PHYSICAL REVIEW VOLUME 95, NUMBER 2 JULY 15, 1954

Microwave Spectrum of TeCS and Masses of the Stable Tellurium Isotopes*

W. A. HARDY† AND G. SILVEY
Columbia University, New York, New York

(Received March 31, 1954)

The microwave spectrum of TeCS has been examined in the rotational transitions $J=6\leftarrow 5$, $J=7\leftarrow 6$, and $J=8\leftarrow 7$. Seven isotopes were observed and from their absorption frequencies mass ratios have been calculated. The mass values are compared with mass spectrographic data and with the recent mass surfaces of Green. The odd-even mass variation is 1.5 milli-mass-units for both Te^{123} and Te^{125}. The Te−C bond distance is 1.904 A and the C−S distance 1.557 A. The molecular dipole moment was measured as 0.172 ±0.002 Debye unit.

THE microwave spectrum of the molecule thiocarbonyl telluride was provisionally analyzed in this laboratory in 1952, but with the apparatus then available the frequency measurements of the spectrum were not sufficiently accurate to allow a satisfactory determination of the tellurium mass ratios.[1] Thus, for Te^{123} the experimental error allowed for the odd-even mass variation was 1.2 milli-mass-units reflecting a 50-kilocycle uncertainty in the measurement of the weak absorption lines due to this isotope. Subsequent to the construction of a highly refined, albeit conventional type, Stark modulation spectrometer the TeCS spectrum was remeasured with increased precision and this paper reports more accurate mass ratios together with the rotational constants of the TeCS molecule. Some account is also given of the spectrometer used in this work.

a. ROTATIONAL CONSTANTS OF TeCS

Microwave rotational transitions of the linear molecule TeCS were observed corresponding to $J=6\leftarrow 5$, $J=7\leftarrow 6$, and $J=8\leftarrow 7$, where J is the rotational quantum number. To each of these belongs an isotopic family due to tellurium nuclei with $A=122$, 123, 124, 125, 126, 128, and 130. Te^{120}, although stable, is only 0.09 percent abundant and was not observed.

The frequency f of the rotational transition of a triatomic linear molecule from the energy level specified by rotational quantum number J to $J+1$ is given by

$$
\begin{aligned}
f &= (2B_v \pm q_l)(J+1) - D[4(J+1)^3 - 2(J+1)l^2],\\
B_v &= B_e - \alpha_1(v_1+\tfrac{1}{2}) - \alpha_2(v_2+1) - \alpha_3(v_3+\tfrac{1}{2}), \qquad (1)\\
B_v &= B_{000} - \alpha_1 v_1 - \alpha_2 v_2 - \alpha_3 v_3.
\end{aligned}
$$

Here B is the reciprocal moment of inertia (times $\hbar^2/2$), D is the centrifugal distortion constant, the α's are rotation-vibration parameters representing the change in the moment of inertia of the molecule in any of the vibrational states specified by the v's, and l is a quantum number refering to the component of angular momentum parallel to the symmetry axis of the molecule. It is different from zero only for the vibrational states of v_2, and $l=\pm 1$ for $v_2=1$, giving the usual l-type doublets. The rotation of the molecule removes the degeneracy of the two bending modes allowed for $v_2=1$, and q_l is a splitting constant giving the separation of the doublets. It can be shown that for $v_2 \geqslant 2$, q_l is essentially zero.[2] B_v is the observed reciprocal moment of inertia, B_{000} that of the molecule in its ground state, and B_e is the equilibrium value neglecting zero-point vibrations.

Molecular parameters are given in Table I from which the TeCS spectrum may be calculated for any transition by the use of (1). Frequencies calculated using this table are exact to better than 40 kc/sec. (Although later measurements of the TeCS spectrum were more precise, Table I includes some earlier data that would have been inconvenient to redetermine in the later work.)

