these objects are quite black and essentially impenetrable by short wavelength radiation. As a consequence the grains are able to protect any molecules inside the clouds from dissociation by the starlight which pervades much of the rest of space and originally thought to pervade *all* space.

These clouds vary in almost all parameters such as: opacity, size, shape, density, temperature, internal turbulence, overall velocity, temperature homogeneity, proximity to stars and emission nebulae, apparent elemental composition, ratio of ions/electrons/ molecules/radicals, whether hot or cool stars or protostars are in the vicinity or embedded, etc.

As a result there are numerous possible classifications and sub-classifications of the clouds, in fact each reviewer can have his own. For the purposes of this review it is convenient to point out that molecules are found in the following regions

1. Diffuse clouds
2. Dark clouds
3. Circumstellar shells
4. Stellar atmospheres
5. Comets

as well as of course planets (in the solar system).

As well as these regions there are interarm regions with $n \sim 10^{-1}\,\mathrm{cm}^{-3}$ and also an intergalactic medium with $n \sim 10^{-4}\,\mathrm{cm}^{-3}$ and two possible effective temperatures due to the radiation field, 10^4 or 10^6 K.

Turner (1979a) has presented a general survey and classification of the regions where interstellar molecules reside. The most important point as far as interstellar chemistry is concerned is cloud opacity. If a cloud is transparent i.e. a diffuse cloud, then molecular lifetimes are limited by photodissociation by the ultraviolet radiation from stars. Such clouds have $T \sim 80$ K, mass $\sim 4 \times 10^2\,\mathrm{M}_\odot$, size ~ 15 ly and number density (H atoms + H_2 molecules) $n \sim 0.1\,\mathrm{cm}^{-3}$. If on the other hand the cloud is opaque to starlight any molecules formed may be very long-lived indeed. For the dark clouds $T \sim 10$ K, mass $\sim$ 10–100 $\mathrm{M}_\odot$, size $\sim$ 1–3 ly and $n \sim 1$–$10\,\mathrm{cm}^{-3}$ (mainly H_2). There are larger inhomogeneous clouds often associated with stars and sometimes called molecular clouds where $T \sim 25$–50 K and $n \sim 10^4$–$10^5\,\mathrm{cm}^{-3}$ in their cores and $T \sim 10$ K and $n \sim 10^3\,\mathrm{cm}^{-3}$ in the less dense outer regions. The masses involved are $\sim 10^4\,\mathrm{M}_\odot$ and sizes range from 3–100 ly. The largest clouds of all are the giant molecular clouds (GMCs) which may have masses $\sim 10^5$–$2.5 \times 10^6\,\mathrm{M}_\odot$ and sizes 100–500 ly. The most recent studies are yielding information about much denser and much hotter regions.

SPECTROSCOPY

Introduction

Quantum mechanics in so far as it applies to spectroscopy can be classified into two problems.

1. The time independent problem, relates to the energy level manifold of the atom or molecule and generates the eigenvalues $E(n)$ and associated eigenstates, $|n\rangle$.
2. The time dependent problem, considers the conditions under which an interstate transition $|n\rangle \leftrightarrow |m\rangle$ can take place either spontaneously or under the influence of a perturbation by radiation or a collision with another molecule or atom.

In the case of molecules the treatment of the first problem almost inevitably starts with the Born-Oppenheimer separation (Born and Huang 1954) which allows the electronic, vibrational and rotational motions to be treated separately and the associated state manifolds to be evaluated independently and then combined. For a finer understanding and indeed for a true insight into the problem one in general then juggles the basic results using a perturbation approach to allow for intermotional effects which are, in our case, mainly vibration–rotation interactions. These are in general small, but interesting, and under high resolution often very important. Into this basic treatment one may often have to inject further, initially disregarded, effects which relate to the specific molecule. The most important interactions that may in certain cases need to be considered are:

1. Internal rotation splitting
2. Conformational isomerism
3. Quadrupole hyperfine interactions
4. Electron spin interactions (for free radicals)

There are others which are *usually* less important. However one should note that in the Universe, anything that one can conceive might happen, undoubtedly does—and then some.

This field has benefitted as much, if not more so than most others, from the ingenuity with which scientists have unravelled the atomic and molecular Hamiltonians. The diverse problems associated with interstellar spectroscopy will be dealt with in the section which deals with the observational data.

As the results of the time dependent problem apply to all the systems in general they can be summarized first and they can usually be put under the heading—the interaction of radiation with matter. In fact, it was this general problem which gave birth to quantum mechanics (Van der Waerden, 1967).

The most important result of the time-dependent analysis of the radiation/molecule interaction lies in the quantitative evaluation of the resonant absorption coefficient $\gamma(\omega)$ in the Beer-Lambert law

$$I(\omega) = I_0(\omega)e^{-\gamma(\omega)l} \tag{1}$$

$I(\omega)$ and $I_0(\omega)$ are transmitted and incident radiation intensities and l the length of the absorbing medium, here assumed homogeneous. The Fermi golden rule (Fermi, 1961) yields the general result

$$\gamma(\omega) = \frac{8\pi^3}{3hc}\,\omega(N_m - N_n)|\langle n|\mu|m\rangle|^2\, S(\omega, \omega_0) \tag{2}$$

(Kroto, 1975) where ω is the frequency, N_m and N_n are the populations* of the connected states, $\langle n|\mu|m\rangle$ is the electric dipole moment matrix element and $S(\omega, \omega_0)$ is a normalized line shape function. From this relation we see that $\gamma(\omega)$ is proportional to ω and thus the higher the frequency the stronger the interaction. Thus microwave transitions at 30 GHz ($\equiv$ 1 cm^{-1}) are inherently 20 000 times weaker than optical transitions at 5000 Å ($\equiv$ 20 000 cm^{-1}). $S(\omega, \omega_0)$ in the case of laboratory microwave studies is usually a Lorentzian peaking sharply at the centre frequency ω_0 (Townes and Schawlow, 1955) and associated with pressure broadening.

