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THE MICROWAVE SPECTRUM AND QUADRUPOLE INTERACTION IN CIS-1, 2-DICHLOROETHYLENE

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The Microwave Spectrum and Quadrupole Interaction in cis-1,2-Dichloroethylene*

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Abstract

The microwave spectrum of cis-1,2-dichloroethylene has been assigned. The rotational constants of cis-$CHCl^{35}$ $CHCl^{35}$ are A = $11,518.3_3$ Mc, B = $2,545.1_5$ Mc, and C = $2,082.5_7$ Mc. The Cl^{35} nuclear quadrupole coupling constants have been measured and are χ_{aa} = 3.7 Mc, χ_{bb} = -35.7 Mc, and χ_{cc} = 31.9 Mc. Various aspects of the nuclear quadrupole interaction and the structure of the molecule are discussed.

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Introduction

In recent years, there has been considerable interest in the application of nuclear quadrupole coupling data from microwave spectroscopy to problems of chemical bonding. In particular, from the number of chlorine containing molecules for which data is now available, one has come to expect a value of the quadrupole coupling tensor component along the C-Cl bond of about -70 to -80 Mc. χ_{zz} values obtained from solid state measurements are typically 5 or 10% smaller than those obtained from the gaseous state.[1] A brief summary of these data is given in Table I.

In view of the uniform trend in these data, one is surprised and interested to note that as a result of their study of the microwave spectrum of cis-1,2-dichloroethylene, Shimizu and Takuma[2] report a value for this molecule of χ_{zz} = -46 Mc. One may justify this value, as these authors do, by asserting that the C-Cl bonding in this molecule exhibits an unusually large degree of ionic character. However, since Livingston[3] reports a solid state value of 70.00 Mc, a re-examination of the microwave spectrum is strongly indicated.

We have made such an examination and find that many of the absorption lines which they have assigned do not exhibit the hyperfine structure patterns required by their assignment. Moreoever, we have been unable to find various

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1 C.T. O'Konski, "Determination of Organic Structure by Physical Methods," (Academic Press, Inc. N.Y., 1961), chapter 12.

2 T. Shimizu and H. Takuma, J. Phys. Soc. Japan 15, 646 (1960).

3 R. Livingston, J. Phys. Chem. 57, 496 (1953).

transitions which they did not observe but whose frequencies should be calculable from their rotational constants. Accordingly, we have concluded that their assignment is incorrect and have proceeded to examine and reassign the spectrum of cis-1,2-dichloroethylene with the results to be described below.

Spectrum and Assignment

The sample of cis-1,2-dichloroethylene was obtained from Matheson, Coleman, and Bell and was used without further purification. Conventional sample handling techniques were employed and, since the vacuum manifold and Stark cell were never subjected to more than 30 microns sample pressure, no difficulty was experienced with the tendency of the sample to dissolve stop-cock grease or with polymerization of the unstabilized vapor.

The microwave spectrometer used in this work has been described previously.[4,5] In its use, the klystron frequency is "locked" by a phase stabilization system to a harmonic of a sum frequency generated by a crystal controlled oscillator and a stable low frequency VFO. The klystron can then be swept slowly by the VFO and one is able to use long time constants and low sample pressures. This, of course, leads to greatly increased resolution and sensitivity. These features, while universally desirable, proved to be indispensable in assigning the spectrum of cis-1,2-dichloroethylene.

Approximate moments of inertia were calculated from an assumed structure. The parameters used and the resultant moments are given in Table II. The only non-zero dipole moment component will lie along the b principal inertial axis

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4 A. Narath and W.D. Gwinn, in press (See also A. Narath, thesis, University of California, 1959).

5 W.H. Flygare, A. Narath, W.D. Gwinn, J. Chem. Phys., in press.

in $CHCl^{35}$ $CHCl^{35}$. Both b-type selection rules and the relatively large moments of inertia of this molecule lead to a very dense spectrum. An additional complication arises from the molecular geometry. In the case of many other two-chlorine molecules that have been studied, the two chlorine atoms are bonded to the same carbon atom (See Table I.). As a result these molecules exhibit complex low J transitions but, as J increases, the quadrupole hyperfine splitting decreases. In the case of cis 1,2-dichloroethylene however, the quadrupole coupling constants along the a and b principal inertia axes are just the reverse of the coupling constants along the same axes in molecules such as CH_2Cl_2, $C_3H_4Cl_2$, CH_2CCl_2, or $COCl_2$. As a result of this, one expects complicated high J multiplets as well as the usual complex low J multiplets.

