in good agreement. The mass of tritium, so far as we know, has not been measured directly, but it has been calculated with high accuracy from nuclear reaction energies. The $m_D=2.014741(\pm 3)$ value which we used here is given by Ogata and Matsuda,[14] and the $m_T=3.016997(\pm 11)$ is that given by Whaling, Fowler, and Lauritsen.[15] This value m_D with our mass ratio leads to the spectroscopy value $m_T=3.01700_8$ for the tritium mass.

After our measurements on TBr were complete we received the Progress Report from the Columbia Radiation Laboratory dated October 30, 1954 which states that A. H. Nethercot and B. Rosenblum[16] have also made measurements on the $J=0\rightarrow 1$ transition of TBr.

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[14] K. Ogata and H. Matsuda, Phys. Rev. **89**, 27 (1953).

[15] Whaling, Fowler, and Lauritsen, Phys. Rev. **83**, 512 (1951).

[16] *Note added in proof.*—The work of Nethercot and Rosenblum has now been published [Phys. Rev. **97**, 84 (1955)].

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Fermi Resonance in the Microwave Spectrum of Linear *XYZ* Molecules*

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Measurements of the rotation-interaction constants α_i for the various vibrational states in the microwave spectrum of OCS and OCSe show little consistency. These discrepancies are explained within experimental accuracy as being due to interaction between adjacent vibrational levels with quantum numbers v_1, v_2, v_3 and v_1-1, v_2+2, v_3. Resonance of this type, called Fermi resonance, has also been found in ICN but the interaction constant is very much smaller.

THE rotational frequency for any vibrational state of a linear *XYZ* molecule is given to a first approximation by

$$\begin{aligned}\nu_{J-1\rightarrow J}&=2JB_v-4D_v(J^3-l^2J),\\ B_v&=B_e-\alpha_1(v_1+\tfrac{1}{2})-\alpha_2(v_2+1)-\alpha_3(v_3+\tfrac{1}{2}),\end{aligned}\tag{1}$$

where B_e is the rotational constant, assuming the nuclei to be in their equilibrium positions, and is inversely proportional to the moment of inertia of the molecule; D_v is the centrifugal distortion coefficient in the vibrational state v; J is the quantum number of the total angular momentum; v_i the quantum number of the ith vibrational mode; and q is the l-type doubling constant.

In this type of molecule, the centrifugal distortion is usually small compared to the effects to be considered and can be neglected. The second vibrational mode v_2, the bending mode, is degenerate. Owing to vibration-rotation interaction this degeneracy is lifted and is split into two levels, called l-type doublet, and is designated by $v_2^{l_1}$ and $v_2^{l_2}$, respectively. The l-type splitting is appreciable only when $l=1$ and is given by $\Delta\nu=2qJ$.[1] The l-type coupling constant varies slightly with J by an amount of the order of $q(B/\omega)J(J+1)$.[2]

The rotation-vibration constants α_i depend in a complex way on the potential function, on the moment of inertia, and on the vibrational frequencies ω of the molecule. Experimentally, one can determine the values of α by measuring the frequency difference between the ground state and the excited vibrational states or between adjacent vibrational states. Thus, for example, the frequency difference between the ground state (000) and the center of the l-type doublet excited vibrational state (010) in the $J=1\rightarrow 2$ transition should equal $4\alpha_2$.

It has been the hope of microwave spectroscopists that rather exact nuclear mass ratios could be determined from the spectra of linear *XYZ* molecules with various isotopic substitutions by measuring the rotational frequencies and the values of the rotation-vibration constants to obtain the equilibrium moments of inertia of the various isotopic molecules. However, discrepancies have appeared in the measurement of the α's from various vibrational states.[3] These discrepancies are illustrated in Table I for OCS. Frequency shifts as high as 17 Mc/sec are found for some vibrational states in the $J=1\rightarrow 2$ transition and similar shifts in the $J=2\rightarrow 3$ transition. The (02^00) line, moreover, does not coincide with the center of the unsplit doublet (02^20), indicating that the perturbations depend not only on the energy of the vibrations but on their symmetry as well. Similar discrepancies have been observed for OCSe and smaller ones for ICN.

These anomalies may be explained as perturbations

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* This work was supported jointly by the U. S. Signal Corps and the Office of Naval Research.

