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NATIONAL BUREAU OF STANDARDS REPORT

4649

MICROWAVE SPECTROSCOPY OF LABILE MOLECULES

I. Transition Types, Frequencies, and Intensities

R. J. Kurland and D. E. Mann
Thermodynamics Section
Heat and Power Division

March 1956

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NATIONAL BUREAU OF STANDARDS

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NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT	NBS REPORT
0302-10-2606	4649

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Sponsored in part by:

United States Air Force through the
Air Force Office of Scientific Research of the
Air Research and Development Command

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U. S. DEPARTMENT OF COMMERCE
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BIBLIOGRAPHICAL CONTROL SHEET

AFOSR TN- -

ASTIA Document No. AD

1. Originating Agency and Monitoring Agency:

O.A. National Bureau of Standards, Washington, C. C.

M.A. Physics Division, Air Force Office of Scientific Research

2. Originating Agency and Monitoring Agency Report Numbers:

O. A. N.S.B. Report No. 4649

M. A. AFOSR TN- -

AD

3. Title and Classification:

Microwave Spectroscopy of Labile Molecules.I. Transition Types, Frequencies, and Intensities. (Unclassified)

4. Personal Authors:

Kurland, R. J.

Mann, D. E.

5. Date of Report:

March, 1956

6. Pages:

7. Illustrative Material:

None

8. Prepared for Contract:

C.S.O. 680-56-19

9. **Prepared for Project:**

AFOSR Physics 1-15

10. **Security Classification**

Unclassified

11. **Distribution Limitations:**

None

12. **Abstract:**

The available data for a number of labile diatomic and some triatomic molecules have been reviewed and summarized in order to classify their expected microwave spectra by type, frequency, and intensity. Estimates are given for lamda-, and rho- type multiplet transitions as well as for pure rotational spectra expected to fall in a readily accessible region of the microwave spectrum. Some discussion of methods of preparation of certain unstable species suitable for microwave investigations is also given.

FOREWORD

This report is the first of a projected series which will describe various stages in an attempt to observe microwave spectra of free radicals and other labile molecular species.

Comments on the research herein described and the exchange of reports are invited. Communications may be addressed to Dr. D. E. Mann, Room 204, Building 8, National Bureau of Standards, Washington 25, D. C.

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MICROWAVE SPECTROSCOPY OF LABILE MOLECULES

I. Transition Types, Frequencies and Intensities[†]

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ABSTRACT

The available data for a number of labile diatomic and some triatomic molecules have been reviewed and summarized in order to classify their expected microwave spectra by type, frequency, and intensity. Estimates are given for lamda-, and rho-type multiplet transitions as well as for pure rotational spectra expected to fall in a readily accessible region of the microwave spectrum. Some discussion of methods of preparation of certain unstable species suitable for microwave investigations is also given.

[†] This work has been supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under C.S.O. 680-56-19.

[‡] National Research Council - National Bureau of Standards Postdoctoral Research Associate for 1956.

THE MICROWAVE SPECTROSCOPY OF FREE RADICALS, LABILE MOLECULES, AND HIGH TEMPERATURE SPECIES

I. Types, Frequencies, and Intensities of Expected Transitions

INTRODUCTION

This report is intended to serve as a preliminary guide in the formulation of a program for the microwave spectroscopy of labile or high-temperature species. Three questions must be answered about any such species to be investigated: do sufficiently intense transitions fall in the accessible microwave frequency range; is there a convenient source for the species; are there means by which the concentration of the species in the absorption cell can be monitored or estimated.

In many cases spectral and kinetic data for a species are not reliable or available. Further study by means of optical spectroscopy might be used to obtain the needed data in some of these cases.

PREDICTION OF THE SPECTRUM

The types of transitions the frequencies of which might fall within the microwave region may be conveniently classified as follows:

1. Electric Dipole Transitions.

   a. Rotational Transitions.

This classification includes those transitions which are essentially between rotational states. Molecules in $^1\Sigma$ states are treated in texts on conventional microwave spectroscopy[1]. For non-linear polyatomic free radicals (e.g. ClO_2 or NO_2[2]), the orbital angular momentum of the odd electron is quenched by the lower than $D_{\infty h}$ symmetry and the effect of the unpaired electron spin is manifested as fine structure in the lines corresponding to rotational transitions. The microwave transitions of those diatomic radicals for which the ρ or λ-type multiplet splitting is small may also be conveniently put in this classification.

(i). Diatomic Molecules

The transition frequencies are given by

$$\nu = 2B \ (J + 1) + \text{fine structure terms.}$$

The fine structure terms may be estimated from the considerations given in 1c. and 2.). The rotational constant $B = h/8\pi^2 I_0$ may be obtained from previous spectroscopic work or estimated by use of a likely value for the internuclear distance. The internuclear distance itself may be estimated from distances in similar diatomics or from values of the appropriate covalent bond radii. The rotational constants of diatomic species observed spectroscopically is given in Table I.

Table I

Rotational Transitions of Diatomics

Species	r* (Å)	B_e (10^4Mc)	Transition**	$2B(J_N + 1)$ (10^4Mc)	Fine Structure***
AgBr($X^1\Sigma$)	2.5	0.18	$4 \leftarrow 3$	1.4	-
AgCl($X^1\Sigma$)	2.2	0.39	$2 \leftarrow 1$	1.6	-
AgI ($X^1\Sigma$)	2.7	0.12	$5 \leftarrow 4$	1.2	-
AlBr($X^1\Sigma$)	-	0.477$^+$	$2 \leftarrow 1$	1.81	-
AlCl($X^1\Sigma$)	-	0.720$^+$	$2 \leftarrow 1$	2.88	-
AlF($X^1\Sigma$)	1.8	1.4	$1 \leftarrow 0$	2.8	-
AlI($X^1\Sigma$)	2.4	0.38	$2 \leftarrow 1$	1.6	-
AgO($X^2\Sigma$)	2.0	0.85	$1 \leftarrow 0$	1.7	ρ-type, ~300Mc
AlO($X^2\Sigma$)	-	1.92$^+$	$1 \leftarrow 0$	3.84	ρ-type, ~600Mc
AsO($X^2\Pi_{\frac{1}{2}}$)	1.7	1.3	$1\frac{1}{2} \leftarrow \frac{1}{2}$	3.9	λ-type, ~1700Mc
AsN($X^1\Sigma$)	1.6	1.6	$1 \leftarrow 0$	3.2	-
BaBr($X^2\Sigma$)	3.0	0.11	$6 \leftarrow 5$	1.3	ρ-type, ~100Mc
BaCl($X^2\Sigma$)	2.9	0.21	$3 \leftarrow 2$	1.3	ρ-type, ~600Mc
BaF($X^2\Sigma$)	2.6	0.45	$2 \leftarrow 1$	1.8	ρ-type, ~800Mc
BaI($X^2\Sigma$)	3.2	0.075	$8 \leftarrow 7$	1.2	ρ-type, ~ 60Mc
BaO($X^1\Sigma$)	-	0.936$^+$	$1 \leftarrow 0$	1.87	-
BaS($X^1\Sigma$)	2.25	0.38	$2 \leftarrow 1$	1.5	-
BBr($X^1\Sigma$)	-	1.47$^+$	$1 \leftarrow 0$	2.94	-
BCl($X^1\Sigma$)	-	2.07$^+$	$1 \leftarrow 0$	4.14	-
BeCl($X^2\Sigma$)	-	(2.4)$^+$	$1 \leftarrow 0$	4.8	ρ-type, ~100Mc

Table 1 (cont'd)