An initial search in the region from 20 to 23 kMc_c showed a very dense spectrum with almost no transitions that were not complex multiplets (see above). In order to identify a multiplet with a particular J it was necessary to use the klystron phase stabilization system. Under high resolution search conditions the hyperfine patterns of a number of these transitions were observed and measured. Possible assignments of these multiplets were then obtained by using the moments of inertia in Table II and estimated quadrupole coupling constants. By comparing these predictions with the observed multiplets a Q branch assignment was soon made. The complexity of these multiplets is illustrated in Fig.1, which shows the trace of the $6_{06} \rightarrow 6_{15}$ transition as observed with the aid of the phase stabilized spectrometer.

By using the parameters obtained from the Q branch assignment and from an assumed value of the inertial defect[6] the value of A + C was calculated and the $0_{00} \rightarrow 1_{11}$ transition was soon found. A trace of the $0_{00} \rightarrow 1_{11}$ transition

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[6] S. Sekino, T. Nishikawa, J. Phys. Soc. Japan, 12, 43(1957).

is shown in Fig. 2. In order to check the R-branch assignment, two other such transitions were found and measured; a trace of the $5_{15} \rightarrow 6_{06}$ multiplet is given in Fig. 3.

The measured and calculated frequencies of the assigned transitions in $CHCl^{35}$ $CHCl^{35}$ are listed in Table III and the resultant rotational constants and principal moments of inertia are listed in Table IV.

Although no quantitative interpretation of Stark effect data can be given here it should be noted that observations on the $0_{00} \rightarrow 1_{11}$ transition reveal a large negative Stark coefficient. This situation arises because the level 2_{02} lies only 26½ Mc above the 1_{11} level and serves to further substantiate the correctness of the assignment.

Quadrupole Interaction

In the case of two chlorine nuclei the nuclear quadrupole interaction can be treated as a small perturbation which couples the nuclear spin angular momentum to the rotation of the rigid asymmetric top. The Hamiltonian describing this interaction is well known and its matrix elements diagonal in J have been given.[7,8] Recently, the theory has been extended to include all off-diagonal elements in J,[9] these being of importance when rotational near degeneracies occur.

For all the cis-$CHCl^{35}$ $CHCl^{35}$ transitions reported here the usual first order theory proves adequate to fit the data. A second simplification is afforded by the fact that the two Cl nuclei occupy equivalent positions. The net result of these facts is that the various members of a given multiplet may be labelled by F_ϵ, where ϵ is a pseudo quantum number related to I, the total nuclear spin. The quadrupole coupling energy is given by $W_Q = \chi^+\lambda(F,\Sigma,J)$, where the λ have been tabulated by Robinson and Cornwell.[10]

The quantity χ^+ is known as the level splitting factor and depends on the quantum number J and τ. Since the nuclei are equivalent and since only the on-diagonal elements of the quadrupole coupling tensor appear in χ^+ we may omit reference to a particular nucleus and use Bragg's expansion[11] to obtain

$$\chi^+ = \chi_{aa}\,\phi^2_{za} + \chi_{bb}\,\phi^2_{zb} + \chi_{cc}\,\phi^2_{zc}$$

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7 H.M. Foley, Phys. Rev. 71, 751(1947).

8 R.J. Myers, W.D. Gwinn, J. Chem. Phys. 20, 1420(1952).

9 W.H. Flygare, W.D. Gwinn, J. Chem. Phys. in press.

10 G.W. Robinson, C.D. Cornwell, J. Chem. Phys. 21, 1436(L953).

11 J.K. Bragg, Phys. Rev. 74, 533(1948).

where the ϕ's are the direction cosines relating the space fixed g axis to the molecule fixed abc axes.