The population factor $N_m - N_n$ determines the nature of the spectrum quite critically. There are three main cases.

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* Note if the states have degeneracies g_m and g_n then $(N_m - N_n)$ must be replaced by $(N_m/g_m - N_n/g_n)$.

1. $N_m > N_n$ and $I(\omega) < I_0(\omega)$: in this case $\gamma(\omega)$ is positive and (stimulated) absorption occurs. This is usually the case in the laboratory where roughly equilibrium conditions (for which $N_m = N_n\,e^{-\Delta E/kT}$) are usually maintained.
2. $N_m = N_n$ and $I(\omega) = I_0(\omega)$. This is the case of saturation and the active volume is effectively transparent.
3. $N_m < N_n$ and $I(\omega) > I_0(\omega)$. In this case we have so-called population inversion, more radiation is emitted than is incident and we have effectively maser or laser amplification.

Selection rules

The selection rules which govern the transitions follow directly from the *electric dipole* matrix element $\langle n|\mu|m\rangle$. In general the most important ones for our purpose are

$\Delta J = 0, \pm 1$, for rotational transitions
$\Delta v = \pm 1$, for vibrational energy changes
$S \not\leftrightarrow T$, singlet-triplet electronic transitions are forbidden.

There are however many loopholes through which the molecule can pass and as we may be dealing with effects over millions of years one must note that even very strongly forbidden processes may take place given enough time (1000 million years!) A more complete study of radiation/molecule interactions indicates that:

1. *Electric dipole* transitions are the strongest.
2. *Magnetic dipole* matrix elements are smaller by the factor $\alpha = 1/137$ (the fine structure constant) and so magnetic interactions are $\alpha^2(\sim 0.5 \times 10^{-4})$ weaker then the electric interaction.
3. *Electric quadrupole* transitions are weaker by the factor $(a/\lambda)^2$ where a is a molecular dimension and λ is the radiation wavelength (Mott and Sneddon, 1963). For optical electronic transitions these are weaker, by $\sim 10^{-8}$, than electric dipole interactions.
4. There are numerous other processes which can, in the absence of other stronger effects, become important. In this class come weak second-order effects such as Rayleigh, Raman and higher order scattering processes.
5. Finally we should note that some other important processes must be taken into account:
   (a) Photoionization
   (b) Photodissociation
   (c) Collisions

The most important recent breakthroughs in this field have come via the marriage of molecular microwave spectroscopy and radio astronomy. The most important aspects of microwave spectroscopy are therefore dealt with in more detail in this section than those of infrared and electronic spectroscopy which are in any case rather more familiar. The latter techniques have however very recently made exciting contributions and undoubtedly will play even more significant rôles in the future and so any relevant points are also highlighted in context with observation.

Spectroscopy is a subject for which many books have been written and almost all aspects have been well covered. More aspects of microwave spectroscopy have been covered by Townes and Schawlow (1955), Wollrab (1967), Gordy and Cook (1970) and Kroto (1975). The books by Herzberg (1944, 1945, 1950, 1966) have covered most aspects of electronic and molecular vibrational spectroscopy.

Microwave spectroscopy

There are several factors which have combined to make microwave spectroscopy a most effective analytical technique. The first is the very high resolution which, together with the high degree of pattern specificity, allows such moderately complex molecules as ethanol (CH_3CH_2OH), glycine (NH_2CH_2COOH) and vinyl cyanide ($CH_2{=}CHCN$) to be unequivocally identified in extremely complex mixtures. Lines at approximately 30 000 MHz ($\equiv 1\ \mathrm{cm}^{-1}$) can be measured routinely to 100 kHz and with specialized techniques to a few kHz if necessary. The interstellar cell in which more than 50 molecules have been detected still yields isolated lines rather than dense long grass though this may change as sensitivity improves.

Another obvious reason is that the atmosphere is relatively transparent to radio waves. Finally we should note that at low temperatures only low frequency transitions are excited to *emit* and so there is no infrared or electronic emission from the cold clouds. These latter techniques would require background radiation to be transmitted through the clouds and allow *absorption* to be detected.

The first microwave experiments were carried out by Cleeton and Williams (1934) at the behest of Dennison who was interested in measuring the ammonia (NH_3) tunneling frequency directly. Cleeton and Williams constructed a 24 GHz valve oscillator and used a leather bag as an absorption cell. The war saw the development of klystron oscillators and more sophisticated cells made from wave guide. Most molecular microwave measurements have been made using the Hughes-Wilson (1947) Stark modulation design which has culminated in the quintessential Hewlett Packard 8460A spectrometer now, regrettably, no longer available.

There are a few general points of which it is important to be aware.