Rotational Transitions of Diatomics

Species	r* (Å)	B_e (10^4Mc)	Transition**	$2B({J \atop N} + 1)$ (10^4Mc)	Fine Structure***
BiBr($X^3\Sigma$?)	2.6	0.13	$5 \leftarrow 4$	1.3	ρ-type(?), ?
BiCl($X^3\Sigma$?)	2.5	0.27	$3 \leftarrow 2$	1.6	ρ-type(?), ?
BiF($X^3\Sigma$?)	2.2	0.60	$1 \leftarrow 0$	1.2	ρ-type(?), ?
BiI($X^3\Sigma$?)	2.8	0.080	$8 \leftarrow 7$	1.3	ρ-type(?), ?
BiO($X^2\pi_{\frac{1}{2}}$?)	2.2	0.69	$1\frac{1}{2} \leftarrow \frac{1}{2}$	2.1	λ-type(?), ?
BrO($X^2\pi_{\frac{1}{2}}$?)	1.8	1.2	$1 \leftarrow 0$	2.4	λ-type(?), ?
CaBr($X^2\Sigma$)	2.0	0.48	$2 \leftarrow 1$	1.9	ρ-type, ~80Mc
CaCl($X^2\Sigma$)	-	$(0.84)^+$	$1 \leftarrow 0$	1.68	ρ-type, ~100Mc
CaF($X^2\Sigma$)	-	$(0.966)^+$	$1 \leftarrow 0$	1.93	ρ-type, ~140Mc
CaI($X^2\Sigma$)	2.2	0.32	$2 \leftarrow 1$	1.3	ρ-type, ?
CaO($X^1\Sigma$)	2.0	1.1	$1 \leftarrow 0$	2.2	-
CaS($X^1\Sigma$)	2.3	0.52	$2 \leftarrow 1$	2.0	-
CBr($X^2\pi_{\frac{1}{2}}$)	1.9	1.3	$1\frac{1}{2} \leftarrow \frac{1}{2}$	3.9	λ-type, ?
CCl($X^2\pi_{\frac{1}{2}}$)	1.8	1.8	$1\frac{1}{2} \leftarrow \frac{1}{2}$	4.8	λ-type, ~200Mc
CSe($X^1\Sigma$)	1.7	1.8	$1 \leftarrow 0$	3.6	-
CP($X^2\Sigma$)	-	2.40^+	$1 \leftarrow 0$	4.8	ρ-type, ~-170Mc
CdBr($X^2\Sigma$)	2.6	0.16	$4 \leftarrow 3$	1.3	ρ-type?, ?
CdCl($X^2\Sigma$)	2.4	0.32	$2 \leftarrow 1$	1.3	ρ-type, ~-100Mc
CdF($X^2\Sigma$)	2.1	0.75	$1 \leftarrow 0$	1.5	ρ-type, ?
CdI($X^2\Sigma$)	2.8	0.11	$6 \leftarrow 5$	1.3	ρ-type, ~-30Mc

Table 1 (cont'd)

Rotational Transitions of Diatomics

Species	r* (Å)	B_e(10^4Mc)	Transition**	$2B({}^{J}_{N}+1)$ (10^4Mc)	Fine Structure***
ClO($X^2\pi_{\frac{1}{2}}$?)	1.7	1.6	$1\frac{1}{2} \leftarrow \frac{1}{2}$	4.8	λ-type, ?
CoBr(?)	?	?	-	-	-
CoCl(?)	?	?	-	-	-
CoO (?)	?	?	-	-	-
CrO (?)	?	?	-	-	-
CuBr($X^1\Sigma$)	2.2	0.30	$2 \leftarrow 1$	1.2	-
CuCl($X^1\Sigma$)	2.0	0.54	$2 \leftarrow 1$	2.2	-
CuF($X^1\Sigma$)	—	1.14^+	$1 \leftarrow 0$	2.28	-
CuI($X^1\Sigma$)	2.4	0.21	$3 \leftarrow 2$	1.3	-
CuO($X^2\Sigma$)	1.8	1.3	$1 \leftarrow 0$	2.6	ρ-type, ?
FeCl($X^6\Sigma$?)	2.2	0.51	$2 \leftarrow 1$	2.0	ρ-type, ?
FeO(?)	1.9	1.2	$1 \leftarrow 0$	2.4	?
GaO($X^2\Sigma$)	?	?	-	-	-
GaBr($X^1\Sigma$)	?	?	-	-	-
GaCl($X^1\Sigma$)	?	?	-	-	-
GaF($X^1\Sigma$)	?	?	-	-	-
GaI($X^1\Sigma$)	?	?	-	-	-
GeBr($X^2\pi_{\frac{1}{2}}$)	2.4	0.24	$2\frac{1}{2} \leftarrow 1\frac{1}{2}$	1.2	λ-type, ~350Mc
GeCl($X^2\pi_{\frac{1}{2}}$)	2.2	0.44	$1\frac{1}{2} \leftarrow \frac{1}{2}$	1.3	λ-type, ~700Mc

Table 1 (cont'd)

Rotational Transitions of Diatomics

Species	r* (Å)	$B_e(10^4\text{Mc})$	Transition**	$2B(\frac{J}{N} + 1)$ (10^4Mc)	Fine Structure***
GeF($X^2\pi_{\frac{1}{2}}$)	1.9	0.90	$1\frac{1}{2} \leftarrow \frac{1}{2}$	2.7	λ-type, ~2000Mc
GeO($X^1\Sigma$)	-	1.41$^+$	$1 \leftarrow 0$	2.82	-
GeS($X^1\Sigma$)	2.0	0.56	$2 \leftarrow 1$	2.2	-
GeSe($X^1\Sigma$)	2.4	0.23	$3 \leftarrow 2$	1.4	-
GeTe($X^1\Sigma$)	2.5	0.18	$4 \leftarrow 3$	1.4	-
HgBr($X^2\Sigma$)	2.5	0.14	$5 \leftarrow 4$	1.4	ρ-type, ~140Mc
HgCl($X^2\Sigma$)	2.2	0.34	$2 \leftarrow 1$	1.4	ρ-type, ~1300Mc
HgF($X^2\Sigma$)	2.0	0.69	$1 \leftarrow 0$	1.4	ρ-type, ~2500Mc
HgI($X^2\Sigma$)	2.7	0.089	$7 \leftarrow 6$	1.2	ρ-type, ?
InBr($X^1\Sigma$)	2.57$^+$	0.161	$4 \leftarrow 3$	1.29	-
InCl($X^1\Sigma$)	-	0.351$^+$	$2 \leftarrow 1$	1.41	-
InI($X^1\Sigma$)	2.86$^+$	0.105	$6 \leftarrow 5$	1.26	-
InO($X^2\Sigma$)	2.2	0.77	$1 \leftarrow 0$	1.5	ρ-type, ~700Mc
IO($X^2\pi_{\frac{1}{2}}$?)	2.1	0.85	$1\frac{1}{2} \leftarrow \frac{1}{2}$	2.6	λ-type, ?
LaO($X^2\Sigma$)	?	—	—	—	ρ-type, ?
MgBr($X^2\Sigma$)	2.2	0.51	$2 \leftarrow 1$	2.3	ρ-type, ~100Mc
MgCl($X^2\Sigma$)	2.1	0.85	$1 \leftarrow 0$	1.7	ρ-type, ~100Mc
MgF($X^2\Sigma$)	-	1.55$^+$	$1 \leftarrow 0$	3.10	ρ-type, ~80Mc
MgI($X^2\Sigma$)	2.4	0.43	$2 \leftarrow 1$	1.7	ρ-type, ?
MgO($X^1\Sigma$)	-	1.72$^+$	$1 \leftarrow 0$	3.44	-

Table 1 (cont'd)

Rotational Transitions of Diatomics

Species	r* (Å)	$B_e(10^4Mc)$	Transition**	$2B(\frac{J}{N}+1)$ (10^4Mc)	Fine Structure***
$MgS(X^1\Sigma)$	2.1	0.90	$1 \leftarrow 0$	1.8	-
$MnBr(X^7\Sigma)$	2.5	0.24	$3 \leftarrow 2$	1.4	ρ-type, ?
$MnCl(X^7\Sigma)$	2.4	0.39	$2 \leftarrow 1$	1.6	ρ-type, ?
$MnF(X^7\Sigma)$	2.1	0.82	$1 \leftarrow 0$	1.6	ρ-type, ?
$MnI(X^7\Sigma)$	2.7	0.18	$4 \leftarrow 3$	1.4	ρ-type, ?
MnO(X ?)	2.1	0.93	$1 \leftarrow 0$	1.9	?
$NiBr(X^2\pi_{\frac{1}{2}}?)$	2.2	0.31	$2\frac{1}{2} \leftarrow 1\frac{1}{2}$	1.6	λ-type, ?
$NiCl(X^2\pi_{\frac{1}{2}}?)$	2.1	0.54	$1\frac{1}{2} \leftarrow \frac{1}{2}$	1.6	λ-type, ~300Mc
$NiO(X^1\Sigma)$	1.8	1.2	$1 \leftarrow 0$	2.4	-
NBr(X?)	1.6	1.7	$1 \leftarrow 0$	3.4	?
$PbBr(X^2\pi_{\frac{1}{2}})$	2.7	0.12	$5\frac{1}{2} \leftarrow 4\frac{1}{2}$	1.3	λ-type, ~2000Mc(?)
$PbCl(X^2\pi_{\frac{1}{2}})$	2.5	0.26	$2\frac{1}{2} \leftarrow 1\frac{1}{2}$	1.3	λ-type, ~4000Mc(?)
$PbF(X^2\pi_{\frac{1}{2}})$	2.2	0.58	$1\frac{1}{2} \leftarrow \frac{1}{2}$	1.7	λ-type, ~4000Mc
$PbI(X^2\pi_{\frac{1}{2}})$	2.8	0.079	$7\frac{1}{2} \leftarrow 6\frac{1}{2}$	1.2	λ-type, ?
$PbO(X^1\Sigma)$	2.1	0.81	$1 \leftarrow 0$	1.6	-
$PbS(X^1\Sigma)$	-	0.318^+	$2 \leftarrow 1$	1.27	-
$PbSe(X^1\Sigma)$	2.5	0.14	$5 \leftarrow 4$	1.4	-
$PbTe(X^1\Sigma)$	2.7	0.085	$7 \leftarrow 6$	1.2	-
$PN(X^1\Sigma)$	-	2.35^+	$1 \leftarrow 0$	4.70	-
SbCl(X?)	2.4	0.32	$2 \leftarrow 1$	1.3	?
SbF(X?)	2.1	0.70	$1 \leftarrow 0$	1.4	?