In order to identify multiplets and to assign their members, relative intensities within the multiplet are required. These may be obtained from line strengths for the Russell-Saunders coupling case (cf., 8,10). In addition, because rotation about the C_2 axis interchanges a pair of protons as well as the two Cl nuclei, one must appropriately apply statistical weight factors of 3 and 1.

Using the above theory one is then able to obtain an "unperturbed" frequency ν_0 and a $\Delta\chi_i^+$ value for each multiplet studied. The molecular parameters χ_{aa} and χ_{bb} (tr $\chi = 0$) are then determined from these $\Delta\chi_i^+$ with the necessary ϕ's being calculated by an IBM 704 computer.[12]

Calculated and observed ν_0's are given in Table III and the coupling constants are given in Table V. The multiplet splittings calculated from the data in Table V are given in Table VI, which compares the calculated and observed splittings. The self consistency of the results in Table VI, when coupled with the results shown in Table III, leaves no doubt that the assignment is correct.

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[12] J.A. Howe, J. Chem. Phys. 34, 1247 (1961).

Discussion

A comparison of the calculated values in Table II with the observed values in Table IV would indicate that the assumed structure is approximately correct. Unfortunately a precise determination of the structural parameters would require observations on a large number of isotopic species with, for example, a determination of $\angle$CCCl requiring a Cl^{37} and a C^{13} species.

However, a consideration of the quadrupole coupling data does lead to further structural information. In the first place, since one generally expects a decrease in the coupling constant along the bond when a chlorinated hydrocarbon goes from the gas to the solid state, one can set a lower limit to $-\chi_{zz}$ of 70 Mc[3]. If, in addition, we make the usual assumption that the C-Cl bond axis is a principal axis of the χ tensor, then in order to satisfy the restriction on χ_{zz} the CCCl angle must be at least 124° (for 124° χ_{zz} = - 68.7 Mc, for 125° χ_{zz} = - 73.7 Mc.) Further support for these values is lent by a molecular orbital calculation[13] which predicts that $\chi_{xx} - \chi_{yy}$ = 8.5 Mc, where y is the out of plane coordinate. The CCCl angle which satisfies this expectation has the value 124° 45' and results in χ_{zz} = - 72.3. As a final indication of self consistency, it may be noted from Table I that vinyl chloride undergoes a decrease in χ_{zz} of 3 Mc on going to the solid state.

Lastly, it is of interest to compare the results obtained here for cis CHCl = CHCl with those previously obtained for CH_2CCl_2.[3] If the properties of the C-Cl bonds were the same in both molecules then the χ tensor for one would become that for the other upon interchange of the a and b axes. To the

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[13] J.A. Howe, et al, "Simple Molecular Orbital Theory of the Dichloroethylenes," in preparation.

contrary, it is found for $CH_2CCl_2^{35}$ that $\chi_{aa} = -42.81$, $\chi_{bb} = 7.69$ and $\chi_{cc} = 35.12$ Mc[14] and that $\angle CCCl = 123^\circ\ 10'$.[33] It seems likely that an explanation of these differences will require examination of the in-plane lone pair interactions as well as those of the π and σ systems.

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[14] J.A. Howe and W.H. Flygare, Stark Effect in the Strong Field Case, in preparation.

Table I. Cl^{35} nuclear quadrupole coupling constants along the C-Cl bond for several molecules

molecule	χ_{zz} obtained in gaseous state from microwave spectroscopy	$\lvert\chi_{zz}\rvert$ in solid state from pure quadrupole spectra
CH_3Cl	-74.74 [a] Mc	68.40 [h] Mc
CH_2Cl_2	-76.2 [b] Mc	72.47 [h] Mc
C_2H_5Cl	-70.07 [c] Mc	65.97 [i] Mc
$C_3H_4Cl_2$	-76.4 [d] Mc	
C_2H_3Cl	-70.16 [e] Mc	67.2 [j] Mc
CH_2CClF	-74.4 [f] Mc	
cis-CHClCHF	-73.7 [g] Mc	

[a] C.H. Townes and A.L. Schawlow, "Microwave Spectroscopy", (McGraw-Hill Book Co., Inc., N.Y., (1955) p. 620.