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

[2] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill Book Company, Inc., 1955), Chap. II has a detailed discussion on vibration-rotation interaction.

[3] These discrepancies were reported for OCS by R. G. Shulman and C. H. Townes, Phys. Rev. **75**, 1318(A) (1949).

between nearly degenerate vibrational states of the same symmetry. Such perturbations between vibrational states have been first recognized by Fermi[4] in the spectrum of CO_2 and are usually called Fermi resonance. The repulsion between adjacent levels due to Fermi resonance changes the effective B value and destroys the expected regularity as predicted by Eq. (1). Figure 1 illustrates the effects of resonance on the rotational levels of OCS in the $J=2\rightarrow3$ transition.[5] The arrows indicate the effect of the perturbations. By allowing for these perturbations consistent values of the α's can be obtained.

THEORY AND RESULTS

Effect of Fermi Resonance on Vibrational Levels

Herzberg has given an elementary theory of perturbation between vibrational levels.[6] This theory will be adapted for the linear XYZ molecule and its effect on the rotational spectrum. If there are n resonating levels on the same symmetry the perturbed energy levels W are given by first-order perturbation theory by the solution of the nth order determinant:

$$\begin{vmatrix} W_1^0-W & W_{21} & W_{31} & \cdots & W_{n1} \\ W_{12} & W_2^0-W & W_{32} & \cdots & W_{n2} \\ \cdots & \cdots & \cdots & & \cdots \\ \cdots & \cdots & \cdots & & \cdots \\ W_{1n} & W_{2n} & W_{3n} & \cdots & W_{nn}^0-W \end{vmatrix}=0, \qquad (2)$$

where W_i^0 are the unperturbed energy levels;

$$W_{ni}=\int\psi_n^0V\psi_i^0d\tau;\ \psi_n^0$$

is the zero approximation of the wave function for the vibrational level n. They must be of the same symmetry type, and therefore must be states of the same angular momentum l about the molecular axis to have matrix elements W_{ni} different from zero. The perturbation interaction is given by the anharmonic terms of the potential function, which, in the case of the linear XYZ molecule, can be written as

$$2V=k_{111}q_1^3+k_{113}q_1^2q_3+k_{122}q_1q_2^2+k_{123}q_1q_3^2 \\ +k_{223}q_2^2q_3+k_{333}q_3^2+\text{quartic terms.} \qquad (3)$$

The constants k_{ijk} are force constants and the q_i are the normal coordinates.

Examples of Fermi resonance between adjacent levels of the same symmetry are shown in Fig. 2. Thus, for example, the two levels (02^00) and (100) perturb each other; similarly, the three levels (04^00), (12^00), and (001).

If only two levels perturb each other, the difference in energy between the perturbed levels is given by

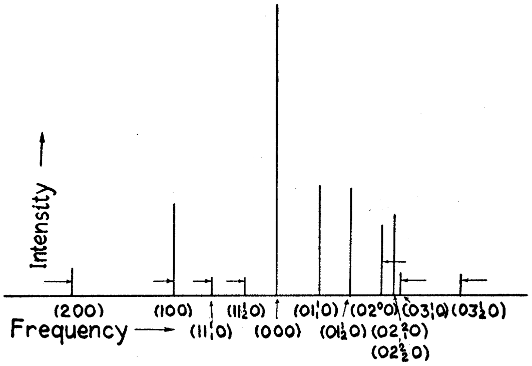

FIG. 1. Rotational transition $J=2\rightarrow3$ of OCS. The arrows indicate the effect of Fermi resonance perturbation in shifting the rotational frequencies. The vibrational state is given by quantum numbers (v_1,v_2,v_3) in brackets, v_2 having a superscript $|l|$. In the case $|l|=1$, the subscript 1 refers to the lower-frequency component and 2 to the higher-frequency component of the doublet. Intensities are calculated for approximately 800°C.