There were two difficulties attendant to the observation of this spectrum which require special mention. The first is the spontaneous decomposition of TeCS at temperatures above its melting point, −54°C. Accordingly, the measurements were made by holding the temperature of the wave-guide absorption cell in the range −55°C to −45°C by circulating chilled acetone around the cell. Under these conditions the molecule was semistable and the spectrum could be observed up to periods of several hours. Deposits of tellurium metal did, however, accumulate in the wave guide. The second and more formidable difficulty concerns the small molecular dipole moment of TeCS, 0.172 Debye unit, with the result that not only is the absorption coefficient considerably smaller than that of comparable molecules, but the Stark modulation fields available were unable to produce Stark splittings greater than a

TABLE I. Molecular parameters of TeCS to be used in Eq. (1). For all the isotopes an average centrifugal distortion constant D was taken as 95 cps. These parameters have the units of Mc/sec.

A of Te	B_{000}	α_2	q_l
130	1559.9303	3.2446	0.6599
128	1565.7022	3.2551	0.6649
126	1571.6524	3.2657	0.6706
125	1574.6925	3.2712	0.6728
124	1577.7898	3.2764	0.6752
123	1580.9261	3.2818	0.6776
122	1584.1224	3.2870	0.6786

---

* Work assisted by the U. S. Atomic Energy Commission.

† National Science Foundation Pre-doctoral Fellow.

[1] Silvey, Hardy, and Townes, Phys. Rev. **87**, 236 (1952).

[2] H. H. Nielsen, Phys. Rev. **75**, 1961 (1949).

fraction of a line width in the ground state of the molecule. It was necessary to make the microwave measurements on the rotational transitions of the excited vibrational states with $v_2=1$ in order to take advantage of the greater Stark effect in this state because of the near degeneracy of the *l*-type doublets.

The measured frequencies of the two *l* doublets with $v_2=1$ in the $J=8\leftarrow7$ transition are given in Table II for each of the tellurium isotopes observed. All these lines were measured with a fixed Stark modulation electric field intensity of 1610 volts/cm. The doublet separations and the change in doublet separation for a unit change in A (the tellurium mass number) are also given. Although the measurements are consistent, the actual absorption frequencies may be displaced from those measured because of Stark distortion of the line shapes. However, this shift is less than 25 kc/sec and will not affect the later determination of the mass ratios because the doublets are exactly symmetric about their average frequency and such a distortion will be cancelled. The measurements listed in Table I were taken by sweeping very slowly over the lines with a stabilized klystron and presenting both the line and frequency standard markers on a recording chart. Using this technique the error in the average of the doublet frequencies is less than 10 kilocycles.

The second-order Stark effect of the TeCS molecule in its ground state is very small both because of the necessarily high J values for microwave transitions and because of the small dipole moment. Lines corresponding to ground-state transitions were only observed after the application of a 700-volt Stark modulation square wave added to a 1200-volt dc source, representing a maximum modulation electric field intensity of 4370 volts/cm in the guide. Even so, the line was only partially separated from its Stark component and could not be used for accurate frequency measurements.

In a strong electric field a linear molecule in a bending vibrational mode behaves like a slightly asymmetric top, permitting a component of angular momentum parallel to the field and thus allowing a first-order Stark effect of considerably larger magnitude than the second-order effect discussed in the previous paragraph.

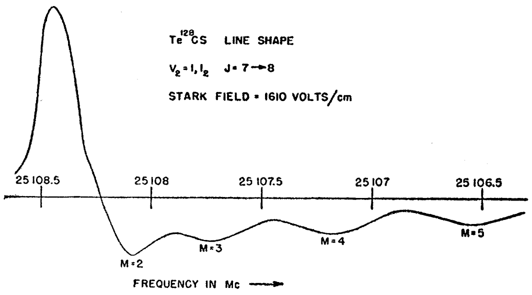

FIG. 1. The line shape of an *l* doublet of TeCS in a Stark field of 1610 volts/cm. In the presentation, the undisplaced line is shown as positive and the Stark components are negative. The minima are shown identified by their *M* component.

TABLE II. TeCS *l*-type doublet measured frequencies in the $J=8\leftarrow7$ rotational transition. The doublet separations and the change in the doublet separations per change in mass number are also given. All frequencies are given in Mc/sec.