[b] W.H. Flygare and W.D. Gwinn, J. Chem. Phys, in press.

[c] R.S. Wagner and B.D. Daily, J. Chem. Phys. 26, 1592(1957).

[d] W.H. Flygare, A. Narath, W.D. Gwinn, J. Chem. Phys. in press.

[e] D. Kivelson, E.B. Wilson, Jr., D.R. Lide, J. Chem. Phys. 32,205(1960).

[f] J.K. Bragg, T.C. Madison, A.H. Sherbaugh, Phys. Rev. 77, 148 (1950).

[g] J.A. Howe, J. Chem. Phys. 34, 1247 (1961).

[h] R. Livingston, J. Chem. Phys. 19, 1434(1951).

[i] R. Livingston, J. Chem. Phys. 20, 1170(1952).

[j] J.H. Goldstein and R. Livingston, J. Chem. Phys. 19, 1613(1951).

Acknowledgement

The authors gratefully acknowledge the aid and encouragement of Professor William D. Gwinn.

Table II. Assumed structural parameters and resultant moments of inertia for cis $CHCl^{35}$ $CHCl^{35}$

d C-C	1.320
d C-Cl	1.724
d C-H	1.079
∢C C Cl	124° 30'
∢C C H	123° 0'
I_a	43.68 a.m.u. A^2
I_b	200.82 a.m.u. A^2
I_c	244.50 a.m.u. A^2

Table III. Measured and calculated frequencies for the assigned transitions in cis-$CHCl^{35}$ $CHCl^{35}$

Transition	Measured frequency in Mc	Calculated frequency in Mc
$3_{03} \rightarrow 3_{12}$	10,668.00	10,668.07
$4_{04} \rightarrow 4_{13}$	11,730.06*	11,729.91
$5_{05} \rightarrow 5_{14}$	13,147.17	13,147.01
$6_{06} \rightarrow 6_{15}$	14,968.41*	14,967.96
$6_{15} \rightarrow 6_{24}$	24,090.1	24,089.83
$8_{08} \rightarrow 8_{17}$	19,977.83*	19,978.35
$11_{1,10} \rightarrow 11_{29}$	24,139.42	24,140.03
$0_{00} \rightarrow 1_{11}$	13,600.90	13,600.90
$3_{13} \rightarrow 4_{04}$	13,445.60	10,445.07
$5_{15} \rightarrow 6_{06}$	20,962.10*	20,962.14

* For these multiplets the ν_0 components are unresolved (see Figs. 1 and 3).

Table IV. Rotational parameters and principal moments of inertia in cis-$CHCl^{35}$ $CHCl^{35}$

A-C	$9,435.7_6$	Mc
A+C	$13,600.9_0$	Mc
$\bar{k}$	$-.90195_2$	
A	$11,518.3_3$	Mc
B	$2,545.1_5$	Mc
C	$2,082.5_7$	Mc
I_A	43.889_9	a.m.u. A^2
I_B	198.628_0	a.m.u. A^2
I_C	242.747_2	a.m.u. A^2
$I_C-I_A-I_B$	.229	a.m.u. A^2

Table V. Cl^{35} nuclear quadrupole coupling constants in cis-$CHCl^{35}$ $CHCl^{35}$

χ_{aa}	3.7 ± .2 Mc
χ_{bb}	-35.6 ± .2 Mc
χ_{cc}	31.9 ± .2 Mc

Table VI. Comparison of observed and calculated multiplet patterns. Only the well-resolved components are compared here

