotopic dependence of the dipole moment is reasonable since the Se actually moves very little in any of the vibrations, and the fractional mass change is small. This may be compared with the slight change in dipole moment when C^{13} is substituted in $O^{16}C^{12}S^{32}$, as reported in reference 1.

The strong dependence of the static dipole moment on the vibrational state is of interest for many reasons. It is obvious that this effect places a limitation on the significance of dipole moments measured in the bulk, e.g., the Debye temperature-dependent polarization method. In OCSe about $\frac{1}{6}$ of the molecules are in excited vibrational states at 20°C. Of course, the change in dipole moment with vibrational excitation is enhanced in OCSe, a molecule pictured as having a resonant bond structure in which the three forms $^{+}O{\equiv}C{-}Se^{-}$, $O{=}C{=}Se$, and $^{-}O{-}C{\equiv}Se^{+}$ participate. The static dipole moment is thus the difference between the electric moment of the molecule with the OC bond as a single- or a triple-bond structure. A vibrational state which tends to increase the OC length, for example, will make the OC single-bond structure more predominant and decrease the contribution to the state due to the triple-bond form. The actual percentage change of the resultant static moment will depend upon how nearly the contributions to the dipole moment of the two structures canceled each other initially.

J. H. Van Vleck, in a private communication, has suggested that data on the change of the dipole moment with vibrational state are of interest, indirectly, in determining vibrational intensities.[9] We measure the average value of the dipole moment in a vibrational state

$$\bar{\mu} = \int \psi_1 \mu \psi_1^* d\tau, \quad (6)$$

where ψ is the vibration wave function of state 1, whereas the vibrational intensities depend upon

$$\mu_{\text{eff}} = \int \psi_1 \mu \psi_2^* d\tau, \quad (7)$$

a quantity measuring the mixing of two vibrational states, 1 and 2, due to the dipole moment. When the vibrational potential of OCSe is known, a connection could be made between the measured dipole moments and the desired vibrational absorption intensity by a calculation of the effective charge[10] from (6), which may then be used to evaluate (7) once the wave functions are known.

With so little knowledge of the vibration

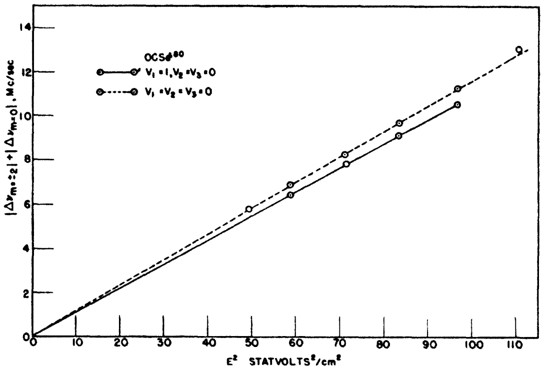

FIG. 2. Observed Stark effect for the ground and excited symmetrical stretching vibration for $O^{16}C^{12}Se^{80}$.

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[9] See, for instance, G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), pp. 259–261.

[10] J. H. Van Vleck, *Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).

potential available at present, we have not pursued these calculations further.

A few words regarding vibration potential are in order. R. C. Lord and R. S. McDonald of the M.I.T. spectroscopy laboratory have kindly measured the vibration frequencies of OCSe for the 0 to 1 transitions of v_1, v_2, and v_3. This information, together with the centrifugal distortion coefficient[11] allows one to solve for the four quadratic force constants. The six cubic force constants may be determined from the α_i and the change of the α_i with isotopic substitutions. We have not carried out these calculations since, at present, we lack the values of α_3 and its variation with isotopic substitution. In this way it is at least theoretically possible to determine the vibration potential to cubic terms.

Although we have the vibration frequencies as determined from infra-red studies by Lord and McDonald, it is interesting to note that these frequencies could be measured from rotational absorption studies alone. The procedure is straightforward. It is known that the absorption coefficients, γ, of a gas depends upon the number of absorbing molecules, N, and the square of the static dipole moment μ.[1] The ratio of the absorption due to molecules in the ground vibrational state to the absorption of one component of the l-doublet due to the molecules in the first excited bending state is (subscripts give vibrational quantum numbers)

$$\gamma_{000}/\gamma_{010}=(N_{000}/N_{010})(\mu_{000}/\mu_{010})^2. \quad (8)$$

Since the populations over the vibrational states follow a Boltzmann distribution, we may immediately write

$$e^{-(W_{000}-W_{010})/kT}=(\gamma_{000}/\gamma_{010})(\mu_{010}/\mu_{000})^2,$$

where W is the vibrational term-value energy. But $W_{000}-W_{010}=-hc\omega_2$ so that we have

$$\omega_2=(kT/hc)\ \ln[(\gamma_{000}/\gamma_{010})(\mu_{010}/\mu_{000})^2]\ \mathrm{cm}^{-1}.$$

The ratio of the absorption intensities is readily measured since the absorptions are not widely separated in frequency. We have measured the dipole moments, and so by also measuring the temperature we may determine the vibration frequency ω_2. Our measurements give ω_2 as 474 cm^{-1}. This has been measured as 464 cm^{-1} by Lord and McDonald. The two percent error is large and corresponds to an error of about five percent in measuring the absorption ratio. These measurements could be further refined to yield more precise vibration frequency data. Large ratios of intensity are best for precise determination of the vibration frequency, since the fractional error is given by

$$d\omega/\omega=(dT/T)+(dR/R\ \ln R),$$

where

$$R=(\gamma_{000}/\gamma_{010})(\mu_{010}/\mu_{000})^2.$$

T is temperature in °K, ω is a vibration frequency. The greater the ratio R is, the less will be the error contributed by the absorption measurements.

If the measurements are performed on the $v_1=1$ and $v_3=1$ states also, one can indeed, by the method described above, determine the vibration potential to cubic terms from rotational-absorption measurements alone.

As a check on our ability to measure absorption ratios, we have measured the ratio of the rotational absorption for the ground vibrational state of the molecules OCSe^{80} and OCSe^{82}. These lines differ in frequency by about 150 Mc/sec. The measured ratio is

$$\mathrm{OCSe}^{82}/\mathrm{OCSe}^{80}=0.196.$$

This ratio is just the ratio of isotopic abundances since both molecules have the same dipole moment. Aston[3] and White and Cameron[12] give the isotopic ratio as

$$\mathrm{Se}^{82}/\mathrm{Se}^{80}=0.195 \text{ and } 0.180.$$

The latter ratio differs by more than a reasonable experimental error of ±5 percent.

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[11] Theoretical expressions for D_v and α_i are available in the literature. See, for instance, A. H. Nielsen, J. Chem. Phys. **11**, 160 (1943).

[12] J. R. White and A. E. Cameron, Phys. Rev. **74**, 991 (1948).