A of Te	$v_2=1,1_1$	$v_2=1,1_2$	Δf	$\Delta(\Delta f)/\Delta A$
130	25 005.326	25 015.884	10.558	
				0.040
128	25 097.805	25 108.444	10.639	
				0.045
126	25 193.132	25 203.861	10.729	
				0.035
125	25 241.844	25 252.608	10.764	
				0.039
124	25 291.465	25 302.268	10.803	
				0.038
123	25 341.714	25 352.555	10.841	
				0.018
122	23 392.929	25 403.788	10.859	

The energy levels in terms of the component M of angular momentum parallel to the electric field E have been given for the bending modes as[3]

$$W=W_{cg}\pm\tfrac{1}{2}[(\Delta W)^2+4\mu^2E^2\varphi^2]^{\frac{1}{2}}. \tag{2}$$

Here φ is a matrix element connecting the *l*-type doublets with $\varphi=M/[J(J+1)]$, W_{cg} is the energy in the absence of doublet splitting, and ΔW is the separation of the doublets in a given J level.

A plot, taken from an actual trace of one of the doublet components and used in the determination of the molecular dipole moment, is shown in Fig. 1. Even at the Stark modulation field strength of 1610 volts/cm used here about one-third of the line is lost due to cancellation by Stark components that are shifted by less than a line width. By measuring the frequencies of the observed minima both the electric dipole moment and the M components corresponding to the minima were determined using (2). The dipole moment was found to be

$$\mu=0.172\pm0.002 \text{ Debye unit.}$$

Calculations using the observed line widths as parameters showed that the observed minima corresponded exactly to their Stark components with negligible error due to overlap of these components and the undisplaced line. The electric field strength in the wave guide was calibrated by measurement of the Stark shift of the molecule OCS whose dipole moment was measured accurately by Shulman and Townes.[3]

The values of α_2 given in Table I and used in the determination of B_{000} are calculated using the separation between the average of the doublet frequencies for which $v_2=1$ and the unsplit line with $v_2=2$. Within the accuracy of the measurement of the ground state transitions no Fermi-type resonance effects were observed. No quardupole hyperfine structure was detected for the odd tellurium isotopes, in agreement with the

---

[3] R. Shulman and C. H. Townes, Phys. Rev. 77, 500 (1950).

spins of $\frac{1}{2}$ measured for these nuclei by the use of optical hyperfine structure.[4]

From the moment of inertia data the Te—C bond distance was determined as 1.904 A and the C—S bond distance as 1.557 A. These values may be interpreted in terms of the percentage contributions of the resonant structures $Te=C=S$, $Te^{+}\equiv C-S^{-}$, and $Te^{-}-C\equiv S^{+}$, together with the usual values of bonding radii of the respective atoms.[5] The small dipole moment of TeCS makes it likely that the last two structures contribute in nearly equal amounts, and the actual percentage must be about 20 percent to give the observed C—S bond distance. The Te—C bond distance then yields the value 1.23 A for the tellurium triple bond radius, which compares favorably with the value 1.20 A that would be interpolated from Pauling's values of bond radii. This indicates that Pauling's bond radii for tellurium taken from solid tellurium are fairly accurate.

b. MASS DATA

If the molecular bonds were rigid, the moment of inertia data would enable the exact determination of the isotopic tellurium masses in terms of any two masses, assumed given, from the expression

$$\frac{m^1-m}{m^2-m}=\frac{M^1}{M^2}\left(\frac{B^2}{B^1}\right)\left(\frac{B-B^1}{B-B^2}\right). \tag{3}$$

The superscripts indicate the isotopes chosen as standards and the M's refer to the total molecular mass. Geschwind has analyzed the errors in these ratios arising from the use of the effective B values (which include molecular vibrational effects) rather than the use of the equilibrium B_e's, and has shown that even in extreme cases the error would be less than a few tenths of a milli-mass-unit.[6] Accordingly, the mass ratios reported in this paper have been determined by substitution of the observed effective B values in (3); it is probable that the error introduced by this approximation is less than a tenth of a milli-mass-unit. It must be noted that all microwave mass ratio determinations using polyatomic molecules involve this assumption, and that there has been excellent agreement with mass spectroscopic and nuclear reaction data.