1. Light diatomic and triatomic molecules such as CO and HCN tend to have their most intense transitions at approximately 100 GHz or higher frequencies and so are studied by millimetre or more readily by far infrared techniques (Dowling, 1967).
2. Most other molecules which have at least three heavy atoms (mass 12 amu or more tend to have accessible rotational transitions in the 8–40 GHz microwave range ($\equiv$ 0.27–1.3 cm^{-1}).
3. If a molecule is very heavy and complicated its spectrum may consist of so many lines that no individual line may be sufficiently strong to be detectable.
4. Often a molecule may not be sufficiently volatile as pressures of 1–100 μm Hg are usually necessary. Raising the temperature may destroy the compound or may populate more states causing line dilution, as in case 3.
5. As far as free radicals and ions are concerned, their microwave spectra are very difficult to detect compared with the success of electronic spectroscopy—mainly due to the very much higher absorption coefficients and superb sensitivity and integrating capabilities of the simple photographic plate.
6. Numerous ingenious techniques have been, and are being, developed to circumvent these problems and astronomy has given the field a shot in the arm.
7. A rather important factor tends to make the spectra of linear molecules more readily detectable than those of non-linear molecules. The linear molecule has only two rotational degrees of freedom and as a consequence that is only *one* line for a given $J + 1 \leftrightarrow J$ transition, whereas for the non-linear species this will in general be a multiplet. In the case of a symmetric rotor it would have $J + 1$ components (see next section) and in the asymmetric rotor case in general even more.

Rotational energy levels

The Hamiltonian for a rigid rotating molecule can be written (Kroto, 1975)

$$H_r = AJ_A^2 + BJ_B^2 + CJ_C^2 \tag{3}$$

where J_A, J_B and J_C are components of angular momentum (units of $\hbar$) along the molecule-fixed principal axes. A, B and C are rotational constants which are related to the principal moments of inertia I_A, I_B and I_C by $A = 1/2I_A \ldots$ etc.* By convention $I_A \leqslant I_B \leqslant I_C$ and therefore $A \geqslant B \geqslant C$. The solution of H_r depends on the type of molecule. Thus for linear molecules such as CO, OCS and HC≡C–C≡N where $B{=}C$ and $J_A \to 0$ the resulting energy is given by the familiar expression

$$E(J) = BJ(J+1) \tag{4}$$

where J is the overall angular momentum quantum number.

Symmetric tops such as $CH_3C{\equiv}N$, $CH_3(C{\equiv}C)_3H$ and SF_5Cl, which are prolate (i.e. cigar shaped) with $A > B = C$, can spin about their symmetry axes, with associated quantum number K, and the energy is given by

$$E(J, K) = BJ(J+1) + (A - B)K^2 \tag{5}$$

A similar expression in which $A \to C$ applies to oblate tops such as NH_3 and C_6H_6 which are discus shaped.

Spherical tops, such as CH_4 and SF_6, have $A = B = C$ and the energies follow a similar expression to that for linear molecules.

Asymmetric top molecules have $A > B > C$ and their energy levels follow much more complicated expressions. It is however very informative to consider a molecule which is not too asymmetric. Consider a *near* prolate molecule in which $A > B \sim C$. In this case the energy, using perturbation theory, is given by

$$E(J, K_A) = \bar{B}J(J+1) + (A - \bar{B})K_A^2 \pm \tfrac{1}{4}\delta_{K_A,1}(B - C)J(J+1)\ldots \tag{6}$$

where $\bar{B} = \frac{1}{2}(B + C)$ and K_A is a *good enough* quantum number ≡ to $|K|$ (which for a symmetric top is *almost* perfect). The last term has a Kronecker delta which indicates that it splits the degeneracy of the $|K| = 1$ levels only. Smaller terms, which shift and/or split other levels, come in only in second order and have been truncated.

If a molecule is very asymmetric the energy level pattern can become very complicated as can the resulting spectrum. A comparison of the energy level patterns for the three cases is given in Fig. 3. For the asymmetric molecule it is necessary to further specify the levels because as can be seen in Fig. 3c levels of a given $|K|$ (or here K_A) are no longer degenerate. It is usual to use the value of $|K|$ with which the level correlates in the oblate limit (K_C). Thus a given level is characterized by $J_{K_A K_C}$.

Rotational spectra

For a linear molecule with a dipole moment $\Delta J = \pm 1$ and the transitions are governed by the expression

---

* $I_A = \sum_n m_n(r_B^2 + r_C^2)$, $I_B = \ldots$ etc. where m_n are the atomic masses and r_A, etc. are the coordinates $A(\mathrm{MHz}) = 505391/I_A(\mathrm{amu\ Å})^2$ or $A(\mathrm{cm}^{-1}) = 16.858/I_A(\mathrm{amu\ Å}^2)$.

Example. For CH_3CN or $CH_3(C{\equiv}C)_nH$, ∠CCH and r(CH) are respectively tetrahedral and ~1.1 Å long. Thus the distance from the A axis is ~1.04 Å ∴ $I_A = 3(1.04)^2 \sim 3.23$ amu Å^2 ∴ $A \sim 5.2\ \mathrm{cm}^{-1}$ or 156.5 GHz.