Rotational transition	F_I transitions $(F'_\epsilon \rightarrow F'_\epsilon) - (F_\epsilon \rightarrow F_\epsilon)$	Differences in Mc Observed	Calculated
$3_{03} \rightarrow 3_{12}$	$(5_2 \rightarrow 5_2) - (6_3 \rightarrow 6_3)$	6.12	6.09
	$(5_2 \rightarrow 5_2) - (3_2 \rightarrow 3_2)$	9.38	9.42
	$(5_2 \rightarrow 5_2) - (3_3 \rightarrow 3_3)$	- 4.71	- 4.66
	$(5_2 \rightarrow 5_2) - (4_3 \rightarrow 4_3)$	-10.97	-11.07
$4_{04} \rightarrow 4_{14}$	$(5_3 \rightarrow 5_3) - (4_1 \rightarrow 4_1)$	21.87	21.96
	$(4_3 \rightarrow 4_3) - (4_2 \rightarrow 4_2)$	17.07	17.12
	$(6_3 \rightarrow 6_3) - (4_2 \rightarrow 4_2)$	15.42	15.42
	$(4_3 \rightarrow 4_3) - (7_3 \rightarrow 7_3)$	14.16	14.22
	$(5_3 \rightarrow 5_3) - (7_3 \rightarrow 7_3)$	18.98	19.05
	$(6_3 \rightarrow 6_3) - (7_3 \rightarrow 7_3)$	12.55	12.52
	$(7_3 \rightarrow 7_3) - (4_2 \rightarrow 4_2)$	2.87	2.90
$6_{06} \rightarrow 6_{14}$	$(4_3 \rightarrow 4_3) - (6_1 \rightarrow 6_1)$	5.22	5.28
	$(9_3 \rightarrow 9_3) - (3_3 \rightarrow 3_3)$	5.35	5.38
	$(7_3 \rightarrow 7_3) - (6_1 \rightarrow 6_1)$	25.94	24.88
	$(7_3 \rightarrow 7_3) - (3_3 \rightarrow 3_3)$	28.96	27.88
	$(8_3 \rightarrow 8_3) - (4_3 \rightarrow 4_3)$	10.50	10.40
	$(8_3 \rightarrow 8_3) - (9_3 \rightarrow 9_3)$	13.70	13.67
	$(8_3 \rightarrow 8_3) - (6_1 \rightarrow 6_1)$	15.93	16.04
	$(8_3 \rightarrow 8_3) - (3_3 \rightarrow 3_3)$	18.97	19.03

Table VI. (cont.) Comparison of observed and calculated multiplet patterns. Only the well-resolved components are compared here

Rotational transition	F_{ϵ} transitions $(F'_{\epsilon} \to F'_{\epsilon}) - (F_{\epsilon} \to F_{\epsilon})$	Differences in Mc Observed	Calculated
$8_{08} \to 8_{17}$	$(10_3 \to 10_3) - (5_3 \to 5_3)$	19.52	19.41
	$(11_3 \to 11_3) - (8_1 \to 8_1)$	2.00	2.09
	$(10_3 \to 10_3) - (8_1 \to 8_1)$	17.08	16.92
	$(6_3 \to 6_3) - (11_3 \to 11_3)$	5.68	5.66
$5_{15} \to 6_{06}$	$(6_3 \to 7_3) - (5_3 \to 6_3)$	2.20	2.18
	$(6_3 \to 7_3) - (7_3 \to 8_3)$	3.70	3.58
	$(6_3 \to 7_3) - (8_3 \to 9_3)$	9.96	9.92
	$(6_3 \to 7_3) - (5_1 \to 6_1)$	11.30	11.26
	$(6_3 \to 7_3) - (2_3 \to 3_3)$	12.98	13.06
	$(5_3 \to 6_3) - (5_1 \to 6_1)$	8.98	9.08
	$(7_3 \to 8_3) - (8_3 \to 9_3)$	6.26	6.34
$0_{00} \to 1_{11}$ *	$3_2 - 2_3$	5.93	5.86
	$3_2 - 3_3$	10.80	10.68
	$3_2 - 4_3$	- 3.54	- 3.56
	$3_2 - 1_1$	- 7.08	- 7.12
	$1_1 - 3_3$	17.80	17.80
	$1_1 - 2_3$	12.93	12.98
	$4_3 - 3_3$	14.28	14.24
	$4_3 - 2_3$	9.41	9.42

* As the 0_{00} rotational level is not split by the quadrupole interaction the differences in the 1_{11} level are given here.