Table I (cont'd)

Rotational Transitions of Diatomics

Species	r* (Å)	B_e (10^4Mc)	Transition**	$2B(\frac{J}{N}+1)$ (10^4Mc)	Fine Structure ***
SbN($X^1\Sigma$)	2.0	0.95	$1 \leftarrow 0$	1.9	-
SbO($X^2\pi_{\frac{1}{2}}$)	2.1	0.81	$1\frac{1}{2} \leftarrow \frac{1}{2}$	2.4	λ-type, ~3000Mc
ScO($X^2\Sigma$)	?	-	-	-	ρ-type ?
SeO($X^1\Sigma$)	1.7	1.3	$1 \leftarrow 0$	2.6	-
SiBr($X^2\pi_{\frac{1}{2}}$)	2.1	0.58	$1\frac{1}{2} \leftarrow \frac{1}{2}$	1.7	λ-type, ~200Mc
SiCl($X^2\pi_{\frac{1}{2}}$)	1.9	0.90	$1\frac{1}{2} \leftarrow \frac{1}{2}$	2.7	λ-type, ~200Mc
SiF($X^2\pi_{\frac{1}{2}}$)	-	1.26^+	$1\frac{1}{2} \leftarrow \frac{1}{2}$	3.84	λ-type, ~ 300Mc
SiN($X^2\Sigma$)	-	2.19^+	$1 \leftarrow 0$	4.38	ρ-type, ?
SiO($X^1\Sigma$)	-	2.18^+	$1 \leftarrow 0$	4.36	-
SiS($X^1\Sigma$)	-	0.906^+	$1 \leftarrow 0$	1.81	-
SiSe($X^1\Sigma$)	2.0	0.58	$2 \leftarrow 1$	2.3	-
SiTe($X^1\Sigma$)	2.2	0.45	$2 \leftarrow 1$	1.8	-
SnBr($X^2\pi_{\frac{1}{2}}$)	2.5	0.16	$4\frac{1}{2} \leftarrow 3\frac{1}{2}$	1.4	λ-type, ~500Mc
SnCl($X^2\pi_{\frac{1}{2}}$)	2.4	0.33	$2\frac{1}{2} \leftarrow 1\frac{1}{2}$	1.6	λ-type, ~1000Mc
SnF($X^2\pi_{\frac{1}{2}}$)	2.1	0.70	$1\frac{1}{2} \leftarrow \frac{1}{2}$	2.1	λ-type, ~3100Mc
SnO($X^1\Sigma$)	-	1.06^+	$1 \leftarrow 0$	2.12	-
SnS($X^1\Sigma$)	-	0.471	$2 \leftarrow 1$	1.84	-
SnSe($X^1\Sigma$)	2.2	0.23	$3 \leftarrow 2$	1.4	-
SnTe($X^1\Sigma$)	2.3	0.16	$4 \leftarrow 3$	1.3	-
SO($X^3\Sigma$)	-	2.11^+	$1 \leftarrow 0$	4.22	ρ-type, ~100Mc

Table I (cont'd)

Rotational Transitions of Diatomics

Species	r* (Å)	B_e(10^4Mc)	Transition**	$2B(J_N + 1)$ (10^4Mc)	Fine Structure***
SrBr($X^2\Sigma$)	3.0	0.13	$5 \leftarrow 4$	1.3	ρ-type, ~100Mc
SrCl($X^2\Sigma$)	2.9	0.24	$3 \leftarrow 2$	1.4	ρ-type, ~200Mc
SrF($X^2\Sigma$)	2.6	0.48	$2 \leftarrow 1$	1.9	ρ-type, ~400Mc
SrI($X^2\Sigma$)	3.2	0.093	$7 \leftarrow 6$	1.3	ρ-type, (small)
SrO($X^1\Sigma$)	-	1.01$^+$	$1 \leftarrow 0$	2.02	- -
SrS($X^1\Sigma$)	2.2	0.44	$2 \leftarrow 1$	1.8	- -
TeO($X^1\Sigma$)	1.9	0.99	$1 \leftarrow 0$	1.9	- -
TlBr($X^1\Sigma$)	2.68$^+$	0.12	$5 \leftarrow 4$	1.2	- -
TlCl($X^1\Sigma$)	2.55$^+$	0.26	$3 \leftarrow 2$	1.6	- -
TlF($X^1\Sigma$)	2.2	0.58	$2 \leftarrow 1$	2.3	- -
TlI($X^1\Sigma$)	2.87$^+$	0.078	$8 \leftarrow 7$	1.2	- -
WO (X?)	-	-	-	-	?
YbCl($X^2\Sigma$)	-	-	-	-	?
YbO(X?)	-	-	-	-	?
YO($X^2\Sigma$)	-	-	-	-	?
ZnBr($X^2\Sigma$)	2.7	0.19	$4 \leftarrow 3$	1.5	ρ-type, ~70Mc
ZnCl($X^2\Sigma$)	2.6	0.33	$2 \leftarrow 1$	1.3	ρ-type, ~140Mc
ZnF($X^2\Sigma$)	2.3	0.65	$1 \leftarrow 0$	1.3	ρ-type, ~240Mc
ZnI($X^2\Sigma$)	2.9	0.14	$5 \leftarrow 4$	1.4	ρ-type, ~50Mc

Table I (cont'd)

Rotational Transitions of Diatomics

Species	r* (Å)	$B_e (10^4 Mc)$	Transition**	$2B(\begin{smallmatrix}J\\N\end{smallmatrix} + 1)$ $(10^4 Mc)$	Fine Structure***
$ZnO(X^1\Sigma)$	1.8	1.2	$1 \leftarrow 0$	2.4	-
$ZnS(X^1\Sigma)$	2.1	0.54	$2 \leftarrow 1$	2.2	-
$ZnSe(X^1\Sigma)$	2.2	0.37	$2 \leftarrow 1$	1.5	-
$ZnTe(X^1\Sigma)$	2.4	0.19	$4 \leftarrow 3$	1.5	-

* Estimated from considerations given in section 1.a.

** $J' \leftarrow J$ for $^1\Sigma$ or $^2\pi_{\frac{1}{2}}$ (Hund's case (a))

$N' \leftarrow N$ for $^2\Sigma$ or $^2\pi$, (Hund's case (b))

*** Estimated from considerations given in Section 1.c and 2; see also tables 2 and 3

† Quoted by Herzberg[3].

(ii) Bent Triatomic Molecules.

For most triatomic molecules the transition frequencies will depend strongly on the valence angle Θ. Since the structure of most triatomic radicals and labile molecules is not well known or predictable, the spectrum cannot be forecast accurately.