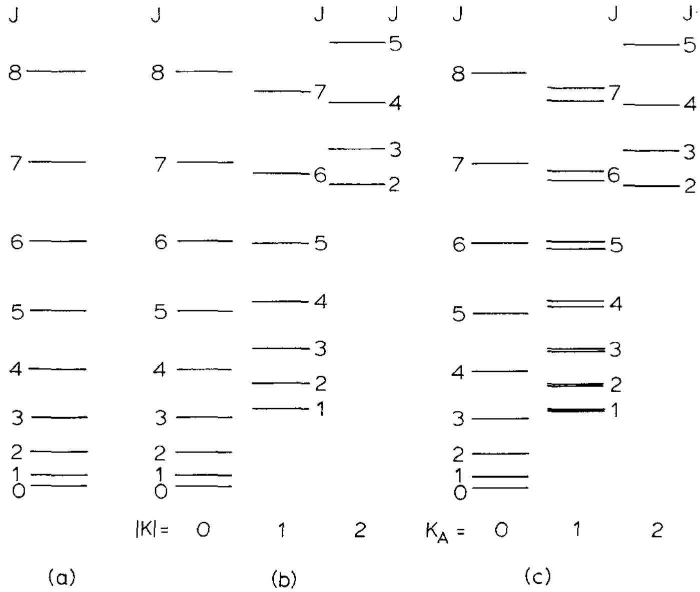

FIG. 3. (a) The rotational energy levels of a linear molecule. (b) The rotational energy levels of a prolate symmetric top. (c) The rotational energy levels of a prolate slightly asymmetric rotor. For this set of diagrams $A \sim 38$ GHz, $B \sim C \sim 30.6$ GHz and $B - C \sim 0.25$ GHz. In all three cases vertical transitions may occur depending on the dipole moment conditions. In such cases the transitions give rise to equidistantly spaced lines for a linear molecule and equidistantly spaced groups of lines in the non-linear cases.

$$\Delta E(J) = 2B(J + 1) \tag{7}$$

This gives rise to a sequence of equally spaced lines (separation $= 2B$) and the textbook example obtained by Dowling (1967) in the far infrared is shown in Fig. 4. The microwave spectrum of $HC{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$ which also shows strong vibrational satellites is shown in Fig. 5.

The selection rules that apply to rigid symmetric tops are $\Delta J = \pm 1$ and $\Delta K = 0$. The selection rule on K essentially means that the radiation field cannot exert a torque about the symmetry axis, as there is no perpendicular dipole component, and cannot therefore make it spin any faster or slower about this axis. Consequently only vertical transitions in

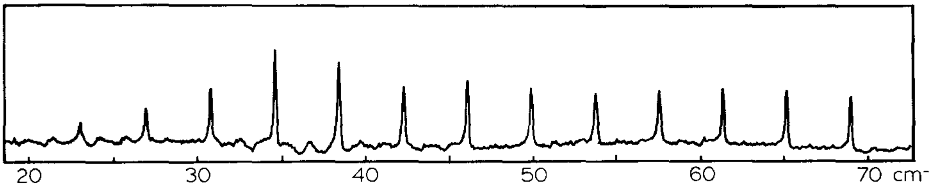

FIG. 4. Part of the far infrared pure rotational spectrum of CO obtained by Dowling (1967). The background intensity varies across the range and so distorts the apparent intensity distribution. The lines are separated by $2B_0$ which can be obtained directly from this spectrum and once this has been determined it is straightforward using eq. (7) to assign the J numbers of the lines.

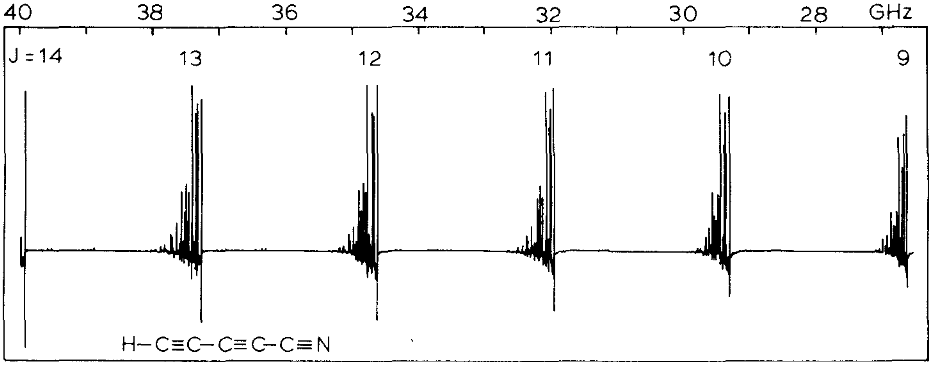

FIG. 5. The laboratory microwave rotational spectrum of cyanobutadiyne, HC≡C–C≡C–C≡N (Alexander, Kroto and Walton, 1976). Instead of a single line, each $J + 1 \leftarrow J$ ground state line is accompanied, to high frequency, by a complicated entourage of bending vibration satellites. The first line at the RH end of each group is the ground state line. The very weak features which lie to the low frequency side are transitions belonging to the ^{13}C and ^{15}N monosubstituted species. Note that the microwave spectra have negative-going Stark lobes as with this Stark spectrometer the zero field spectrum is presented positively and the field split spectrum negatively.

the $|K|$ manifolds of Fig. 3b may occur, giving rise to a spectrum governed by the same expression as for a linear molecule, Eq. (7). Such a spectrum in the microwave range is shown in Fig. 6 for $CH_3(C{\equiv}C)_2C{\equiv}N$. A nice example of a far infrared spectrum is given by Ozier, Ho and Birnbaum (1969) for CH_3D. There is an added complication in that vibrational satellites are also detected in microwave spectra as discussed in the next section. The various $|K|$ components for a given value of $J + 1 \leftarrow J$ overlap if centrifugal distortion (next section) is negligible as is the case in the low resolution run shown in Fig. 6. Although a spherical top has no permanent dipole moment it distorts on rotation and gives rise to a distortion-induced rotational spectrum (Watson, 1971, Rosenberg, Ozier and Kudian, 1972).