$$\Delta W=(4|W_{12}|^2+\delta^2)^{\frac{1}{2}}, \qquad (4)$$

where $\delta=W_n^0-W_i^0$ is the separation between the unperturbed levels. In the special case of interest when the two levels with quantum numbers $(v_1,v_2^{|l|},v_3)$ and $(v_1-1,\ v_2+2^{|l|},\ v_3)$ resonate, the interaction potential W can be evaluated:

$$W_{(v_1,\ v_2^{|l|},\ v_3;\ v_1-1,\ v_2+2^{|l|},\ v_3)} \\ =\frac{-h^{\frac{3}{2}}}{16\sqrt{2}\pi^3c^{\frac{3}{2}}\omega_1^{\frac{1}{2}}\omega_2}k_{122}v_1^{\frac{1}{2}}[(v_2+2)^2-l^2]^{\frac{1}{2}}, \qquad (5)$$

where ω_1, ω_2, ω_3 are the fundamental frequencies of the XYZ molecule. It is noteworthy that the center of gravity of the perturbed and unperturbed levels coincide.

The eigenfunctions of the new states are a mixture of the unperturbed eigenfunctions and are given by

$$\psi_1=a\psi_1^0-b\psi_2^0,\quad \psi_2=b\psi_1^0+a\psi_2^0,$$

where

$$a^2=\frac{[4|W_{12}|^2+\delta^2]^{\frac{1}{2}}+\delta}{2[4|W_{12}|^2+\delta^2]^{\frac{1}{2}}}=\frac{1}{2}+\frac{\delta}{2[4|W_{12}|^2+\delta^2|^{\frac{1}{2}}}, \qquad (6)$$

and

$$a^2+b^2=1.$$

In the case of resonance, the B values for the various vibrational states as determined from Eq. (1) refer now to the perturbed value. The unperturbed B values can be found as follows. Let B_1, B_2, $\cdots B_n$ refer to the measured rotation levels which resonate, and B_1^0, B_2^0, $\cdots B_n^0$ the unperturbed values in absence of resonance; then

$$B_i=a_i^2B_1^0+b_i^2B_2^0+c_i^2B_3^0+\cdots,$$

$$a^2+b^2+c^2+\cdots=1, \qquad (7)$$

$$\sum_i^n B_i=\sum_i^n B_i^0,$$

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[4] E. Fermi, Z. Physik 71, 250 (1931).

[5] Figure 1 is taken from reference 2 with the kind permission of Professor Townes.

[6] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945).

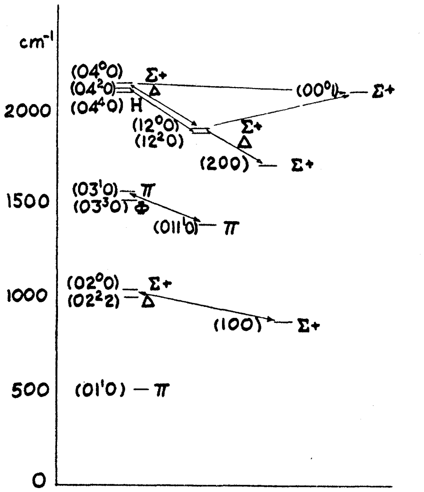

FIG. 2. Vibrational states in OCS. Arrows indicate possible interaction between vibrational levels.

where the summation is carried out over all levels. In the case of interest of the two resonating levels (v_1,v_2,v_3) and $(v_1+1,\ v_2+2,\ v_3)$, a knowledge of the two experimental values of $B_{(v_1v_2v_3)}$ and $B_{(v_1-1,\ v_2+2,\ v_3)}$ and the unperturbed value of $B_{(010)}{}^0$ is necessary to determine the unperturbed values of α_1 and α_2. From Eqs. (4) and (7) and the separation ΔW between the vibrational levels (known from infrared data) the unperturbed separation δ and the interaction constant W_{12} can be evaluated.

OCS

Figure 2 shows the energy levels of the various vibrations and the arrows indicate the possible interactions which might cause Fermi resonance. Table I lists the observed frequencies for $J=1\rightarrow2$ and $J=2\rightarrow3$ transitions (interacting levels are bracketed). The unperturbed value of α_2 is found from the separation between the rotational levels of states (000) and (01^{1}0). The frequency shift of the (02^{0}0) level due to Fermi resonance may be obtained from the known value of α_2. The unperturbed value of α_1 is now determined since the frequency change of the (100) state must be equal and opposite to that of (020). From Eq. (7), one finds $a^2=0.9434$ and $b^2=0.0566$. The perturbed separation between the vibrational levels has been measured by Bartunek and Barker.[7] (The $l=0$ and $l=2$ transitions are interchanged in their paper.) Using their results, one finds for the interaction energy $W_{12}=43.2$ cm^{-1} and the unperturbed separation $\delta=166.6$ cm^{-1}. The more recent measurements by Callomon *et al.*[8] give the separation ΔW as 188.8 cm^{-1}, and one finds $\delta=167.4$ cm^{-1} and $W_{12}=43.6$ cm^{-1}. The correction factors due to Fermi resonance are now calculated using the latter values and Eq. (5), and reversing the process. They are listed in column 4. Some small discrepancies remain, possibly because Eq. (1) is a first-order approximation and, therefore, varies slightly with the vibrational state. Slightly improved values are obtained using 171.6 cm^{-1} and 45.8 cm^{-1}. They are given in parentheses in column 4.