The situation may be illustrated by considering MX_2 molecules of C_{2v} symmetry (e.g. CF_2). The rotational constants may be written

$$A = \frac{\alpha}{1+\cos\Theta} \; \frac{M}{m},$$

$$B = \frac{\alpha}{1+\cos\Theta},$$

$$C \cong \frac{AB}{A+B},$$

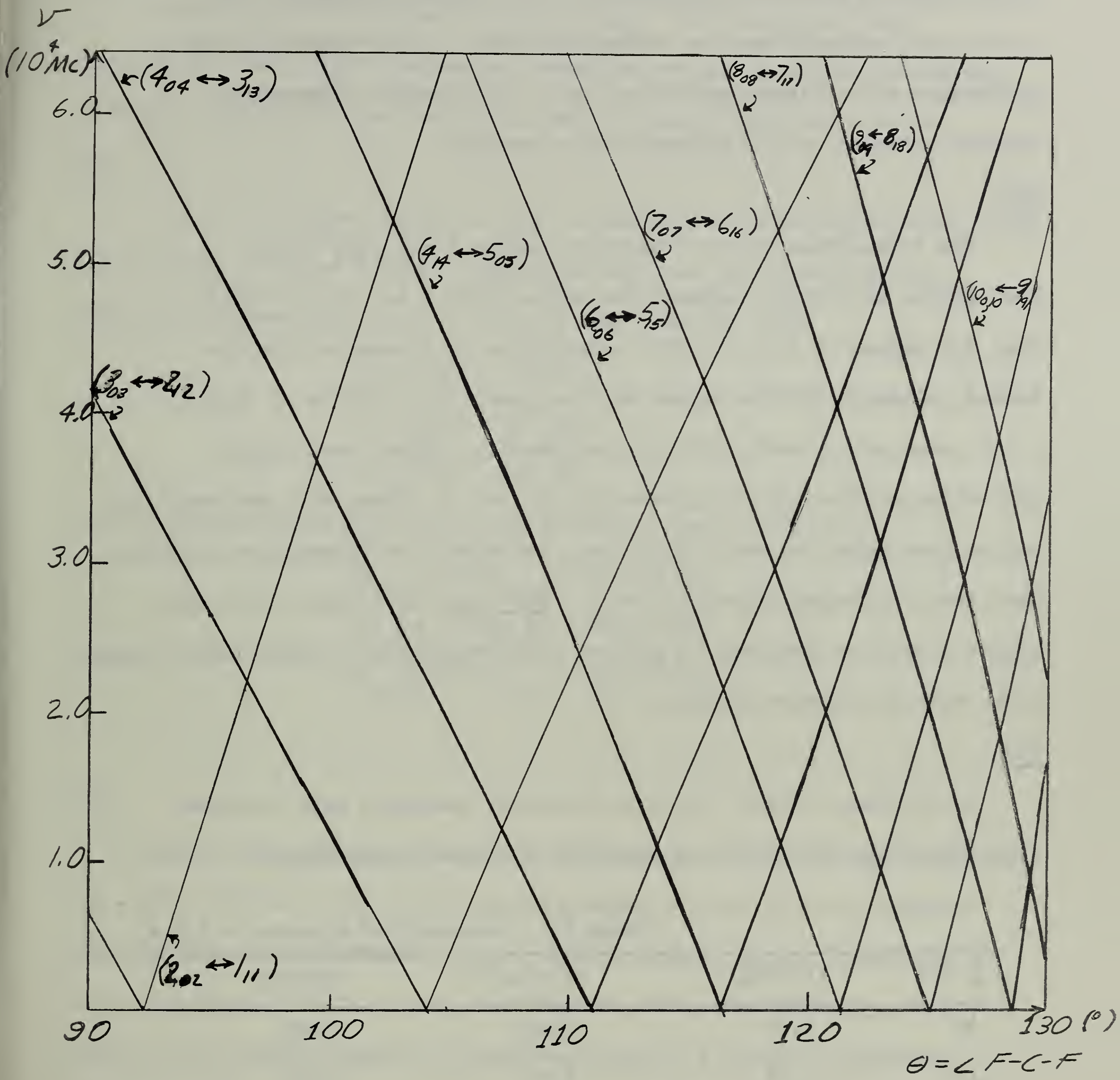
where $\alpha = \dfrac{h}{8\pi^2 m' d^2}$; here m is the mass of atom M, m' is the mass of atom X, M is the total mass of MX_2, d is the M-X bond distance and Θ is the X-M-X angle. Usually the bond distance can be predicted much more accurately than the angle, which is very sensitive to the type of bonding present.

Moreover, for Θ greater than 90° (which is nearly always the case) 'b'-type selection rules will hold for MX_2 type molecules: $\Delta K_{-1} = \pm 1, \ldots$, $\Delta K_1 = \pm 1, \pm 3$, in the notation of King, Hainer and Cross. This requires that the relatively large rotational constant $A - \frac{B+C}{2}$ enters into the transition frequencies:

$$W = \left(\frac{B+C}{2}\right) J\,(J+1) + \left(A - \frac{B+C}{2}\right) K_{-1}^{\;2} + \ldots,$$

$$\text{or } \nu \cong \left|\,(B+C)\,(J+1) + \left(A-\frac{B+C}{2}\right) \Delta(K_{-1}^{\;2})\right|,$$

(where, for purposes of illustration, only the symmetric rotor approximation to the energy has been explictly written). Consequently large J will be involved in those transitions occurring in an accessible frequency range.



CF$_2$ Transitions: $(J - 1)_{1,J-1} \leftrightarrow J_{o,J}$. For $d_{C-F} = 1.30$Å.

Figure 1

This situation makes the prediction of the spectrum difficult; the rotational constants must be accurately known if the relatively small difference of two large quantities is to yield useful information. Several examples will illustrate the situation:

CF_2

The frequencies of the transition series $(J-1)_{1,J-1} \longleftrightarrow J_{0,J}$ are plotted in figure 1 against the angle F-C-F = θ. It is evident that for values of θ up to 130°, transitions will occur within the K-band, although for the larger θ, the transitions will be of higher J and consequently more difficult to identify. Also, centrifugal distortion effects will be greater for larger J. There will be transition series for higher values of K_{-1}, also, but since the frequencies of these have even a stronger dependence on $A - \frac{B+C}{2}$ and, therefore, on θ, even higher J will be involved. A plot of the frequencies of these latter transitions will not be very useful.

NH_2

As is shown in Table II, the rotational constants must be known very accurately in order to predict the spectrum successfully.

Table II. (Assumed N-H distance = 1.0 Å)

θ (°)	A(10^5Mc)	B(10^5Mc)	C(10^5Mc)
90	5.69	5.05	2.69
110	8.68	3.77	2.63
130	15.88	3.07	2.54

CH_2

The situation is similar to that for NH_2. It is possible that for both of these light species no transition occurs within an accessible frequency region, or that, as in the case of water, only one occurs.

NS_2

If a structure similar to NO_2[1] is assumed for NS_2: angle S-N-S = 134° and N-S bond distance = 1.19 + 0.33Å (the N-O bond distance plus the difference between the O and S covalent bond radii[4]), then

$$A = 1.251 \times 10^5 \text{ Mc} ,$$

$$B = 4.045 \times 10^3 \text{ Mc} ,$$

$$C = 3.907 \times 10^3 \text{ Mc},$$

and the transitions occurring in the microwave region would be

$$15_{1,15} \rightarrow 16_{0,16} : 12,200 \text{ Mc.}$$

$$17_{1,17} \rightarrow 18_{0,18} : 28,400 \text{ Mc.}$$

$$12_{0,12} \rightarrow 11_{1,11} : 25,000 \text{ Mc.}$$

HCO

Ramsay[5] gives for the rotational constants of HCO, $B = 4.498 \times 10^4$ Mc, $C = 4.209 \times 10^4$ Mc. The corresponding moments of inertia are consistent with the following structure: $r_{C-H} = 1.08 \pm 0.02$ A, $r_{C-O} = 1.19 \pm 0.01$ A, and angle H-C-O = 120 ± 4°. It is therefore likely that the major component of the dipole moment is along the a-axis. A series of Q-branch transitions between asymmetry doublet components should fall in the K-band region ($\Delta J = 0$, $K_{-1} = 1$, $\Delta K_{-1} = 0$, $\Delta K_1 = 1$). The frequencies of these transitions are given approximately by

$$\nu = \frac{(B - C)}{2} J (J + 1) = 1.445 J (J + 1) \times 10^3 \text{ Mc.},$$

or

$$\nu = 17{,}340 \text{ Mc.}, 3_{13} \rightarrow 3_{12},$$

$$\nu = 28{,}900 \text{ Mc.}, 4_{14} \rightarrow 4_{13},$$

$$\nu = 43{,}350 \text{ Mc.}, 5_{15} \rightarrow 5_{14}.$$

HO_2

The lack of information about the structure of HO_2 precludes a reliable prediction of its spectrum.

b. Lambda-doublet Transitions.

