MICROWAVE SPECTROSCOPY PART–2

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Selection rules of Microwave spectroscopy

In order for a molecule to give rise to rotational spectrum, it becomes essential that the molecule must have a dipole moment but all transitions are not permitted.

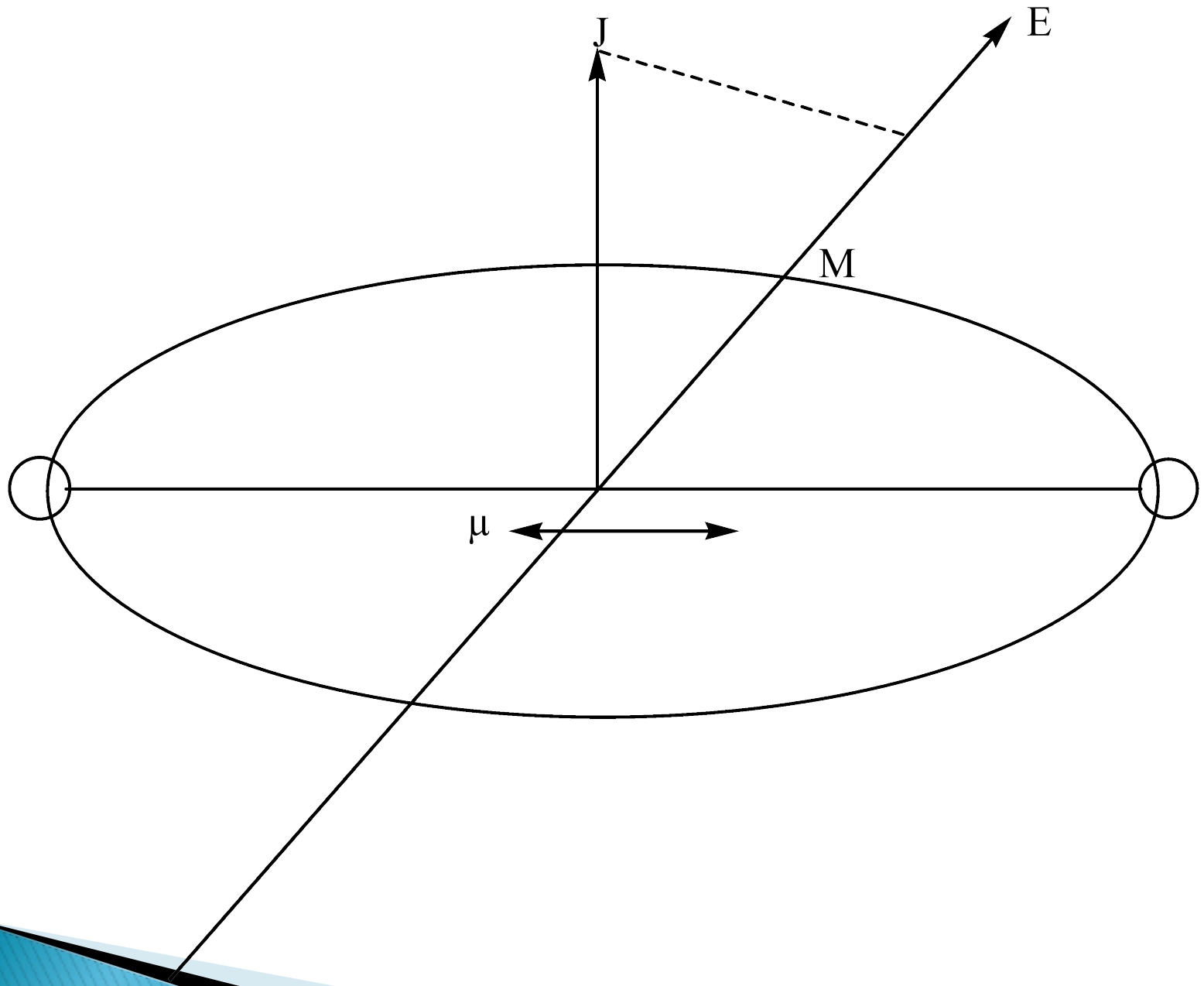
selection rule which is given as

$\Delta J = +\_1$

From the above rule, It is evident that that only those transitions are permitted in which there is an increase or decrease by unity in the rotational quantum number. It means that J=0 → J=2 J=4…transitions are not possible. In other word ,these transitions are spectroscopically forbidden.