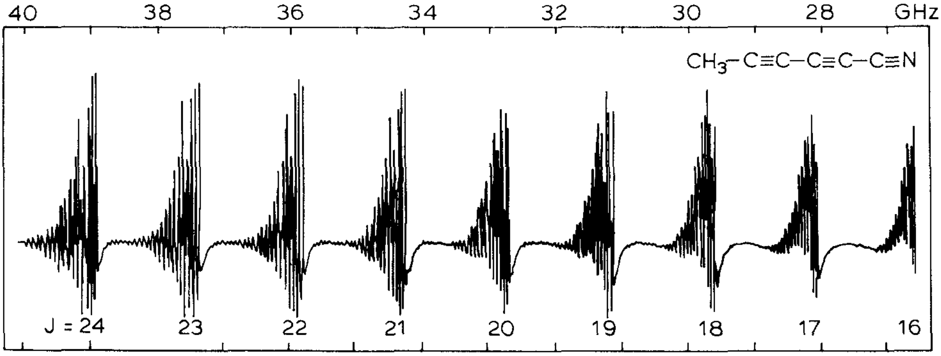

FIG. 6. Wide band scan of the microwave spectrum of $CH_3C{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$ (Alexander *et al.*, 1978). As in the case of cyanobutadiyne the first line at the RH end of each group belongs to the vibrational ground state and the rest to bending vibrational satellites. The ground state transitions can be resolved into $|K|$ multiplets under higher resolution (Fig. 10).

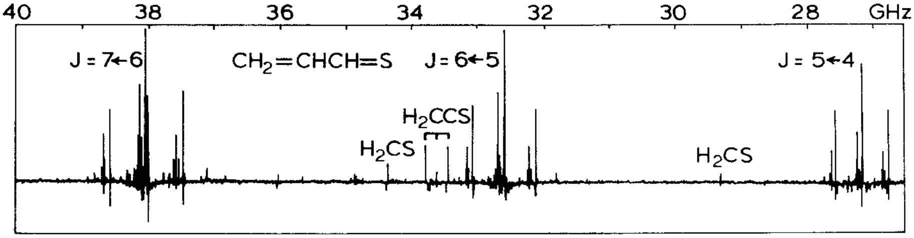

FIG. 7. The microwave spectrum of trans-2-propenethial $CH_2{=}CHCH{=}S$ produced by pyrolysis of diallylsulphide (Georgiou and Kroto, 1980). The most prominent features are the three groups of R-branch transitions which display the characteristic pattern of a slightly asymmetric rotor. The $K_A = 1$ lines flank the central ($K_A \neq 1$) group roughly symmetrically. Lines of H_2CS and H_2CCS are also observed.

Asymmetric rotor molecules may have very complex spectra. However the most frequently observed transitions often occur for near prolate molecules with a dipole component μ_A along the long A axis. Accordingly we will deal only with the spectra for this special and most important case in detail. The most important effect of asymmetry as we have noted is the splitting of the $K_A = 1$ levels (Fig. 3c). The *main* μ_A selection rules are analogous to those for a symmetric rotor i.e. $\Delta J = \pm 1$ and $\Delta K_A = 0$ and thus an analogous type of spectrum occurs. Transitions occur from upper to upper and lower to lower $K_A = 1$ split levels and so the transition energy relation from Eq. (6) is

$$\Delta E = 2\bar{B}(J + 1) \pm \tfrac{1}{2}\delta_{K_A,1}(B - C)(J + 1) \tag{8}$$

This splits the $K_A = 1$ lines out as two single lines which symmetrically flank the central bunch for a given J. This effect is shown under low resolution in Fig. 7 for $CH_2{=}CHCH{=}S$. These are called μ_A R-branch lines because they have $\Delta J = +1$ and are associated with the μ_A dipole moment. An asymmetric rotor may have other non-zero dipole moment components and these will generate other types of transitions. For instance a dipole moment perpendicular to μ_A, either μ_B or μ_C, will allow the molecule to be twisted about by its long axis by the radiation and this allows K_A to change by $\Delta K_A = \pm 1$. The splitting is the quantum effect equivalent to classical wobbling which occurs for an object which is not a good top. Under high resolution, as is shown in Fig. 8, we see the effect in detail. In fact we can also see that second order effects of asymmetry also split $K_A = 2$ lines. The splitting is much smaller for, as one expects, wobbling gets less important as the molecule spins more rapidly about the axis i.e. as K_A increases relative to J.

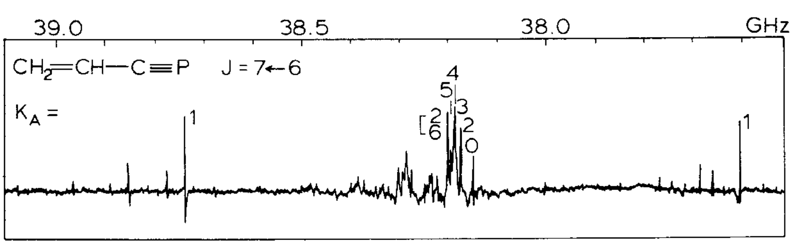

FIG. 8. A moderate resolution microwave scan of the $J = 7 \leftarrow 6$ transition of $CH_2{=}CHC{\equiv}P$ the phosphorus analogue of $CH_2{=}CHC{\equiv}N$, vinyl cyanide. The vibrational ground state lines have been labelled by the value of K_A (Ohno, Kroto and Nixon, 1981).