These transitions occur for molecules in π states. The transitions are between electronic states whose degeneracy is removed by the interaction of the electronic angular momentum with the molecular rotation. The frequencies of the transitions depend on the rotational states involved. The following summarizes material given in reference 1, chapter 7 and reference 3, chapters 2 and 3. Only $^2\pi$ states are of interest here.

(i) For Hund's coupling case a, the frequency of a transition between the lambda doublet components is given by

$$\nu = a(J + 1/2), \Omega = 1/2,$$

$$\nu = b(J^2 - 1/4) (J + 3/2), \Omega = 3/2$$

(case a corresponds to the electronic orbital angular momentum and spin angular momentum coupled strongly to the figure axis; $\Omega = \Lambda + \Sigma$, the sum of the projection of the orbital and spin angular momentum on the figure axis. J is the resultant of Ω and O, the angular momentum corresponding to the molecular rotation. $\Omega = 1/2$ is the ground state when the spin coupling constant A is positive; $\Omega = 3/2$ is the ground state for A negative.)

(ii) Hund's case b:

The lambda-doublet separation is given by

$$\nu = q\ N(N + 1),$$

where N is the quantum number for the resultant of the nuclear rotation, O and Λ. (In Hund's case b the electronic spin angular momentum is coupled more strongly to the overall rotation than to the figure axis.)

(iii) Intermediate Coupling:

As the rotation energy becomes comparable to the spin doubling energy a transition between Hund's case a and b takes place. Thus, for the lighter diatomic molecules (e.g. hydrides) we may have intermediate coupling for fairly low values of J (or N).

For the general case of intermediate coupling Van Vleck[6] gives

$$\nu = \frac{q}{2}\ (J+1/2)\ [(2+A'/B')(1+ \frac{2-A/B}{x})+4(\frac{J+3/2)(J-1/2)}{x}],$$

where

$$X = -[A/B(A/B-4) + 4(J+1/2)^2]^{1/2}$$

here, A positive corresponds to the $^2\pi_{\frac{1}{2}}$ state, A negative to the $^2\pi_{3/2}$. For A positive and the $^2\pi_{3/2}$ state the positive square root is taken equal to X, as for A negative and the $^2\pi_{\frac{1}{2}}$. A'/B' is approximately equal to A/B but is actually proportional to the quotient of the matrix elements of AL_y and BL_y, taken between the $^2\pi$ state and excited Σ states.

(iv) Estimation of the constants q and a.

The constants q and a may be estimated by means of formulas given by Mulliken and Christy[7]. These formulas are based on the hypothesis of 'pure precession' which considers that Λ, the projection on the figure axis of the electronic orbital angular momentum, is the projection of the orbital angular momentum of the odd electron. This orbital angular momentum has quantum number ℓ and precesses about the figure axis. The molecular rotation interacts, both magnetically and mechanically, with the angular momentum of the odd electron thus giving the π state a small amount of Σ state character. This hypothesis holds best for molecules for which the 'united atom' representation of the electronic wave-function is not a bad approximation. It still may be useful, however, in setting the order of magnitude of q or a for other diatomics. From the pure precession hypothesis Mulliken and Christy obtain for the constants a and q:

$$a \cong \frac{2AB\ell(\ell+1)}{hv(\pi,\Sigma)} = \frac{4\,AB}{hv(\pi,\Sigma)}$$

$$q \cong \frac{2B^2\ell(\ell+1)}{hv(\pi,\Sigma)} = \frac{4\,B^2}{hv(\pi,\Sigma)}$$

where $hv\,(\pi,\Sigma)$ is the energy difference between the ground π state and the excited Σ state mixed in by the interaction of the molecular rotation and the electronic orbital angular momentum.

(v) Intensities.

The absorption coefficient α may be evaluated by means of the expressions given in reference 1, chapter 1, for the rotational transition absorption coefficient of diatomic molecules, if the dipole matrix element for a pure rotational transition is replaced by that for a transition between lambda-doublet components. The resulting formulas are, at T = 300°K,

case a:

$$\alpha \cong 5.5\mathrm{x}10^{-18} \quad \frac{B\Omega^{2}\ \mu^{2}\ \nu^{2}}{(J + 1)} \quad \exp \frac{[-hBJ(J+1)]}{kT}$$

case b:

$$\alpha = 5.5\mathrm{x}10^{-18} \quad \frac{B\Lambda^{2}\ \mu^{2}\ \nu^{2}}{(J + 1)} \quad \exp \frac{[-hBN(N+1)]}{kT}$$

where ν and B are in Mc, and μ, the dipole moment, is in Debyes. The dipole moment may be estimated from bond moments, when reported, or from the electronegativities of the two atoms. The line width parameter for pressure broadening has been assumed to be 10 Mc/mm. Hg.

Table III gives calculated, and when available, observed values for the lambda-doubling constants and the frequencies and intensities of any transitions occurring in the microwave region. The data has been taken, for the most part, from reference 3 and Table 1. The principal uncertainty is in B, where this has to be determined from an estimated internuclear separation.

2. Magnetic Dipole Transitions

The material in this section has been summarized from reference 1, chapter 7.

Radicals in $^{2}\Sigma$ and $^{3}\Sigma$ states exhibit ρ-type multiplet splitting. While electric dipole transitions between the components of these multiplets are forbidden, magnetic dipole transitions are not. Although the magnetic dipole of a radical or biradical is several orders of magnitude less than that of the usual electric dipole (several Bohr magnetons compared to several Debyes), the trnasition may still be quite strong.

a. $^2\Sigma$ states

The components of the ρ-type doublet have energies given by

$$W'' = BN(N+1) + \frac{\gamma}{2} N, \quad J = N + \tfrac{1}{2};$$

$$W' = BN(N+1) - \gamma (N+\tfrac{1}{2}), \; J = N - \tfrac{1}{2}.$$

The frequency of the ρ-type doublet transition is then

$$\nu = /\gamma/ \; (N+\tfrac{1}{2})$$

Using the "pure precession" hypothesis, Mulliken and Christy obtain

$$\nu = 2AB \frac{\ell \; (\ell+1)}{h\nu(\pi, \Sigma)} \quad ,$$

where A is the spin coupling constant of the $^2\pi$ state "mixed" in by the interaction of the electronic spin with the molecular rotation.

In Table IV are given the coupling constants calculated from the Christy and Mulliken formula or obtained from Herzberg's compilation.[3]

The intensities of these transitions are given by

$$\alpha \cong 9 \times 10^{-21} \; B \; \frac{(N+1)^2}{(2N+1)} \quad \nu^{,2} \quad \exp \frac{[-BN(N+1)]}{kT} \quad ,$$

where B, ν are in Mc and the temperature is taken to be 300°K. A pressure broadening parameter of 10 Mc/mm. Hg. has been assumed.

Table III

Species	a(Mc)	q(Mc)	Transition	ν(Mc)	$\gamma^*(\mathrm{cm}^{-1})$
$\mathrm{AsO}(X^2\pi_{\frac{1}{2}})$	1700		$J=9\frac{1}{2}$	17,000	5×10^{-6}
$\mathrm{BN}(X^3\pi)$	Insufficient data		-	-	-
$\mathrm{BrO}(X^2\pi_{\frac{1}{2}})$	Insufficient data		-	-	-
$\mathrm{CCl}(X^2\pi_{\frac{1}{2}})$	200	-	-	-	-
$\mathrm{CF}(X^2\pi_{\frac{1}{2}})$	308	-	-	-	-
$\mathrm{CH}(X^2\pi_{\frac{1}{2}})$		800	$N=4$	16,000	5×10^{-6}
$\mathrm{ClO}(X^2\pi_{\frac{1}{2}})$	Insufficient data		-	-	-
$\mathrm{GeBr}(X^2\pi_{\frac{1}{2}})$	350		-	-	-
$\mathrm{GeCl}(X^2\pi_{\frac{1}{2}})$	680		-	-	-
$\mathrm{GeF}(X^2\pi_{\frac{1}{2}})$	2000		$J=9\frac{1}{2}$	20,000	2.1×10^{-5}
$\mathrm{NiCl}(X^2\pi_{\frac{1}{2}})$	300		-	-	-
$\mathrm{NO}(X^2\pi_{\frac{1}{2}})$	600 (calc.) 355 (obs.)[2]		-	-	-
$\mathrm{NS}(X^2\pi_{\frac{1}{2}})$	700 (~330 obs)[9]		-	-	-
$\mathrm{OH}(X^2\pi_{\frac{3}{2}})$		1300(calc.) 1090(obs.)-intermediate[1] 1190 (case b)		-	4.4×10^{-5}
$\mathrm{HS}(X^2\pi_{\frac{3}{2}})$		320	$J=9\frac{1}{2}$	19,200	1.3×10^{-7}
$\mathrm{PbBr}(X^2\pi_{\frac{1}{2}})$	~2000(if $A = 10^4\ \mathrm{cm}^{-1}$)		$J=9\frac{1}{2}$	20,000	2.57×10^{-6}
$\mathrm{PbCl}(X^2\pi_{\frac{1}{2}})$	4000(if $A = 10^4\ \mathrm{cm}^{-1}$)		$J=4\frac{1}{2}$	20,000	2×10^{-6}
$\mathrm{PbF}(X^2\pi_{\frac{1}{2}})$	4000($A = 8.2\times10^3\ \mathrm{cm}^{-1}$)		$J=4\frac{1}{2}$	20,000	1×10^{-5}
$\mathrm{PbH}(X^2\pi_{\frac{1}{2}})$	3.2×10^5		-	-	-