TABLE III. Mass defects $(M-A)$ for the stable tellurium isotopes expressed in millimass units.

A of Te	Halsted	Data of Hogg-Duckworth[a]	Green *et al.*	Microwave†
130	-51.47 ± 0.10	-52.3 ± 0.4	-49.44	-50.5 ± 0.2
128	-53.51 ± 0.13	-56.2 ± 0.6	-52.68	-53.5
126	-55.80 ± 0.07		-55.21	-55.6 ± 0.2
125	-55.40 ± 0.31		-55.35	-55.0 ± 0.2
124	-57.22 ± 0.11	-60.8 ± 0.4	-57.05	-57.2
123	-56.32 ± 0.39		-56.75	-56.1 ± 0.2
122	-58.07 ± 0.08	-60.1 ± 0.6	-58.05	-57.8 ± 0.2

[a] These results depend slightly on the mass value assumed for carbon. See reference 8.
† Using Halsted masses for Te^{128} and Te^{124}.

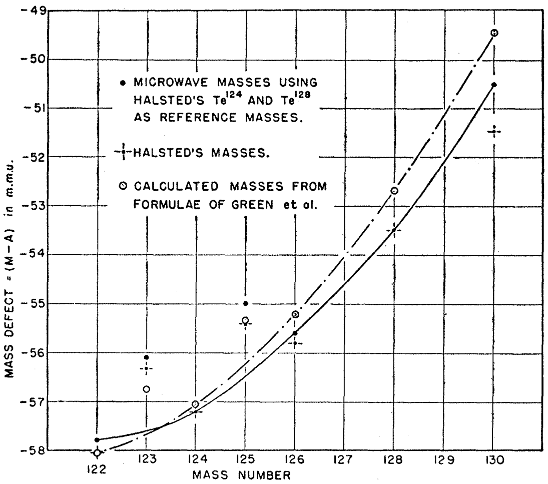

FIG. 2. The mass defects of tellurium shown as a function of tellurium mass number.

The tellurium mass data is given in Table III and the mass defect is plotted as a function of the mass number of tellurium in Fig. 2. It will be seen that the data of Halsted and that of Hogg and Duckworth do not agree within the experimental errors quoted by these authors.[7,8] Although the two reference masses used in computing the microwave mass ratios were chosen from the Halsted masses because of the smaller quoted uncertainty, comparison of these data is strongly conditioned by the specific masses chosen. For example, the choice of Te^{124} and Te^{128} used in the data indicates a disagreement with the Halsted data of 1.0 mMU for Te^{130}. Alternately, a choice of Te^{124} and Te^{130} as reference masses causes a disagreement of 0.7 mMU for Te^{128} and 0.5 mMU for Te^{122}. The above discrepancies may be seen from Table III to be considerably larger than the experimental errors quoted for the separate measurements, and accordingly no attempt has been made to combine data to achieve "adjusted" mass values.

On the other hand, the odd-even mass variations determined from the microwave data are relatively unaffected by the trend for even isotopes that is set by the choice of reference masses, and one of these may be directly compared with nuclear reaction data. Thus, the $Te^{125}(\gamma,n)$ threshold is determined by Sher, Halpern, and Mann as 6.5±0.2 Mev, comparing very favorably with the 6.4±0.2 Mev deduced from the microwave data.[9] The odd-even mass variation for Te^{125} is 1.5±0.2 mMU and for Te^{123} it is the same.

---

[4] Mack, Marakawa, Ross, Pick, and van den Bosch, Phys. Rev. **83**, 654 (1951).

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

[6] S. Geschwind, thesis, Columbia University, 1951 (unpublished).

[7] R. Halsted, Phys. Rev. **88**, 666 (1952).

[8] B. G. Hogg and H. E. Duckworth, Can. J. Phys. **30**, 628 (1952).

[9] Sher, Halpern, and Mann, Phys. Rev. **84**, 387 (1951).