CAPTIONS FOR FIGURES

Figure 1 - $CHCl^{35}$ $CHCl^{35}$ $6_{06} \rightarrow 6_{15}$ transition

Figure 2 - $CHCl^{35}$ $CHCl^{35}$ $0_{00} \rightarrow 1_{11}$ transition

Figure 3 - $CHCl^{35}$ $CHCl^{35}$ $5_{15} \rightarrow 6_{06}$ transition

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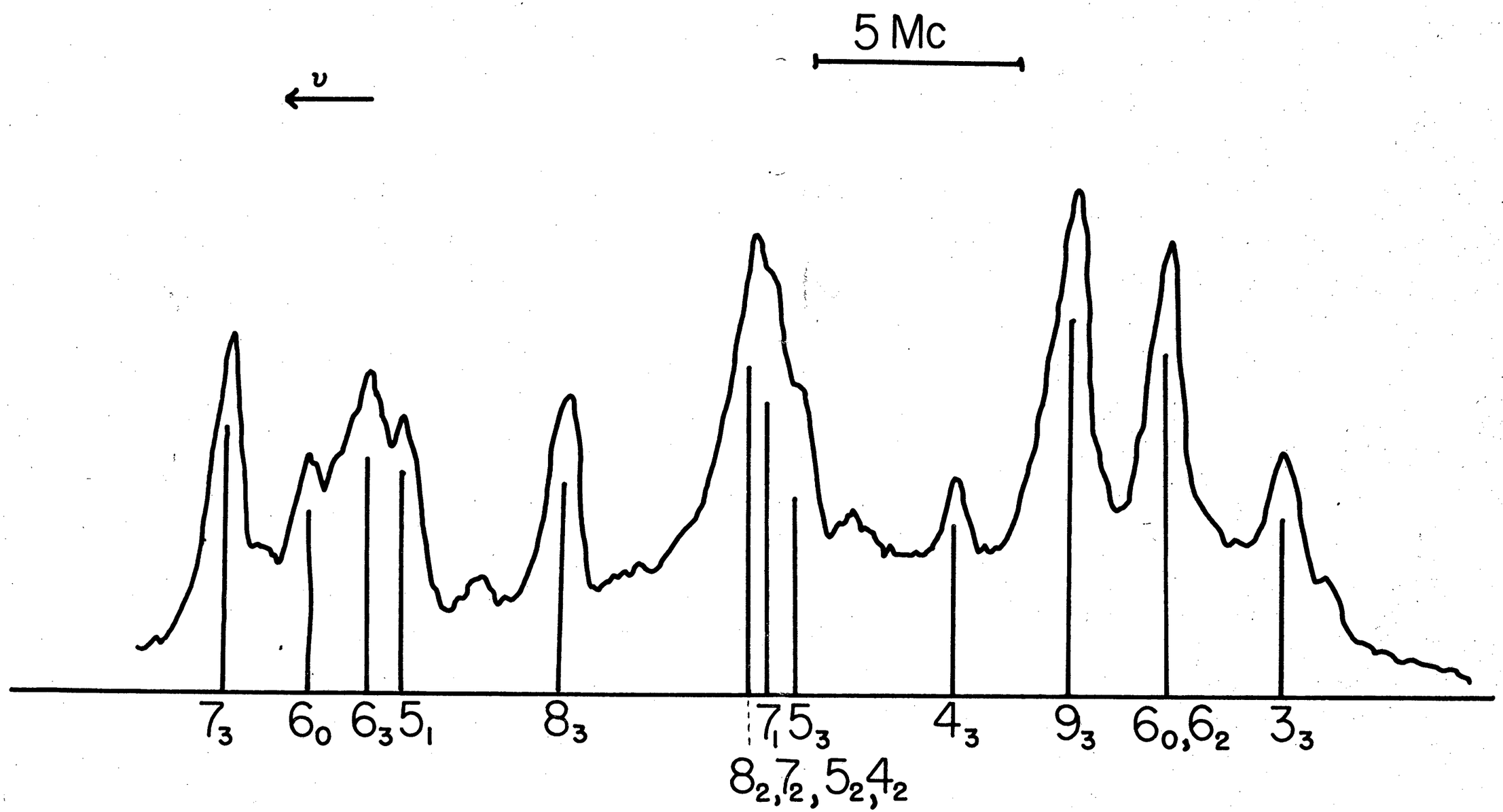

FIG. 1.