Table III (cont'd)

Species	a(Mc)	q(Mc)	Transition	ν(Mc)	*(cm^{-1})
$PO(X^2\pi_{\frac{1}{2}})$	500		-	-	-
$SbO(X^2\pi_{\frac{1}{2}})$	~3000		$J=7\frac{1}{2}$	24,000	$3x10^{-6}$
$SiBr(X^2\pi_{\frac{1}{2}})$	250		-	-	-
$SiCl(X^2\pi_{\frac{1}{2}})$	200		-	-	-
$SiF(X^2\pi_{\frac{1}{2}})$	320		-	-	-
$SiH(X^2\pi_{\frac{1}{2}})$	$4.0x10^3$*	~200* (if ν (π, Σ) = $3x10^4$)	$J=9\frac{1}{2}$	19,500	$1x10^{-7}$
$SnBr(X^2\pi_{\frac{1}{2}})$	480		-	-	-
$SnCl(X^2\pi_{\frac{1}{2}})$	1000		$J=9\frac{1}{2}$	10,000	$5x10^{-7}$
$SnF(X^2\pi_{\frac{1}{2}})$	3100		$J=4\frac{1}{2}$	16,500	$1x10^{-5}$
$SnH(X^2\pi_{\frac{1}{2}})$	5400		$J=3\frac{1}{2}$	21,600	$8x10^{-5}$

b. $^3\Sigma$ States

In addition to the sort of interaction that occurs in $^2\Sigma$ states, the two unpaired spins of a bi-radical may interact with each other. If this interaction is small compared to the rotational energy, a first order expression given by Kramers for the multiplet splitting can be used.

$$W = BN(N+1) - \frac{\lambda}{1+\frac{1}{2(N+1)}} + \gamma(N+1), \quad J=N+1;$$

$$W = BN(N+1), \qquad J=N$$

$$W = BN(N+1) - \frac{\lambda}{1-\frac{1}{2N}} - \gamma N, \qquad J=N-1.$$

If the spin-spin interaction is large compared to the rotational energy or of comparable magnitude, then a second order expression given by Miller and Townes should be used:

$$W = BN(N+1) -\lambda- \frac{\gamma}{2} + [\lambda^2 - 2\lambda(B- \frac{\gamma}{2})+ (2N-1)^2(B- \frac{\gamma}{2})^2]^{\frac{1}{2}}$$

$$-(2N-1)B, \qquad J = N-1,$$

$$W = BN(N+1), \qquad J = N$$

$$W = BN(N+1) -\lambda - \frac{\gamma}{2} - [\lambda^2 - 2\lambda(B \frac{-\gamma}{2}) + (2N+3)^2(B \frac{-\gamma}{2})^2]^{\frac{1}{2}}$$

$$+(2N+3)B, \qquad J = N+1.$$

The intensities are given as

$$\alpha = 2.4\text{x}10^{-20} \, B \, \frac{N(2N+3)}{N+1} \, e^{\frac{-BN(N+1)}{kT}}, \quad J= N \leftrightarrow J=N+1$$

$$\alpha = 4.8\text{x}10^{-20} \, B \, \frac{(2N-1)(N+1)}{2N} \, e^{\frac{-BN(N+1)}{kT}}, \quad J=N \leftrightarrow J=N-1$$

at 300°K and for an assumed pressure broadening parameter of 10 Mc/mm.Hg. If the species is non-polar, then the line width will be much smaller, and one will gain in intensity by a factor of 5-10.

In Table V are listed the expected frequencies and intensities for a number of transitions of $^3\Sigma$ molecules. The fine structure constants are taken from reference 3, except where otherwise noted.

Table IV

Species ($X^2\Sigma$)	γ (Mc)	Transition (ρ-type doublet)	ν (Mc)	α (cm^{-1})
AgO	340			
AlO	633*			
BaBr	120			
BaCl	650			
BaF	820			
BaI	60			
BaH	(10,000) 5,580*	N=4	25,100	2×10^{-8}
BeCl	100			
BeF	-90			
BeH	125			
BO	$\sim$ -1000			
CaBr	$\sim$ 80			
CaCl	$\sim$ 100			
CaF	$\sim$ 140			
CaH	(1250) 1350*	N=9	13,000	5×10^{-8}
CaI	?			
CdCl	100			
CdH	32,000	N=1	48,000	1×10^{-6}
CN	-1270	N=19	25,000	3×10^{-8}

Table IV (cont'd)

Species ($X^2\Sigma$)	γ (Mc)	Transition (ρ-type doublet)	ν(Mc)	α (cm^{-1})
CP	(-150) -170*			
CuO	?			
GaO	?			
HgBr	140			
HgCl	1260	N=19	24,600	7×10^{-8}
HgF	2500	N=9	23,600	3×10^{-8}
HgH	(90,000) 64,500*			
HgI	?			
InO	~700			
LaO	?			
MgBr	100			
MgCl	100			
MgF	80			
MgH	(105) 750*			
MgI	?			
ScO	350			
SiN	?			
SrBr	100			
SrCl	200			
SrF	400			

Table IV (cont'd)

Species ($X^2\Sigma$)	γ (Mc)	Transtion (ρ-type doublet)	ν (mc)	α (cm^{-1})
SrH	(9000) 3660*	N=5	19,600	$2x10^{-7}$
YbCl	$\sim 10^3$			
ZnBr	70			
ZnCl	140			
ZnF	240			
ZnH	(11,300) 7,620*	N=3	26,600	$5x10^{-8}$
ZnI	50			

* Quoted by Herzberg

Table V

ρ-Type Triplet Transitions of $^3\Sigma$ Molecules

(A) B_2 Insufficient data

(B) N_2 ($A^3\Sigma_u$) $\lambda = 39{,}000$ Mc[10]

$B = 43{,}200$ Mc

$\gamma = -90$ Mc[10]

$N+1 \leftarrow N$

N	ν(Mc)	α (cm^{-1})
2	29500 31100*	4×10^{-5}
4	36000*	1×10^{-4}

(C) NH $\lambda = 13500$ Mc

$B = 449500$ Mc

$\gamma = 1200$ Mc

$N \leftarrow N+1$

N	ν*(Mc)	α(cm^{-1})
1	13200	5×10^{-6}
2	15200	6×10^{-6}
3	16800	7×10^{-6}
4	18300	8×10^{-6}
⋮	⋮	⋮
8	23450	5×10^{-7}

$N \leftarrow N-1$

N	ν^*(Mc)	α(cm^{-1})
1	25800	1.6×10^{-5}
2	15600	3×10^{-6}
3	12600	2×10^{-6}

(D) PH.