THE STARK EFFECT

- When a rotational spectrum is recorded in the presence of a strong electric field E, the lines will in general be split and shifted. The effect was first of all observed by Stark in atomic spectra and is known as Stark effect. Consider a diatomic molecule in the presence of an external electric field as shown in the figure below:


J
E
M
μ

- In the above figure, M is the projection of J along the external electric field. The energy E_{JM} in the presence of the field is given by

$$E_{J,M} = E_J + a_J, M \in +1/2 b^2 J, M \in^2$$

Where E_J is the energy of the rotation in the absence of the field and aj, M are the first and second order Stark effects. If the dipole μ has a component along the direction of J, we get the second Stark effect, this is shown in the figure above.

The difference between the first order and second order Stark effects lies in the dependence of the energy on the energy in the electric field. For a linear molecule having no component of μ in the direction of J, we have

$$E_{J,M} = \frac{h}{8\pi^2 cI} J(J+1) + 1/2 b_J, E\varepsilon^2$$

- The vaues of b_J, m are given by

$$b_{0,0} = -\frac{16}{3h}\pi^2 Ic\mu^2 \text{ cm}^{-1} \quad \text{for } J = 0$$

$$b_{J,M} = -\frac{16\pi^2 Ic\mu^2}{h} * \frac{3M^2 - J(J+1)}{J(J+1)(2J-1)(2J+3)} \text{ cm}^{-1} \quad \text{for } J \neq 0$$

- The selection rules are

$$\Delta J = \pm 1 \qquad \Delta M = 0$$

It can be shown that the shift in the $J = 0 \mapsto 1$ line when the field is applied is given by $32\pi^2 Ic/15h$ and the $J=1 \mapsto 2$ line will be split into two with a separation of $64\pi 2Ic\mu/105h$.

Splitting of the rotational levels by an external electric field. The energy levels on the left are without external electric field, and on the right, with external field.

INSTRUMENTATION FOR MICROWAVE SPECTROSCOPY

A microwave spectrometer consists of the following essential components:

- **THE SOURCE AND MONOCHROMATOR :**
- Reflex klystron valve is the main source of radiations in microwave region. As the klystron valve emits radiation of a very narrow frequency range, it acts as its own monochromator. Furthermore , the frequency of the emitted radiation depends on the voltage that is applied to the klystron valve. As the voltage is varied over a given range, the emitted radiation can thus be made to sweep through a region of the microwave range.

Klystron are readily available from 3000 to 5000Mc/second and weaker signals up to 250000Mc/second may be obtained with harmonic generators.

One slight disadvantage of the klystron valve is that it radiates out very small energy which is of the order of 30 milliwatts. However, since the energy radiated is concentrated into very narrow frequency band, a sharply tuned detector may be activated to produce a strong signal.

- **THE BEAM DIRECTION:** The radiation emitted by klystron cannot be handled with mirrors and lenses, but can be most advantageously transmitted through hollow metallic conductors of such geometry that the electric and magnetic fields can be utilised to the greatest extent.

These are known as ***wave guides.*** These are hollow tubes of copper or silver of rectangular cross section inside which the radiation is confined. In order to maintain the direction of the beam as well as its focussing, the wave guides may be bent or tapered. The waveguides are generally evacuated because if air is present in them, considerable absorption of the radiation will occur. The waveguides used in microwave spectrometer is now commonly used in chemical research facilities.