Finally, the tellurium mass values given by the semiempiric formulas of Green, Engler, and Edwards, including shell corrections, are also shown.[10,11] It is significant that the fit of the data, particularly the shape of the mass defect parabola, is much better than that given by any of the other mass-surface equations commonly used, such as the Bohr-Wheeler equation.

c. THE SPECTROMETER

The Stark modulation microwave spectrometer used in this work was constructed with three principal objectives—high sensitivity, capability of precision frequency measurements, and adaptability as a general purpose instrument to a wide variety of microwave problems. Some discussion of the general features of this instrument and of the technique used in the frequency measurements of the TeCS lines is given below. The spectrometer consists basically of a 14-foot wave-guide cell with an inner septum that is Stark modulated at a frequency of 89 kc/sec. A minimum sensitivity of 3×10^{-10} cm^{-1} has been demonstrated and the line width at half-maximum intensity is 150 kc/sec.

Townes and Geschwind have derived an expression for the limiting sensitivity of a microwave spectrometer which may be written for this instrument as $\alpha_{\min}=4\times10^{-11}(N\Delta f)^{\frac{1}{2}}$.[12] Here N is a noise figure and Δf is the band width of the detecting system. It must be noted that although increased sensitivity may be achieved by the use of very small band widths, the time required for observation of an accurate line shape is at least ten times the reciprocal band width. Further, it is assumed that the microwave radiation is very nearly monochromatic and varies in a smooth and continuous manner during the tracing of the line. In practice, this requirement (particularly for the 2*K*33- and *QK*-type klystrons used in this work) is rather formidable. For example, a 25 to 40 CFM blower directed upon the klystron in a gentle stream produces more than 300 kilocycles microphonic modulation. In the present apparatus the klystron is rigidly fixed upon a shock-mounted 250-lb concrete block and is connected to the wave guide cell by flexible wave guide. Cooling is effected by means of oil flowing at a constant rate within a jacket surrounding the shell of the klystron. Mechanical tuning of the klystron cavity is accomplished by a gear reduction, remotely activated by selsyns to avoid vibration, that provides mechanical tuning with a precision of better than 30 kc/sec and with negligible backlash. Finally, the klystron power supply is regulated to within 10 millivolts of ripple and drift. These precautions have enabled us to achieve a clean microwave signal with a frequency width of about 15 kc/sec and with very slow drift. This increased the sensitivity and also gave considerably more accurate frequency measurements. A continuous high sensitivity search over a region of more than 100 Mc/sec while mechanically tuning the klystron at a rate of 5 (Mc/sec) per minute could be automatically recorded in a very satisfactory manner.

For band widths of the order of 1 cycle/sec additional stability is obtained by stabilizing the klystron with respect to a frequency standard harmonic, using discriminator detection and dc control of the klystron repeller voltage. This technique makes the microwave signal still more nearly monochromatic and permits arbitrarily slow sweeping over the absorption line. It was used in the measurements of the *l*-type doublets of TeCS. Further decrease of the band width is limited in the present apparatus by saturation of the lock-in detector due to noise voltages when the receiver gain is increased to enable detection of weaker absorptions than 3×10^{-10} cm^{-1}.

Features which increase the utility of the spectrometer include a temperature control of the wave-guide cell from −70°C to 95°C and the use of a wave-guide cell constructed entirely of copper, brass, and Teflon to permit analysis of reactive molecules such as fluorides.

d. CHEMISTRY

The TeCS was prepared[13] by the action of an arc under CS_2 between a graphite anode and a tellurium-graphite cathode, the latter containing 10–15 percent graphite. The material was purified by distillation at −78°C. Considerable amounts and several varieties of unknown impurities were obtained and were only partially removed by further fractional distillation.

e. ACKNOWLEDGMENT

The authors wish to acknowledge the courtesy of Dr. A. E. S. Green and Mr. Kiuck Lee for sending us their tellurium mass values calculated from the mass-surface equations of Green *et al.*[10,11]

---

[10] A. E. S. Green and N. A. Engler, Phys. Rev. **91**, 40 (1953).

[11] A. E. S. Green and D. F. Edwards, Phys. Rev. **91**, 46 (1953).

[12] C. H. Townes and S. Geschwind, J. Appl. Phys. **19**, 795 (1948).

[13] A. Stock and P. Praetorius, Ber. deut. chem. Ges. **47**, 131 (1914).