λ = 21990 Mc

B = 253300 Mc

γ = -2340 Mc

$N \leftarrow N+1$

N	ν^*(Mc)	α(cm^{-1})
1	22280	7×10^{-6}
2	25870	1×10^{-5}
3	28910	2×10^{-5}
4	31700	2×10^{-5}
⋮	⋮	⋮
7	39420	1×10^{-5}

$N \leftarrow N-1$

N	ν^*(Mc)	(cm^{-1})
1	41650	2×10^{-5}
2	24620	7×10^{-5}
3	19280	4×10^{-6}
4	15740	3×10^{-6}
5	12800	1×10^{-6}

(E) S_2 $\lambda \sim 10^5 - 10^6$ Mc [11]

$B = 7920$ Mc [11]

$\gamma \sim -10^3$ Mc [11]

$N \leftarrow N-1$

N	ν(Mc)	$\alpha^{\dagger}$(cm^{-1})
3	$47520 - X^{\ddagger}$	3×10^{-7}

(F) SO $\lambda \sim 30000 - 50000$ Mc [12]

$B = 21099$ Mc

$\gamma \cong 90$ Mc [12]

$N \leftarrow N+1$

N	ν*(Mc)	α (cm^{-1})
1	~40000 Mc	2.0×10^{-6}
⋮	⋮	⋮
N	$+\lambda + (N+1)\gamma$	-

$N \leftarrow N-1$

N	ν*(Mc)	
2	~40000 Mc	4×10^{-6}
⋮	⋮	⋮
N	$+ \lambda + N\gamma$	-

* Calculated by use of Kramer's first-order formula.

† Intensity calculated for T = 700°K; the temperature dependence of the line width for non-polar S_2 has been assumed to be of the form $\Delta\nu \propto \left(\frac{1}{T}\right)^{\frac{1}{2}}$; the temperature dependence of α is then $\left(\frac{1}{T}\right)^{5/2}$.

‡ $X \cong \dfrac{2N(N-1)(B-\gamma/2)^2}{\lambda + \gamma/2 - B} \sim 4\times10^3$ Mc

PRODUCTION OF RADICALS, METASTABLES AND HOT MOLECULES

Since the field of free radical reactions is so wide, only the particular cases relevant to the present microwave program will be discussed here in any detail. A recent survey of free radical and atomic reactions, with particular attention to organic systems, is given by Steacie[13]. Earlier work dealing with the role of atomic and free radical species in electrical discharge processes is reviewed by Glockler and Lind[14].

The survey herein given is neither complete nor detailed with regard to the number of systems or to the explicit experimental techniques that can be used. It was thought more desirable to cull from the general references cited and from other sources those systems of most interest from a spectroscopic point of view. When a choice of particular species is made as being most suitable for further investigation, the less general considerations can be brought forth.

Radicals or metastables may be produced by thermal, photolytic, or discharge techniques. The radicals may result either from direct dissociation of the parent species or from chemical reactions with other species.

Thermal Methods

In the thermal production of radicals two cases may be distinguished: (1) the radicals or metastables are in thermal equilibrium with the parent species; (2) the radicals are short-lived (from 10^{-4} to 0.1 seconds) intermediates in pyrolytic reactions.

For the first case, fairly high temperatures are required to get even a moderate concentration of radicals. For example, in the thermal dissociation of water vapor, $2H_2O \rightarrow H_2+2OH$, a temperature of 1700°K is required to get an equilibrium partial pressure of about 0.05 mm. Hg. OH from 1 mm. Hg. H_2O.[15] Temperatures of the order of 10^3°C are required to get appreciable partial pressures of most inorganic free radicals - e.g. HgI, HgCl.[16] If the bond to be broken in the pyrolysis is weak, then the required temperature will be lower. For example, the dissociation of I_2 is 99 percent complete at about 800°K[17] - the I-I bond energy is about 35 kcal/mol. as compared with an O-H bond energy in H_2O of about 100 kcal/mol. Several particular cases are of interest where an adequate vapor pressure of the radical or molecule is achieved for moderate temperatures ($\angle$ 700°C, say).

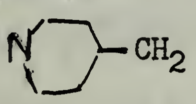
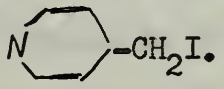
S_2:[18] At 400°C and a total pressure of 0.1 mm. Hg., sulfur in the vapor phase is almost completely S_2.[18] At 350°C and a total pressure of 0.1 mm. Hg. the partial pressure of S_2 is 0.07 mm. Hg.; the other species in the sulfur vapor are S_6 and S_8. At 300°C and a total pressure of sulfur vapor of 0.1 mm. Hg., the partial pressure of S_2 is 0.013 mm. Hg.

In Table V are listed some molecules whose vapor pressure should be sufficient for microwave purposes in the given temperature range. The data are taken from Stull's compilation[19].

Table VI

0-300°C	300-500°C	500-700°C	p≥1mm.Hg.
TlF	GeO	GeSe	
TlCl	GeS	GeTe	
TlI		InBr	
		InCl	

For the situation where the radicals are not in thermal equilibrium with the parent species, as is the case for most organic free radical reactions, the variety of species which usually occur in the reactions of the pyrolytic intermediates complicate the picture. It also should be noted that the radicals themselves may be thermally unstable at sufficiently high temperatures. The strength of the bond to be broken may, even for the non-equilibrium situation, give a measure of the temperature required for sufficient yield. For example, benzyl iodide is quantitatively pyrolyzed to benzyl radicals at a temperature of 670°C,[20] while at a temperature of 1150°C only about 10 percent benzyl radicals are detected in the pyrolysis of toluene[21].

It may be noted in passing that the picolyl radical should have kinetic properties similar to the benzyl as was shown by Swarzc [22,23] in studies on the pyrolysis of toluene and picoline. Thus it should be possible to prepare  by the pyrolysis of  The picolyl radical should be more suitable for microwave study than the benzyl, having a larger dipole moment.

In general one might expect the pyrolysis of Iodides, RI → R + I, to be effected at lower temperatures than those of other halides. The reverse reaction is fast, however, so that silver or some other I fixing agency is required. Also, reactions among the intermediates, as mentioned above, may complicate the picture. Although one might in principle be able to obtain such radicals as CF_2Cl, CH_3CFCl, etc. by the pyrolysis of the corresponding iodides, the kinetics of such reactions are not yet well enough known to be sure that these radicals would be the principal steady-state constituents. The pyrolysis of other organic systems is more likely to be complicated by many intermediate species. The pyrolysis of organometallic, e.g. $Hg(CH_3)_2$, compounds proceeds at fairly low temperatures (200-700°C) but the resulting radicals, having a low dipole moment, are not likely to be particularly suitable for microwave studies.

SO has been prepared "in considerable yield" by the reaction

$$2Ag + SOCl_2 \xrightarrow{180° - 350°C} 2AgCl + SO,$$

the yield increasing at higher temperatures.[24]

A whole class of similar reactions, the sodium diffusion flame reactions, has been reviewed by Steacie[25]. The reactions are of the type

$$RX + Na(g) \xrightarrow{200 - 300°C} NaX + R,$$

where X is any halogen. For Iodides, corresponding to the weaker C-I bond, reaction occurs at almost every collision, while for F, less than one collision in 10^6 is effective. In principle one might obtain such radicals as CF_2Cl from such reactions as

$$CF_2ClI + Na(g) \longrightarrow CF_2Cl + NaI_{(s)},$$

since, as in photolysis, the reaction is selective to the C-I bond. The partial pressure of Na in these reactions is about 10^{-3} mm Hg. and that of RX about 0.1 mm. Hg., so that the yield is small; however, the Na partial pressure could be increased. Because of the lack of information about the lifetime of the radicals and about reactions subsequent to $RX + Na \longrightarrow NaX + R$, one cannot say that R• would be present in high concentration in the steady state.

Photolysis

The production of radicals by photolysis may be effected in two ways: by steady irradiation or by short bursts of very intense radiation (flash photolysis). The yield of radicals by use of the former technique will be much less, in general, than by use of the latter, as is illustrated in Ramsay's experiments with the continuous[26] and flash[27] photolysis of NH_3 to give NH_2.

A number of radicals suitable for microwave study have been produced by flash photolysis: CH,CN,OH[28], HCO[29], NH[30], NH_2[27], ClO[31,32]. All but the last of these have lifetimes of the order of milliseconds. ClO has a lifetime (i.e. the time required for the pressure of ClO to go from 0.1 mm. Hg. to 0.01 mm. Hg.) between 0.05 seconds and three seconds, as indicated by the kinetic studies of Porter and Wright[32].

The continuous photolysis of a number of organic compounds has been studied extensively. Although the initial step, the breaking of some weak bond - e.g. a C-I bond-is simple and well-established, the ensuing reactions may be, as in pyrolyses, quite complicated. CH_2 produced by the photolysis of ketene has a lifetime of approximately 0.2 seconds[33].