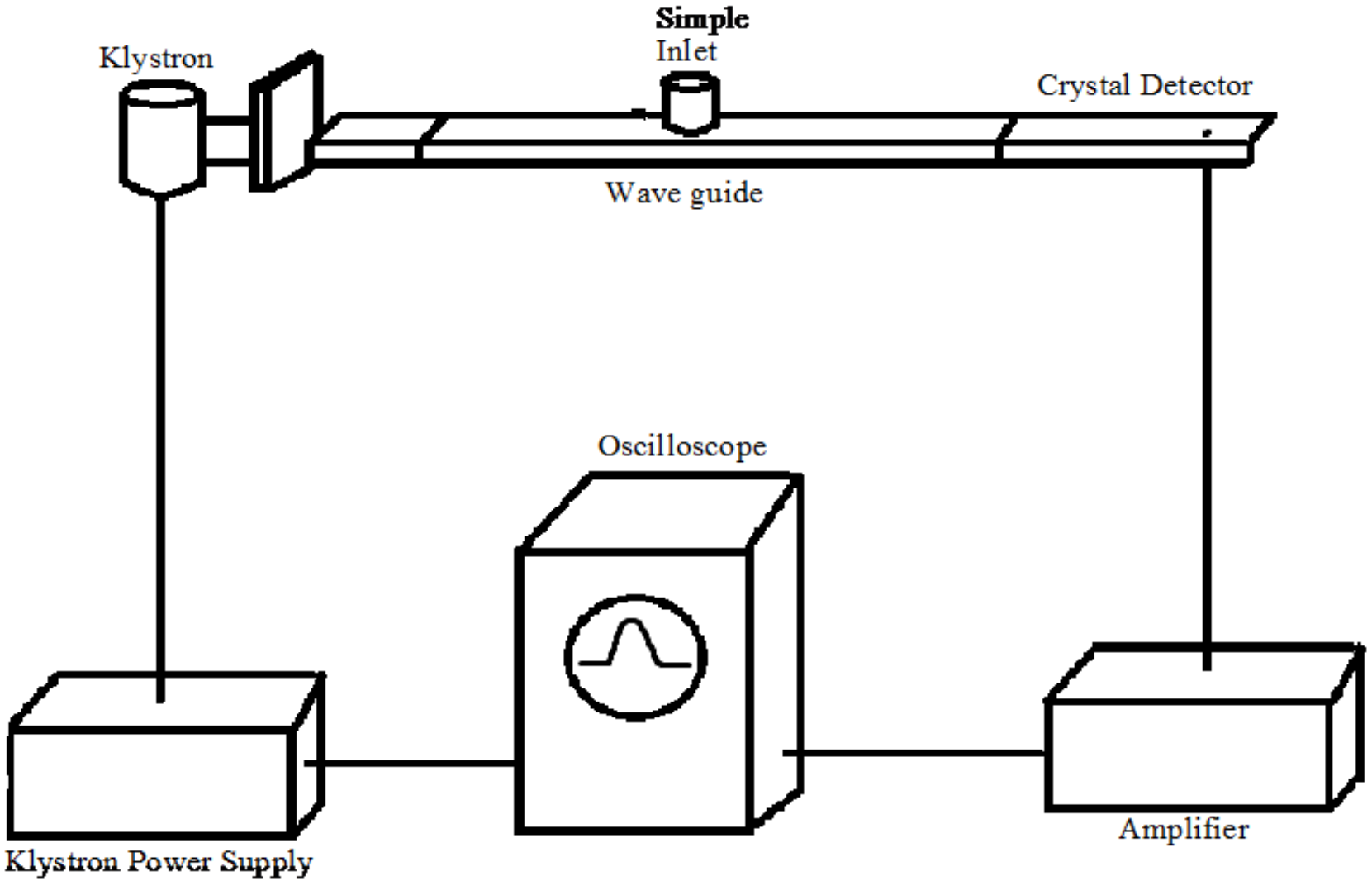
- **SAMPLE AND SAMPLE SPACE:** The sample is placed in a piece of evacuated wave-guide which is closed at both ends by thin mica windows. Round holes are made in the tube for evacuation purposes and for introduction of the gas under test. The pressure of the gas is adjusted to make the absorption line sharp.

The sample must be in the gaseous state for studying in the microwave region. The pressures of the order of 0.01 mm mercury are generally required to give absorption spectrum. Many solids or liquids substances can be studied by the microwave techniques provided their vapour pressures are above the value of 0.01mm of mercury.

- **DETECTOR:** A quartz crystal is generally used as a detector. It is mounted on a cartiridge made up of tungsten whisker held in point contact with the crystal. In place of crystal detector, an ordinary superheterodyne radio receiver can be used provided it may be tuned to the appropriate high frequency. But a simple quartz crystal is more sensitive and easier to use.

- **SPECTRUM ANALYSER:** It consists of an amplifier of detected energy and an indicator which may be either a cathode ray oscillograph or a pen- and ink-recorder. The vibrations emitted by the quartz crystal produce an electrical signal which is amplified and then displayed as a pattern on an oscilloscope screen or a recording on a chart by the pen- and -ink recorder.

  A diagrammatic sketch of one of the simplest type of microwave spectrometers is shown in the figure below:



Simplified diagram of microwave spectrometer.