An important transition, called a K-doubling transition, can occur *between* the $K_A = 1$ *split* levels. From Eq. (6) we see that the transition energy is given by

$$\Delta E = \tfrac{1}{2}(B - C)J(J + 1) \tag{9}$$

Spin statistics

In a molecule such as H_2CO with two identical H atoms the rotational states with odd and even values of K_A have different spin statistics. The situation is similar in the rotational

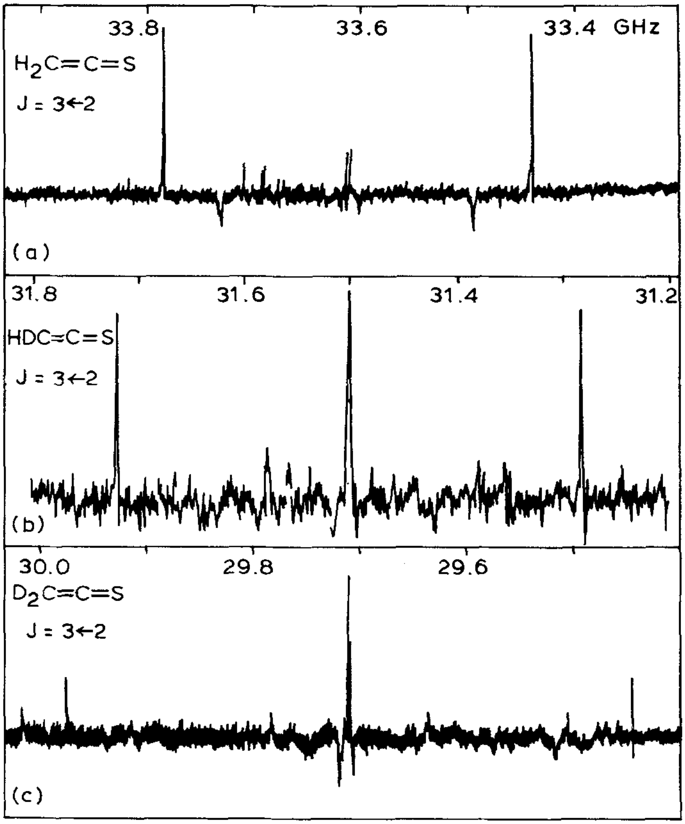

FIG. 9. The microwave spectra of $J = 3 \leftarrow 2$ transitions of the thioketenes $H_2C{=}C{=}S$, $HDC{=}C{=}S$ and $D_2C{=}C{=}S$ (Georgiou, Kroto and Landsberg, 1979). These are slightly asymmetric rotors with central lines having $K_A = 0$, 2 and outer lines $K_A = 1$. In H_2CCS and D_2CCS rotation about the axis exchanges equivalent nuclei and so the generalised Pauli Exclusion Principle controls the statistical weights of states with odd and even K_A. A similar effect occurs for H_2 where it explains the *ortho* -*para* ratio (Kroto, 1975). For H_2CCS the ortho states with statistical weight 3 have K_A odd and *para* states with statistical weight 1 have K_A even. Thus the outer lines are 3 × as intense as the central lines. The D nuclei are bosons so the statistics reverse and yield *ortho*:*para* (K_A even : K_A odd) 2 : 1. In HDCCS the statistics do not apply and the intensities are normal. Note that transitions do not occur between the *ortho* and *para* manifolds and so one can essentially think of them as two different molecules.

states of H_2 for which ortho H_2 may only have odd J and para H_2 even J. For molecules like H_2CO, H_2CCO and H_2CCS, levels with K_A odd have three times the statistical weight of levels with K_A even, a factor reflected directly in the intensities of associated transitions. For D_2CCS this changes to 2 to 1 for K_A even and K_A odd because D nuclei are bosons and in HDCCS permutation statistics do not apply. This is a nice example of the generalized Pauli Exclusion principle (Kroto, 1975) and the experimental effect is shown in Fig. 9. This effect is also important in symmetric tops as indicated below. One can consider the two sets of levels as effectively different molecules between which transitions do not occur.

Centrifugal distortion

Centrifugal effects which tend to increase the molecular dimensions with increasing J are usually quite adequately taken into account by J^4 corrections introduced using perturbation theory. For a linear molecule the centrifugal distortion correction to the