60.535-2

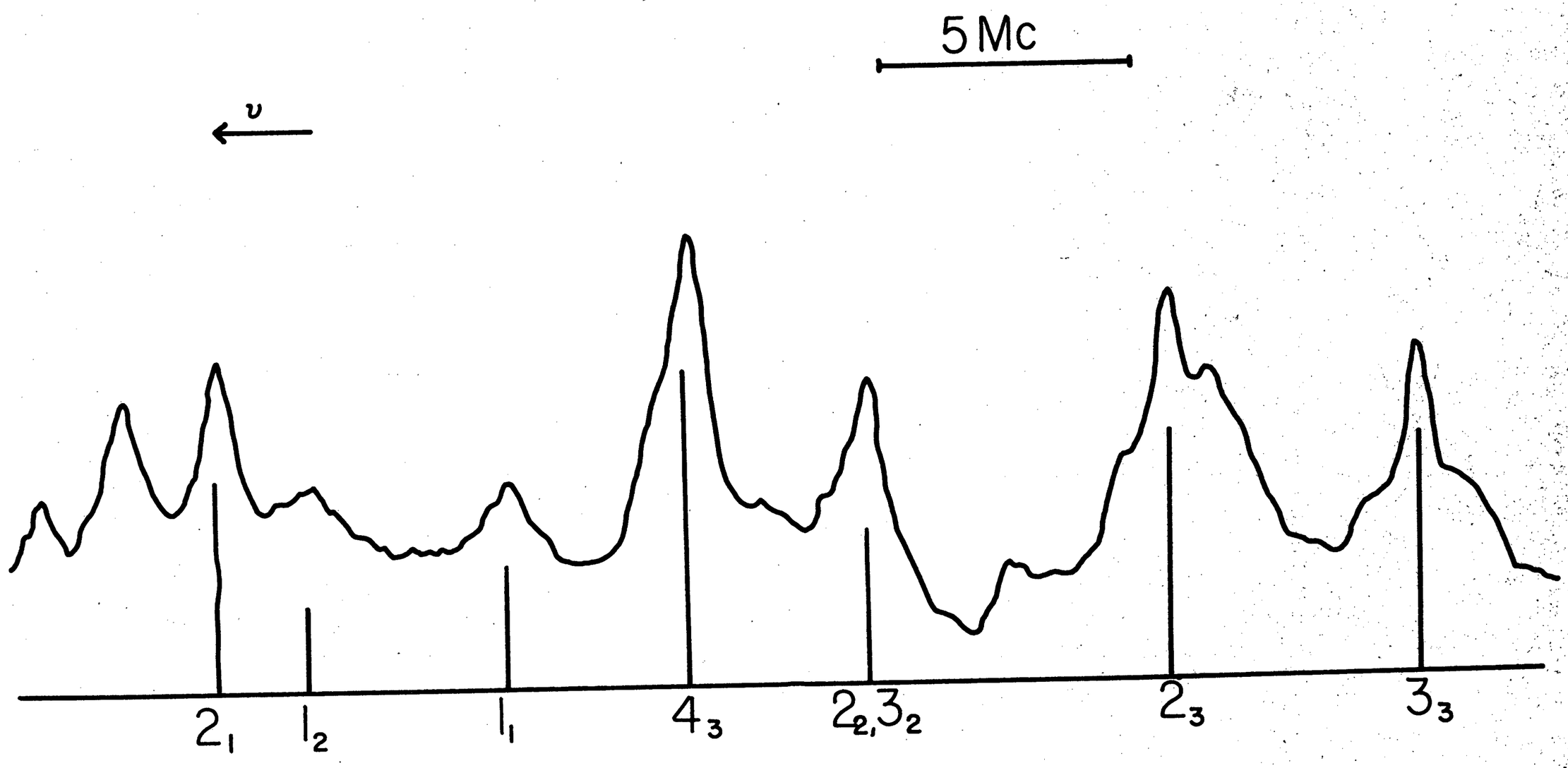

FIG. 2.

