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 $\Lambda$-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 $\Lambda$-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.

*Temperature.* Temperature is really only a well defined quantity when equilibrium conditions apply and the distribution of the molecules among the energy levels obeys the Boltzmann relation. This is not in general the case in the ISM and the distributions are governed by a subtle interplay of collisional and radiative processes. It is convenient to describe any individual two level distribution $N_n/N_m$ by an effective (Boltzmannian) temperature and call this the excitation temperature $T_{ex}$. In the case of the molecular radio lines this will in general be the rotational excitation temperature and it may often vary from one *pair* of rotational levels to another. In a similarly parochial and suspect manner one can define a kinetic temperature $T_k$ which describes the velocity distribution (assumed Maxwellian) of the bulk of gas which is being observed. There is also the temperature of the radiation field which bathes the molecule $T_{rad}$. The grains may be at yet another temperature.

*The number density.* As a telescope can only see an object in plan the length of the active volume is never known exactly. As a consequence in a simple case such as that governed by Eq. (1) only the *column density nl* (cm$^{-2}$) is obtainable directly. It is usual however to assume that a cloud is about as deep as it is wide and so derive an estimate of the number density $n$ (cm$^{-3}$).

*Cloud velocities.* Along the line of sight there may be several pockets of gas each with its own characteristic set of temperatures and travelling with either the same or different mean bulk velocities relative to the observer. The velocity relative to the observed is called $v_{LSR}$ the radial velocity relative to the *local standard of rest* (*LSR*). The frequencies ($\omega$) will thus be shifted (by $\Delta\omega$) according to the Doppler relation, $\Delta\omega = (v_{LSR}/c)\omega$. Each pocket of gas will thus contribute some roughly gaussian line shape to an overall intensity/velocity line profile which may or may not be susceptible to deconvolution. Collisions are so infrequent in general that the pressure broadening mechanism that gives Lorentzian line shapes to microwave lines in the laboratory (Townes and Schawlow, 1955) can be neglected.

### The equation of radiative transfer

In some cases, and in radioastronomy in particular, the simple Beer-Lambert relation Eq. (1) is not sufficient and the more complete *radiative transfer equation* must be used. Consider a slice of active medium of thickness $dx$. Then

$$dI(\omega) = -\gamma(\omega)I(\omega)\,dx + \varepsilon(\omega)\,dx \tag{12}$$

The Beer-Lambert relation Eq. (1) is derived directly from the first R.H. term. The second is an additional term which takes spontaneous emission with coefficient $\varepsilon(\omega)$ into account. We can set $\gamma(\omega)\,dx = d\tau(\omega)$ (where $\tau(\omega)$ is called the *optical depth*) and take into account that at thermal equilibrium Kirchhoff's law indicates that absorption and emission are equal, i.e.

$$\frac{\varepsilon(\omega)}{\gamma(\omega)} = B_\omega(T_{ex}) \tag{13}$$

where $B_\omega(T_{ex})$ is the Planck function

$$B_\omega(T_{ex}) = \frac{2h\omega^3}{c^2}\frac{1}{e^{h\omega/kT_{ex}} - 1} \tag{14}$$

We will take the easy way out and assume that temperature and therefore $B_\omega(T_{ex})$ are independent of $\tau(\omega)$ and integrate Eq. (14) from $I_0(\omega)$, the incident intensity, to $I(\omega)$, the emergent intensity, and from $\tau(\omega) = 0 \rightarrow \tau(\omega)$ (i.e. the optical depth equivalent to $x = 0 \rightarrow l$ the length of the active volume). Thus

$$I(\omega) = I_0(\omega)\, e^{-\tau(\omega)} + B_\omega(T_{ex})(1 - e^{-\tau(\omega)}) \tag{15}$$

If the line is narrow and sits on top of a broad flat background which is independent of $\omega$ then setting $I_0(\omega) \rightarrow I_0$ the excess line intensity can be defined as

$$\Delta I(\omega) = I(\omega) - I_0 = (B_\omega(T_{ex}) - I_0)(1 - e^{-\tau(\omega)}) \tag{16}$$

In the Rayleigh-Jeans limit $h\omega \ll kT$ and thus Eq. (14) simplifies and allows the following definitions:

1. *The excess line brightness temperature* $T_L(\omega) = a\Delta I(\omega)$
2. *The excitation temperature* $T_{ex} = aB_\omega(T_{ex})$
3. *The background brightness temperature* $T_0 = aI_0$

where $a = (c^2/2\omega^2 k)$. As a consequence Eq. (16) becomes

$$T_L(\omega) = (T_{ex} - T_0)(1 - e^{-\tau(\omega)}) \tag{17}$$

In general $T_0 = T_S + T_{BB}$ where $T_S$ is a background source contribution and $T_{BB}$ is the Universal 3K blackbody radiation. The *total* line intensity is expressed by the *total line brightness*, $T_L$, an integral over the line shape

$$T_L = \int T_L(\omega)\, d\omega \tag{18}$$

There are two particularly important limiting cases

1. The *optically thick case* for which $\tau(\omega) \gg 1$ where the line brightness is independent of optical depth. In this case

$$T_L = T_{ex} - T_0 \tag{19}$$

   and the brightness temperature gives the cloud excitation temperature directly and is independent of optical depth. It is essentially the case of a black body radiation which is independent of the material.
2. The *optically thin* case for which $\tau(\omega) \ll 1$ for which Eq. (17) becomes

$$T_L(\omega) = (T_{ex} - T_0)\tau(\omega) \tag{20}$$

In the simplest homogeneous cloud model in which $\gamma(\omega)$ is independent of cloud depth along the line of sight $\tau(\omega) = \gamma(\omega) l$ and so

$$T_B = (T_{ex} - T_0) l \int \gamma(\omega)\, d\Omega \tag{21}$$

From Eq. (2) and the following set of definitions and approximations for a linear molecule:

1. The line shape integral $\int S(\omega, \omega_0)\, d\omega = 1$
2. At *LTE* $(N_m - N_n) = N_m(h\omega/kT)$ for $h\omega \ll kT$
3. $N_m = (N/Q)(2J + 1) \exp[-hBJ(J + 1)/kT]$ where $N$ is the total number density and $Q$ the rotational partition function which $\approx kT/hB$ for the case where $hBJ(J + 1) \ll kT$ (Herzberg, 1950),

Eq. (21) becomes

$$T_B = \frac{8\pi^2}{3ck^2}\frac{T_{ex} - T_0}{T_{ex}^2} hB(2J + 1)Nl\omega^2 |\langle J|\mu|J - 1\rangle|^2 e^{-E(J)/kT} \tag{22}$$

For a $J \to J - 1$ emission line

$$|\langle J|\mu|J - 1\rangle|^2 = \mu^2 \left(\frac{J - 1}{2J + 1}\right) \tag{23}$$

A consequence of Eq. (19) is that in a case such as that of CO, where in general the $^{12}C^{16}O$ line is optically thick, $T_{ex}$ is obtained directly from the brightness temperature. From $T_B$ for $^{13}C^{16}O$, which is often optically thin, one can *then* obtain the column density $Nl$ according to Eq. (22).

The excitation temperature $T_{ex}$ results from a subtle blend of various factors which can affect the populations of the connected states. To determine this, *statistical equilibrium calculations* should be carried out. The simplest case of a two level system subject to collisions with a surrounding gas with kinetic temperature $T_k$ and to radiation field characterized by temperature $T_r$ has been studied by Purcell and Field (1956). In the simplest form

$$T_{ex} = (\tau_r T_k + \tau_c T_r)/(\tau_r + \tau_c) \tag{24}$$

(Rank, Townes and Welch, 1971) where $\tau_c$ is the collision lifetime and $\tau_r$ is the radiative lifetime. Winnewisser, Churchwell and Walmsley (1979) have discussed this problem in further detail with some appropriate examples.

### *Radioastronomy*

Radiotelescopes are essentially glorified radios with large, steerable, highly directional aerials and expensive amplifying electronics, which can tune in to very weak sharp frequency signals. The modern parabolic reflector is, like an optical telescope, diffraction limited in that it can distinguish between beams from two sources separated by $\delta\theta \sim \lambda/D$ (in radians) where $\lambda$ is the operating wavelength and $D$ the diameter of the mirror. Theoretically the limit is governed by the *half power beam width HPBW*. For a parabolic reflector this is $HPBW = 1.22\ \lambda/D$ radians. One can obtain higher spatial resolution by increasing $D$ or by reducing $\lambda$, i.e. increasing the frequency. $D$ can also effectively be increased by interferometric aperture synthesis techniques.