OCSe^{80}

In OCSe^{80}, a shift of 4.22 Mc/sec due to Fermi resonance was observed as indicated in Table II. Using vibrational frequencies[9] of OCSe, $\omega_1=642\pm4$, $\omega_2=466\pm4$, $\omega_3=2022\pm4$ (all in units of cm^{-1}), one obtains the unperturbed values $\alpha_1=14.01$ Mc/sec, $\alpha_2=-6.88$ Mc/sec, $a^2=0.975$, $b^2=0.025$, $W_{12}=45$ cm^{-1} and $\delta=275$ cm^{-1}.

ICN

The spectrum of ICN is complicated by quadrupole interaction. The excited states $v_2=2$, $l=2$, and $v_2=2$, $l=0$ are separated by quadrupole effects. After correcting for second-order corrections for quadrupole

TABLE I. Fermi resonance perturbations in the rotational spectrum of OCS.

Rotational transition	Vibrational state $v_1\ v_2{}^{\lvert l\rvert}\ v_3$	Frequency Mc/sec	Correction due to Fermi resonance perturbation Mc/sec[a]	Intensity cm^{-1}
$J=1\rightarrow2$	0 0 0	24 325.92[b]	0	5.5×10^{-5}
	0 1^{l_1} 0	24 355.50[b]	0	4.4×10^{-6}
	0 1^{l_2} 0	24 381.07		4.4×10^{-6}
	1 0 0	24 253.51[c]	− 9.52 (− 9.85)	8.7×10^{-7}
	0 2^0 0	24 401.0[d]	+ 9.52 (9.85)	3.2×10^{-7}
	2 0^0 0	24 179.62[c]	−16.4 (−17.5)	1.3×10^{-8}
	1 2^0 0	...	+16.4 (17.5)	...
	1 1^{l_1} 0	24 289.97	−16.2 (−17.15)	6.2×10^{-8}
	1 1^{l_2} 0	24 316.76		6.2×10^{-8}
	0 3^{l_1} 0	24 411[d]	+16.2 (17.15)	2.8×10^{-8}
	0 3^{l_2} 0	24 459		2.8×10^{-8}
$J=2\rightarrow3$	0 0 0	36 488.82[e]	0	1.5×10^{-4}
	0 1^{l_1} 0	36 532.47	0	1.3×10^{-5}
	0 1^{l_2} 0	36 570.83		1.3×10^{-5}
	0 2^2 0	36 615.3	0	2.2×10^{-6}
	0 2^0 0	36 600.81	−14.28 (−14.83)	1.1×10^{-6}
	1 0^0 0	...	+14.28 (14.83)	...

[a] Calculated with the values $\delta=167.4$ cm^{-1}, $W_{12}=43.6$ cm^{-1}. Values in parentheses were calculated with $\delta=171.6$ cm^{-1} and $W_{12}=45.8$ cm^{-1}. Interacting levels are bracketed.
[b] Townes, Holden, and Merritt, Phys. Rev. 74, 1113 (1947).
[c] Bianco and Roberts (private communication).
[d] R. G. Shulman, Thesis, Columbia University, 1949 (unpublished).
[e] Strandberg, Wentink, and Kyhl, Phys. Rev. 75, 270 (1949).

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[7] P. F. Bartunek and E. F. Barker, Phys. Rev. 48, 518 (1935).

[8] Callomon, McKean, and Thompson, Proc. Roy. Soc. (London) **A208**, 341 (1951).