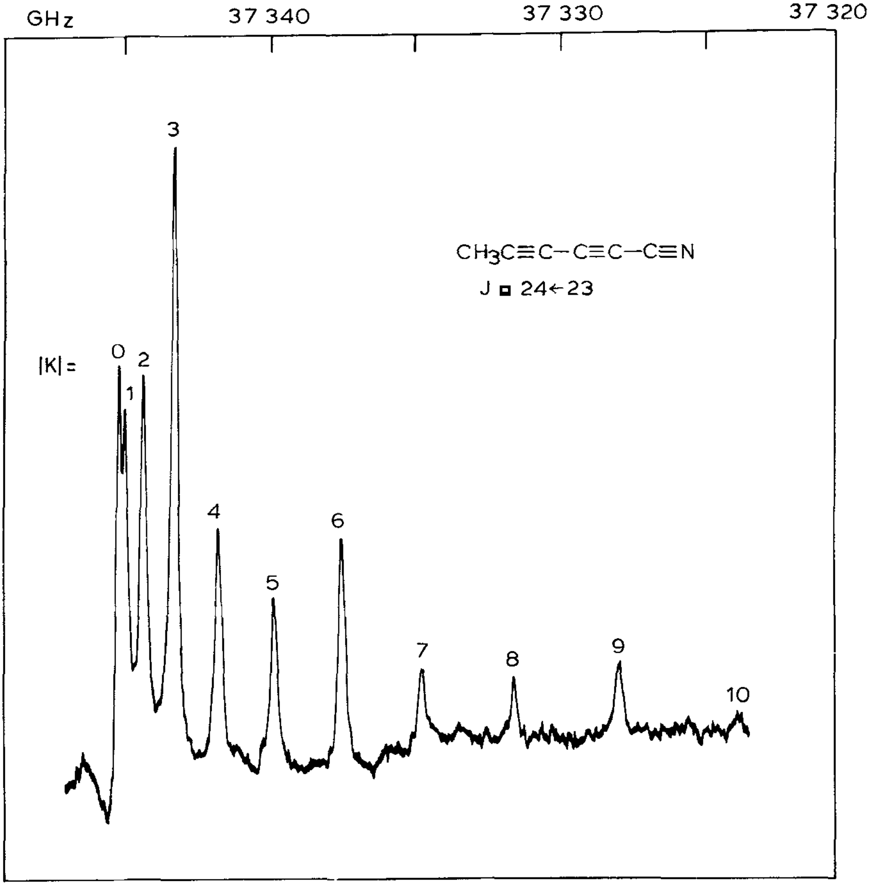

FIG. 10. Part of the $|K|$ structure of the $J = 24 \leftarrow 23$ transition of $CH_3C{\equiv}C{-}C{\equiv}C{-}C{\equiv}N$ (Alexander *et al.*, 1978). The higher $|K|$ levels are not sufficiently populated to be detected at this temperature (~ –60 K). Note that statistical weights of levels with $|K|$ a multiple of 3 are twice those for the rest.

energy (Eq. (4)) is $-DJ^2(J+1)^2$ where $D \sim 10^{-6}\,B$ (for a diatomic molecule $D = 4B^3/\omega^2$ where ω is the vibrational frequency). The resulting transition expression is

$$E(J) = 2B(J+1) - 4D(J+1)^3 \tag{10}$$

For the symmetric top, the correction which must be added involves three centrifugal distortion terms $-D_J J^2(J+1)^2 - D_{JK}J(J+1)K^2 - D_K K^4$ (Slawsky and Dennison, 1939; Kroto 1975) which results in transitions governed by the expression

$$\Delta E(J, K) = 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)K^2 \tag{11}$$

As a consequence a given $J+1 \leftarrow J$ symmetric top transition is split by the small D_{JK} term into a sequence of close quadratically spaced $|K|$ components as is shown in Fig. 10 for $CH_3(C{\equiv}C)_2C{\equiv}N$. Note here how spin considerations cause transitions with $|K|$ a multiple of 3 to have twice the statistical weight of the others (Kroto, 1975).

More complex centrifugal corrections apply for the general asymmetric rotor (Watson, 1967) which as far as qualitative patterns are concerned are in general masked by the larger shifts and splittings due to asymmetry.

Ground and vibrationally excited states

Many molecules have vibrational frequencies sufficiently low that their laboratory spectra show rotational transitions of vibrationally excited states. Bending vibrations associated with low force constants, and therefore low frequencies, are often observed. They tend, in the case of linear chains, to yield shorter effective bond lengths, the moments of inertia tend to decrease and the rotational constants to increase. Good examples of this are shown in Figs. 5 and 6 where long sequences of vibrational satellites are shown. In a linear molecule such as $N{\equiv}C{-}C{\equiv}P$ shown in Fig. 11 we see that the $v = 1$ level is split into a doublet by an effect which can be related to the $K_A = 1$, splitting in asymmetric rotors (Watson, 1965). This effect, known as *l*-doubling (Herzberg, 1945, Nielsen, 1950), occurs in all cases where the bending vibration quantum number v is odd. In general the effect is treated as a vibration-rotation coriolis interaction (Nielsen, 1950).

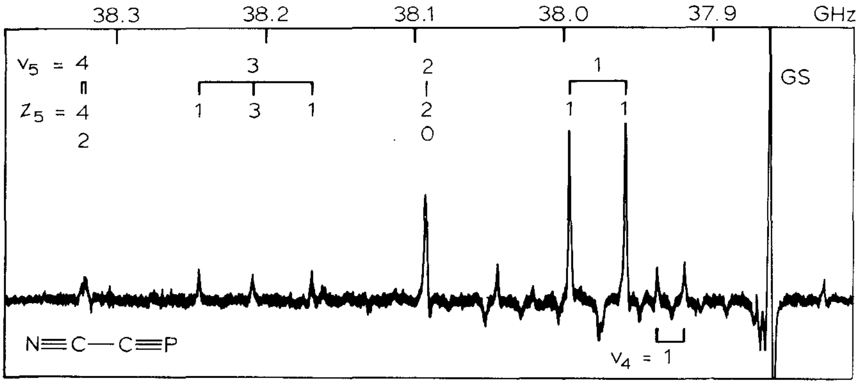

FIG. 11. The microwave spectrum of the $J = 7 \leftarrow 6$ transition of $N{\equiv}C{-}C{\equiv}P$ (Cooper *et al.*, 1979). The spectrum is very similar to that of $HC{\equiv}C{-}C{\equiv}N$. The vibrational satellite pattern is characteristic of a simple linear molecule with a low bending frequency. The $v = 1$ satellite consists of two lines split apart by *l*-doubling, a vibration-rotation counterpart of asymmetry *K*-doubling and electron-rotational Λ-doubling.