WORKING

- Monochromatic radiations of various wavelengths in the microwave region emitted by klystron valve are allowed to pass through the simple space containing the gaseous sample of the substance under investigation. Then, the radiations are made to conduct along a rectangular tube called a waveguide. After this the radiations are received by the quartz crystal detector which is situated at the far end of the waveguide. After receiving the radiations from the wave guide it vibrates and produces an electrical signal which is amplified by the amplifier and then displayed either as a recording on a chart or as a pattern on an oscilloscopic screen. The pattern obtained on the chrt or on the screen of the oscillograph enables one to determine the frequency or the range of frequencies of the detected microwave radiation.

The microwave spectrometer described above is usually used for the measurements of the highest accuracy because the absorption lines are narrow and fairly faithful in shape and relative intensities. The use of oscilloscope poses a serious problem that the amplifiers bandwidth cannot be narrowed to remove noise and, thus, the sensitivity is not exceptionally high. At the same time the new lines for unknown substances cannot be obtained very easily unless their frequencies are known within narrow limits.

By changing the frequency of the oscillator and observing the intensity of transmitted beam, moment of inertia and internuclear distances upto ±0002 Å can be calculated- Datanobtained for bond lengths and bond angles calculated for linear molecules and symmetrical top molecule by microwave spectroscopy.

SOME MOLECULAR DATA DETERMINED BY MICROWAVE SPECTROSCOPY

S. No.	Molecules	Bond	r(Å)	Bond	r(Å)
1	HCN	C–H	1.06317	C–N	1.15535
2	ClCN	C–Cl	1.629	C–N	1.163
3	BrCN	C–Br	1.790	C–N	1.159
4	NNO	N–N	1.126	N–O	1.191
5	OCS	C–O	1.164	C–S	1.559
6	CH_3Cl	C–H	1.0959	C–Cl	1.178
7	CH_3F	C–H	1.109	C–F	1.385
8	SiH_3Br	Si–H	1.570	Si–H	2.209

BOND ANGLES FOR SOME MOLECULES

S.No.	Molecules	Bond Angle	Value of Bond Angle in degrees
1	$CHCl_8$	Cl–C–Cl	110°24’
2	CH_3Cl	H–C–H	108°0’
3	CH_3F	H–C–H	110°0’
4	SiH_3Br	H–Si–H	111°20’

APPLICATIONS OF MICROWAVE SPECTROSCOPY

Wireless Communications (space, cellular phones, cordless phones, WLANs, Bluetooth, satellites etc.)

Radar and Navigation (Airborne,vehicle, weather radars, GPS etc.)

Remote sensing (Meteorology, mining, land surface, aviation and marine traffic etc.)

RF Identification (Security, product tracking, animal tracking, toll collection etc.)

Broadcasting (AM,FM radio, TV etc.)

Heating (Baking, Food process, Ovens, Drying, Mining, rubber industry)

Bio-medical application(Diagnostics)

a)Structure of xenon oxyfluoride molecule- the microwave spectrum of this molecule is a characteristic of a symmetric top and is consistent with the C4vsymmetry of the molecule.

b) For the determination of structure of OCSmolecules.

c) It was at one time thought that the compound with thestoichiometric composition FNS should have the structure S-N-F. Microwave spectroscopic experiments, however, provide evidence for a non-linear molecule with the atomic order N-S-F and an angle of 117º.

d) One of the most noteworthy studies in the field of structural organic chemistry was the exact determination ofthe geometry of benzonitrile. It is interesting to note the deformation of the benzene ring from the regular hexagonal structure.

e)The inversion Spectrum of Ammonia- It was the first molecule to be studied by microwave spectroscopy, byBleaney and by Townes. In the spectrum of ammonia molecule, each of the linesis split into a double due to the inversion of the molecule.

Measurement of Barrier Heights- Microwave spectroscopy can be useful in measuring the barrier heights of certain molecules. If a part of a molecule can rotate about a single bond the internal potential energy of the molecule will depend on the orientation of this part with the rest of the molecule The structure of ozone molecule- microwave spectroscopy is successful to deduce the correct triangular structure of the simple ozone molecule. Previously, its correct structure could not be established by optical spectroscopy and electron diffraction technique. The abundance of isotopes- The microwave spectroscopy is successful in determining the isotope abundance because each molecule possesses a unique moment of inertia depending upon the particular nuclei present.


Thank You