[9] We are grateful to Professor R. F. Lord for informing us of the unpublished vibration frequencies of OCSe.

effects,[10] a small discrepancy of 0.35 Mc/sec is found between these lines. This yields a value of $W_{12}=3$ cm^{-1}, $\delta=171$ cm^{-1}, $\alpha_1=9.33$ Mc/sec, and $\alpha_2=-6.88$ Mc/sec.

Tetenbaum[10a] has made a detailed analysis of the spectrum of BrCN. Unlike our value of the interaction constant W_{12} for ICN he finds a much larger value of 61.5 cm^{-1} for BrCN. This large difference is somewhat puzzling. It is intended to make measurements on the higher vibrational states of ClCN and to compare it with these two molecules.

TABLE II. Fermi resonance perturbations in the rotational spectrum of OCSe^{80} and ICN.

Molecule	Vibrational state $v_1\ v_2^{\lvert l\rvert}\ v_3$	Frequency Mc/sec	Correction due to Fermi res. perturbation Mc/sec	Intensity cm^{-1}
OCSe^{80} $J=2\rightarrow3$	0 0 0	24 105.85[a]	0	6.8×10^{-6}
	0 1^{l_1} 0	24 137.80	0	7.2×10^{-7}
	0 1^{l_2} 0	24 156.46	0	7.2×10^{-7}
	1 0 0	24 026.26[b]	−4.22	3.1×10^{-7}
	0 2^0 0	24 183.97	+4.22	8.1×10^{-8}
	0 2^2 0	24 188.18	0	1.6×10^{-7}
ICN $J=3\rightarrow4$ $E_i=11/2\rightarrow$ $F_l=13/2$	0 0 0	25 823.08[c]	0	7.5×10^{-5}
	1 0 0	25 748.18[c]	−0.35	7.0×10^{-6}
	0 2^0 0	25 979.72	+0.35	1.7×10^{-6}
	0 2^2 0	26 046.32	0	3.5×10^{-6}

[a] Geschwind, Minden, and Townes, Phys. Rev. **78**, 174 (1950).
[b] Strandberg, Wentink, and Hill, Phys. Rev. **75**, 827 (1949). Frequency corrected by 0.13 Mc/sec so that the ground state should coincide with that in reference a.
[c] Townes, Holden, and Merritt, Phys. Rev. **74**, 1113 (1948).

TABLE III. Summary of results.

Molecule	Vibrational frequencies cm^{-1} v_1	v_2	v_3	Interaction constant cm^{-1}	Rotation-vibration interaction in Mc/sec α_1	α_2	α_3
CO$_2$[a]	1342.8	667.3	2349.3	51.2	13.2	−21.6	92.1
OCS	865	524	2066[b]	43.6(45.8)	20.5	−10.59	
OCSe	642	466	2022[c]	45	14.0	− 6.88	

[a] Taylor, Benedict, and Strong, J. Chem. Phys. **20**, 1884 (1952); Benedict, Herman, and Silverman, J. Chem. Phys. **19**, 1325 (1951).
[b] See reference 8.
[c] Professor F. C. Lord (private communication).

Table III summarizes these results. It is interesting to note the similarity in values of W_{12} for CO$_2$, OCS, and OCSe.

Because of these types of perturbations in polyatomic molecules it will be very difficult to determine the equilibrium moments of inertia for several isotopic species with sufficient accuracy to take full advantage of the accuracy of microwave measurements for nuclear mass determinations. In some cases, allowance can be made for Fermi resonance. But in others, as in the determination of the third vibrational mode, it may be very difficult since the level may be perturbed by several adjacent levels as seen from Fig. 2. On the other hand, isotopic mass ratios can be determined with good accuracy from the effective rotational constants of polyatomic molecules if two isotopic masses are known.[11]

This work was carried out at the Department of Physics, Columbia University, in 1949, and was reported at the American Physical Society meeting at Washington in 1950.[12] The author would like to thank Professor C. H. Townes for the constant advice and help which made this work possible.

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[10] J. Bardeen and C. H. Townes, Phys. Rev. **73**, 627 (1948).

[10a] S. J. Tetenbaum, Phys. Rev. **86**, 440 (1952).

[11] Townes, Holden, and Merritt, Phys. Rev. **74**, 1113 (1948).

[12] W. Low and C. H. Townes, Phys. Rev. **79**, 224(A) (1950).