Sensitizers may be used to absorb the radiation and transfer it to the species to be dissociated. That is,

$$M + h\nu \longrightarrow M^*$$

$$M^* + AB \longrightarrow M + A + B.$$

CF_2 is probably produced by the Xenon sensitized photolysis of CF_4. Hg, Cd and Zn may also be used as sensitizers:

$$M + h\nu \longrightarrow M^*$$

$$M^* + RH \longrightarrow MH + R$$

$$MH \longrightarrow M + H$$

HgH is very unstable; its lifetime is probably 10^{-5} that of CdH, for which latter the resonance absorption has been observed. It is probable that even though CdH molecules in the ground state are produced in the photolysis of Cd vapor in H_2, the yield is small[34].

Electrical Discharges

Electrical discharges may be used to produce radicals and metastables in two ways: (1) by direct dissociation or chemical reaction in the discharge, or (2) by production of an active species in the discharge and reaction of it outside the discharge to give another labile species. Many diatomic and a few triatomic labile molecules have been produced by reactions in a discharge. The discharge processes are in general more violent and less selective than those occuring in continuous photolysis or pyrolysis, so that polyatomic radicals do not result. However a number of polyatomic radicals have been postulated as intermediates when relatively long-lived species-H, O, OH, active nitrogen, for example - are flowed from the discharge and attack stable molecules. Steacie[13] cites a number of such reactions, which are supported by more or less indirect evidence.

Among those radicals produced directly within the discharge for which kinetic data is available are the following:

NH has been produced by discharges through HN_3[35]; its lifetime should be about the same as NH produced by the pyrolysis of HN_3: 10^{-3} seconds at a pressure of HN_3 of 0.07 mm. Hg.[36], NH and NH_2 have also been produced by discharges through ammonia and hydrazine[37].

HO_2 is produced from discharges through H_2O_2 in yields of about 0.1 to 1 percent at moderate flow rates.[38]

$^3\Sigma_u$ N_2 is the lower state in the transition corresponding to the first positive bands present in the active nitrogen afterglow. This afterglow can be made to persist, by suitable wall conditioning, for several hours after a discharge through N_2 is cut off. Since the transition to the $^1\Sigma$ ground state is forbidden, the radiative lifetime of the $^3\Sigma$ state is relatively long. However, mass spectrometric studies of the afterglow at N_2 pressures of about 1 mm. Hg. indicate that N atoms rather than excited N_2 molecules are the principal constituent of the afterglow[39]. ClO should result when a discharge is passed through mixtures of Cl_2 and O_2. The kinetic properties of ClO produced from a discharge should be similar to those of ClO produced by photolysis, although the initial yield from the discharge might be smaller.

SO has been prepared by passing SO_2 through a discharge; the yield of 10% is increased to 40% if sulfur vapor is mixed with the SO_2[24].

The spectra of a number of other diatomic radicals have been observed in emission and absorption in discharges. However, detailed kinetic data are not available for these.

Several relatively long-lived metastable molecules have been produced by dissociation in a discharge.

CH_2 has been detected by the formation of $(TeCH_2)_n$ polymers when the products of a discharge through ketene or methane are passed over tellurium mirrors[40]. Its lifetime should be about the same as when produced by photolysis - about 0.2 seconds. CH_2 has not yet been observed spectroscopically, however.

CF_2 has been studied by means of its ultraviolet absorption spectrum and its lifetime estimated to be of the order of several seconds[41]. It has been prepared by the dissociation of compounds containing CF_2 groups, although it was not observed in discharges through CF_4[42]. Wall conditions, it should be noted may be important; CF_2 was not observed when the discharges were carried out in glass tubing whose diameter was less than about 40 mm. CSe might be expected to have a lifetime of several seconds, if the relative lifetimes of CO (stable) and CS (about 30 minutes when produced by a discharge through CS_2[41]) are any indication. CSe has been seen in emission in discharges through CH_2Cl_2 and Se[43]; it should be possible to prepare it by passing CSSe through a discharge.

Among those species produced by reactions of active species flowed from the discharge, and for which there is spectroscopic evidence are those occurring in the following reactions:

$$H + O_3 \longrightarrow OH^* + O_2,$$ [44]

(where OH* is vibrationally excited $(v \leqslant 9)$);

$$\text{active nitrogen} + Br_2 \longrightarrow NBr;$$ [45]

$$\text{active nitrogen} + S_2(g) \rightarrow NS;$$ [9]

(the lifetime of NS has been reported to be of the order of seconds)[46];

$$O + HCHO \longrightarrow OH + CHO;$$ [47]

$$O + CH_3OH \longrightarrow OH + CH_3O;$$ [47]

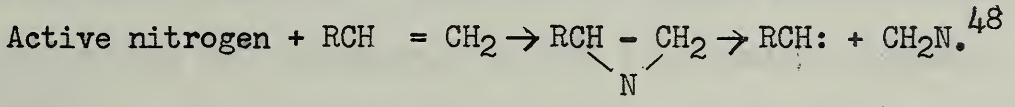
(the OH and HCHO were observed spectroscopically; further data would be required before one could say that a sufficiently high steady-state concentration of CH_3O could be maintained: also the OH and HCO were observed in emission - the reaction is luminescent - rather than absorption so that no estimate of the yield could be made).

Among those reactions for which the intermediates are inferred are those of the types[13]

$$H + RH \longrightarrow H_2 + R\cdot,$$

$$O + RH \longrightarrow OH + R\cdot,$$

(here one interesting possibility is $O + CH_3COH \rightarrow OH + CH_3CO$),



$$\text{Active nitrogen} + RCH = CH_2 \rightarrow \underset{\diagdown\, N \,\diagup}{RCH - CH_2} \rightarrow RCH: + CH_2N.$$ [48]

In all these cases the variety of intermediates is likely to produce situations as complicated as those occurring in photolysis and pyrolysis.

MONITORING THE CONCENTRATION OF RADICALS

Inasmuch as the experimental conditions required for an optimum concentration of radicals in the absorption cell will not be known a priori, there should be available some device which can detect the radicals in concentrations less than that required for the observation of their microwave spectra. The experimental conditions can then be varied to maximize the radical concentration to a point where their spectra should be observable. This monitoring device is particularly required if there is a lack of information for positively predicting the frequencies and intensities of the microwave lines. Even in such a relatively simple system as that of H_2O passed through a discharge to give OH, a history of the microwave investigations shows that a means, independent of the microwave line itself, for estimating the concentration of OH in the absorption cell would be desirable and almost necessary. Obviously the monitoring device need not be used in conjunction with the spectrograph, but may be used to estimate concentrations on a set-up similar to that which will finally be used.

Three sorts of monitoring systems might be used.

Chemical Tests

A number of specific reactions, such as the color change of certain oxides on reaction with atomic hydrogen, have been used for particular radicals. The most general method, however has been to analyze directly the products of reactions involving free radicals or the products of the reaction intermediates with various test substances. For example, the formation of a dark blue paramagnetic solid, with composition $(NH)_x$, in a cold trap through which is passed the products of a discharge through HN_3, has been used to infer the presence of the NH radical[36]. However, in that the analysis of products is not a direct indication of the concentration of radicals at a particular site and instant, it may be misleading. Such was shown to be the case for the microwave work on the OH radical[50]. In even such a relatively simple system as H_2O passed through a discharge, the amount of H_2O_2 trapped out did not correlate with the actual concentration of OH in the microwave absorption cell.

Absorption Spectra

The minimum partial pressure which may be detected in absorption by a spectrograph with good resolving power and dispersion is of the order of 10^{-3} mm. Hg. However only diatomic and a few triatomic species can be observed at these pressures. Porter[31] gives the requirements that an optical spectrograph for the study of labile molecules in absorption must meet.

Paramagnetic Resonance Absorption

A paramagnetic resonance spectrograph such as that used by Dehmelt[51] in his study of atomic phosphorus would be capable of detecting a minimum partial pressure of about 10^{-3} mm. Hg. of free radicals and would therefore be ideal for the detection of polyatomic free radicals whose optical spectra could not be observed. The searching problem present in microwave spectroscopy would be minimized. Furthermore, valuable information about the free radicals could be obtained from their paramagnetic resonance spectra. However the construction of such a spectrograph would certainly be almost as major an undertaking as the construction of a microwave spectrograph.

Mass Spectrometer

A mass spectrometer would be the ideal tool for monitoring not only radical concentrations but also those of stable species in free radical reactions. However the same objection which might be applied to a paramagnetic resonance spectrograph as a possible monitoring device can be applied to the mass spectrograph - its construction would be as big and complex a task as that for the microwave spectrograph itself.

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