60-336-2

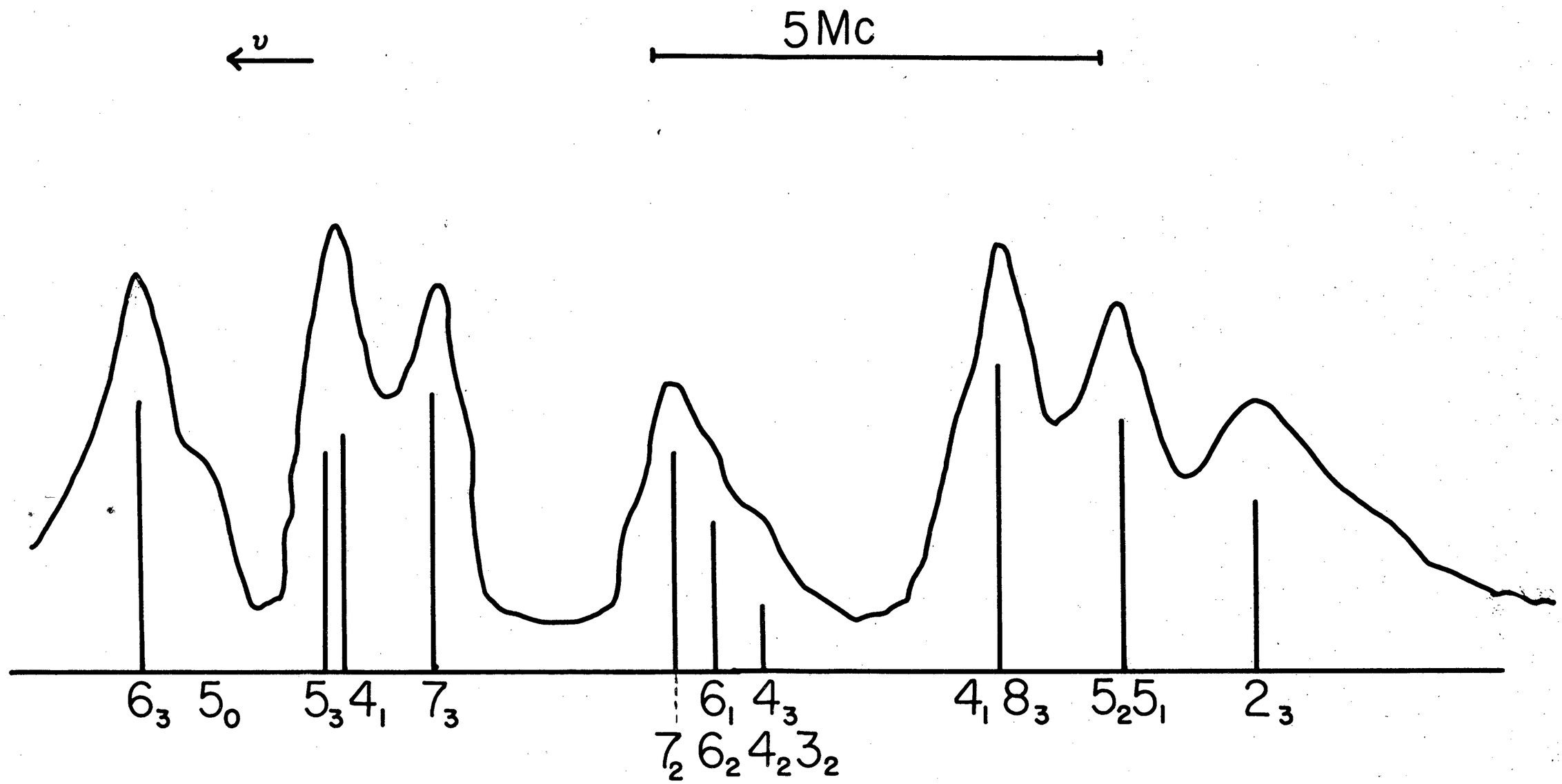

FIG. 3.

60,537-2