The rotational constants are usually identified by the appropriate vibrational quantum number subscripts and for the ground state in particular they are written A_0, B_0 and C_0 associated with I_A^0, I_B^0 and I_C^0 respectively.

Conformers and internal rotation effects

Some molecules have rotational isomers. For instance the molecule isocyanotoethene CH_2=CHNCO with an angle of about 140 degrees at N has two conformers, *cis* and *trans* species (Bouchy and Roussy, 1978; Kirby and Kroto, 1978). The moments of inertia of the two isomers are quite different as are the dipole moments and hence the rotational spectra (Fig. 12) are also quite different and it is important to note that although the *cis* spectrum is clearly very weak this isomer is present in approximately 35 per cent proportion.

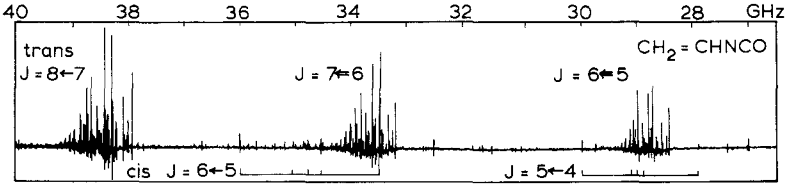

FIG. 12. The microwave spectrum of CH_2=CHNCO (Kirby and Kroto, 1978). The strong groups of lines belong almost entirely to trans CH_2=CHNCO (∠CNO ~ 140 degrees). Some very weak features, the strongest of which are assigned below the baseline, belong to the *cis* conformer. Though the *cis* species is present in ~35 per cent abundance the lines are very much weaker due to greater asymmetry and lower dipole moment.

The barrier between rotational conformers in some cases is sufficiently low that appreciable tunnelling occurs during the timescale of the experiment. This can cause internal rotation splittings to be observable.

Other types of isomerism can occur such as in the case of cyanides and isocyanides. The rotational spectra of both CH_3CN and CH_3NC were well known but, as discussed later, the interstellar spectrum of HNC was detected before the laboratory measurement was made.

Quadrupole splittings

Nuclei with spin $I \geqslant 1$ possess non-spherical charge distributions and therefore quadrupole moments which can interact with electric field gradients of molecular charge distributions. This causes hyperfine splittings which are largest for low J and high K. The splitting pattern depends qualitatively on I and quantitatively on the nucleus in question and its bond location. These hyperfine patterns have been very valuable in interstellar identifications as shown later. The splittings tend to decrease roughly as J^{-3} so in general only low J lines show these splittings. For linear molecules with N atoms, for which the quadrupole parameters are only a few MHz or less, only the lowest J lines with $J \sim 0$–2 show resolvable structure in general. In symmetric tops the highest $|K|$ lines, for a given J, show splittings.

Dipole moments

The most accurate dipole moments are in general obtained by studying the Stark effect in rotational spectra. These values are particularly important in molecular radio astronomy as the line intensities are so dependent on their values through the relation for the absorption coefficient $\gamma(\omega)$ in Eq. (2). Many values are listed by Gordy and Cook (1970).

Free radicals

Some molecules have unpaired electrons which give rise to electronic angular momenta that interact in complicated ways with the rotational motion. The energy level patterns produced depend quite critically on the molecule in question. Suffice it to say that further splittings can, and often do, occur. In fact the first molecule detected, OH, was detected by a transition which occurs *between* two levels split apart by a Λ-doubling interaction, an interaction and therefore a type of transition which does not occur in diamagnetic molecules. The radio spectrum of CH has also been detected by this type of transition. The hyperfine splittings that can arise in these systems have, as we shall see, been very important in the identification of some unexpected and exciting species. The Λ-doubling splitting arises by a type of coriolis splitting of the electronic angular momentum about the bond axis caused by interaction with overall rotation (Townes and Schawlow, 1955; Carrington, 1974; Kroto, 1975).

Most free radicals have been detected by electronic spectroscopy and their electronic properties are discussed by Herzberg (1950, 1966). Some have also been detected by gas-phase paramagnetic resonance as discussed by Carrington (1974). Laser magnetic resonance is proving to be one of the most powerful and sensitive techniques for studying these species (Evenson *et al.*, 1979) and much effort is also being applied to detect their zero field microwave spectra.

Electronic and vibrational spectra

The first interstellar molecules were indeed diatomic molecules detected by their electronic spectra. The main characteristics of these spectra are rather more familiar to the non-specialist than are those of microwave spectra and so a detailed introduction is not given in this review. Important features will however be discussed in context with the astrophysical results. A complete discussion covering most major aspects of electronic as well as vibrational and rotational spectra of diatomic molecules has been given by Herzberg (1950). So far no interstellar polyatomic molecules have been detected by their electronic spectra though the species C_3 and H_2O^+ have been detected in comets. Their electronic spectra have been discussed in detail by Herzberg (1966).

The problems involved in detecting vibrational spectra are only just being solved and the first results are very exciting. The vibrational spectra of polyatomic molecules have also been discussed by Herzberg (1945) and, in this review, will also only be discussed very briefly in context with observations. It is possible that infrared spectroscopy will yield as much data in the future as radio spectroscopy is doing at present.

Astronomical observation

The main information which can be derived from molecular spectra, apart of course from the molecular identity, relates to the abundance and the physical conditions that pertain in the molecular clouds. This information is buried in the transition intensities, the line shapes and the observed line frequencies. There are three main problems that tend to confuse the issue: namely temperature, number density and cloud velocity.