The way in which the radiation is processed depends on the frequency ranges and the particular philosophy of the telescope designers. In general the radiation from a distant source is collected and focused by a radiotelescope's parabolic reflector into a cooled parametric or maser amplifier ($<100$ GHz) or a Schottky barrier system ($>100$ GHz) located at the focal point. The focal point may be at the primary focus or a secondary mirror may be used to produce a secondary focus through a hole in the centre of the main reflector. In general the radiation having been amplified is converted to an intermediate frequency by a mixer, amplified further and detected. As the signal usually consists of a range of frequencies, the final stage is a spectrometer such as an electronic multichannel filter bank which can effectively analyse the signal and display it as a function of frequency. The data collection and processing is usually carried out by a computer as is the telescope pointing and guidance. A particular observation may consist of several hours of observations in which data is collected by tracking a particular source across the sky. During the observation some telescopes are designed to follow a continuous cycle in which they collect data from the source for a period say $\frac{1}{2}$ minute, jump off the source by a small angle to a patch of clear sky for $\frac{1}{2}$ minute, and subtract this data from that in the on-source store. In doing so, instrumental and atmospheric features can often be continuously eliminated.

The signal is usually detected as an *antenna temperature* $T_A$ which is a function of frequency and sometimes displayed as such. It is however more usual to display the spectrum as a $T_A$ vs $v_{LSR}$, which can be determined if the laboratory rest frequency is known. In general the peak of the $T_A$ vs $v_{LSR}$ line shape will be the same for all molecules in the same cloud and so appropriate telescope frequency adjustment for the Doppler effect is straightforward.

If the cloud is an extended source i.e. its angular size is larger than the telescope's *HPBW* then the antenna temperature and cloud brightness temperature are the same i.e. $T_A = T_L$. If the cloud is smaller then so-called *beam dilution* occurs and $T_A = (\Omega_C/\Omega_A)T_L$ where $\Omega_C$ is the cloud solid angle and $\Omega_A$ is the antenna pattern acceptance solid angle (Winnewisser, Churchwell and Walmsley, 1979). As if the numerous temperatures met so far are not enough, there is yet another one, the *system noise temperature* $T_{sys}$. $T_{sys}$ is the parameter that scales the random background noise level that occurs in any electronic system. In an ordinary amplifier this is the background hiss which determines the basic signal-to-noise level attainable. $T_{sys} \sim$ 50–80 K at cm wavelengths and 300–1000 K at mm wavelengths.

The signal-to-noise can be reduced as usual by integration as $T_{min} \propto t^{\frac{1}{2}}$ where $T_{min}$ is the minimum detectable signal and $t$ is the integration time. In practice, how long $t$ is depends on a multitude of fairly obvious parameters, not least the strength of the line. CO can be detected using a 4 foot pocket instrument in the middle of New York and the signal in Fig. 21 of $HC_7N$ after 6 hours of integration with a 46 m dish located ~200 miles away from civilization in Algonquin Park, Ontario to reduce interference.

### *Coordinates*

Astronomical objects must be found by some sort of coordinate system. The usual ones are Right Ascension (RA or $\alpha$) and Declination (Dec. or $\delta$) defined in the first few pages of any introductory book on astronomy (*cf* Unsöld, 1977). A good example of these coordinates is shown in the map in Fig. 26 which should be compared with the photograph in Fig. 2. Most recent observations are specified with respect to the year 1950 which is usually specified on the diagrams, note however maps may differ in the reference year.

### *Useful astrophysical quantities*

There are finally a few miscellaneous astronomical terms, definitions and facts that are useful in understanding the literature.

In this review distances have been given in light years (ly) which is of course the distance travelled by light ($c = 3 \times 10^{10}$ cm s$^{-1}$) in one year ($\sim 3.2 \times 10^7$ s) which is $\sim 9.46 \times 10^{17}$ cm or $\sim 10^{13}$ km. The main distinguishing feature between astronomers and the rest is that they give distances in parsecs (pc). One pc is the distance at which a star exhibits an angular parallax shift of one arc second against the background fixed stars (which are too distant to show any parallax) between two positions separated by 1 AU (Unsöld, 1977). 1 pc $= 3.086 \times 10^{13}$ km $\equiv 3.26$ ly.

To get a feel for astrophysical distances it is worth noting that the radius of the Earth's orbit is $\sim 150 \times 10^6$ km $\equiv$ 1 astronomical unit (AU). Pluto's semi-major axis is $5.9 \times 10^9$ km. Thus $R_{Earth} \sim 1.5 \times 10^{-5}$ ly. $R_{Pluto} \sim 40 \times R_{Earth} \sim 0.6 \times 10^{-3}$ ly. So the solar system can be considered to be contained in a volume of diameter $\sim 1/1000$ ly. The distance to the nearest star, Proxima Centauri, is ~4.2 ly and the distance to one of the nearest galaxies, Andromeda, is $\sim 2.2 \times 10^6$ ly.