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Molecular Spectroscopy Prompted by Astrophysical Observations

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Molecular spectroscopy prompted by astrophysical observations

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Observations of molecules in the Galaxy, whether by absorption, spontaneous emission or maser action, have shown that for all that molecular spectroscopy has long been studied in great detail, there are large gaps in our knowledge of even simple molecules, both in general and in detail. At the most basic level, a number of unidentified radio frequency lines were detected some while ago, and with the extension of observations into the millimetre wave region, many more unidentified lines have been found. Despite earlier extensive work at the National Bureau of Standards of the U.S.A. there remains a great need for measurements of frequencies of transitions in many molecules. The fact that galactic concentrations of molecules are often associated with strong sources of far infrared or ultraviolet radiation has shown that there are many gaps in our knowledge of molecular spectra in those technically difficult ranges of the spectrum and has led to attempts to develop improved techniques for studying them, as well as to interest in some theoretical problems.

1. Introduction

The interpretation of astronomical observations evidently depends on having accurate and extensive data about the spectra and structures of molecules that may occur in astronomical objects. Sufficiently accurate measurements of frequencies of transitions must be available to permit the identification of molecules, but beyond that the understanding of conditions in astronomical objects requires a knowledge of transition probabilities and cross sections for such processes as photodissociation, collisional excitation and so on. As observations in the millimetre range of wavelengths are extended to higher frequencies, a great many unidentified transitions are being found, many of which no doubt occur in molecules that are unstable under laboratory conditions. Molecules that had been supposed to be well understood have shown new phenomena, new forms of interaction within molecules have been detected, new types of interaction with photons or particles were either found for the first time or seen to have greater significance than laboratory studies had indicated, and the observations of astronomy and attempts to understand them continue to present the laboratory spectroscopist with problems to be solved: transition frequencies to be determined, new ranges of spectra to be explored, and theoretical understanding to be enlarged.

Most molecules are observed through transitions in the radio frequency range (1 mm to 20 cm wavelength, roughly speaking), but of course visual observations of molecules have been made long since, in cool stars, in comets and in the interstellar medium. In recent years, satellite-borne telescopes (for example in the Copernicus satellite (Morton 1975), have enabled ultraviolet absorption by H_2 molecules in the interstellar medium to be investigated. Further, while most molecules are detected by radio-frequency observations, the processes by which they are excited so that they become detectable may involve collisions with electrons or ions or neutral atoms or molecules, or the absorption of radiation of very much higher frequency, and so the understanding of radio-frequency spectra may involve investigations of transitions in the infra-red or ultraviolet. The most striking instances of that class of problem are to be found in the search for processes that may lead to maser action (Cook 1977).

A useful summary of recent work in molecular spectroscopy has been given by McPherson & Barrow (1979). I shall review briefly the present state of work on the problems I have indicated and shall emphasize those studies that involve something novel.

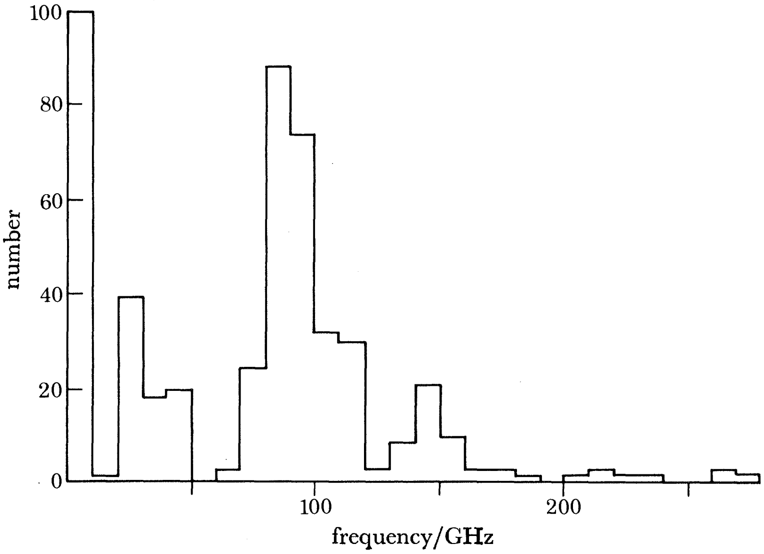

FIGURE 1. Distribution of observed interstellar microwave transitions.

2. TRANSITION FREQUENCIES UP TO 300 GHz

In the early 1970s the Institute of Basic Standards of the National Bureau of Standards of the U.S.A. began the publication of a series of reports under the general title 'Microwave spectra of molecules of astrophysical interest' (Johnson *et al.* 1972). The correlation and reduction of the data, as well as some of the laboratory observations, were made or coordinated by a group within the N.B.S. led by Dr D. R. Johnson. One of the related publications is a list of all microwave transitions observed in astronomical sources (Lovas *et al.* 1979*b*), and some of the statistics to be drawn from that list are instructive. In all, 46 interstellar molecules are known from their microwave spectra, to which must be added H_2 observed in the ultraviolet in interstellar space and CH, CN and C^+ in the visible. Isotopes of the commoner elements have also been detected in many molecules (table 1). Altogether, 478 distinct transitions have been recorded and figure 1 shows how they are distributed. Some notable concentrations of lines occur, which, however, do not represent the real distribution of transitions of interstellar molecules with respect to frequency but rather facts such as the intensive study of Ori A with the NRAO 36ft telescope. Twenty lines are unassigned: they lie below 115 GHz and mainly in three groups (table 2) However, only ten lines, sporadically distributed, are listed above 180 GHz and that is no doubt due to there being, up to 1979, few telescopes that could work in that range, as well as to absorption by atmospheric water. The list contains nothing observed by the Berkeley Hat Creek telescope, and I have been told (privately) that tens of unassigned lines have been found there.

TABLE 1. INTERSTELLAR MOLECULES

(*a*) *inorganic*

H_2	hydrogen	HNO	nitroxyl hydride
NO	nitric oxide	HN_2^+	diazenylium
NS	nitric sulphide	H_2O	water
OH	hydroxyl	H_2S	hydrogen sulphide
SiO	silicon monoxide	NH_3	ammonia
SiS	silicon monosulphide	N_2O^+	nitrous oxide
SO	sulphur monoxide	SO_2	sulphur dioxide

(*b*) *organic*

C^+	carbon	HCCN	cyanoethynyl	HC_4	butadiynyl
CH	methyladyne	HCCCN	cyanoacetylene	CH_3CCH	methylacetylene
CN	cyanogen	HC_5N	cyanodiacetylene	HCHO	formaldehyde
CO	carbon monoxide	HC_7N	cyanohexatriyne	HCHS	thioformaldehyde
CS	carbon monosulphide	HC_9N	cyanooctatetrayne	H_2CCO	ketene
HCC	ethynyl	CH_3CN	methyl cyanide	CH_3OH	methanol
HCN	hydrogen cyanide	CH_2CHCN	vinyl cyanide	CH_3CHO	acetaldehyde
HNC	hydrogen isocyanide	CH_3CH_2CN	ethyl cyanide	CH_3CH_2OH	ethanol
HCO	formyl	CH_2NH	methylenimine	CH_3OCH_3	dimethyl ether
HCO^+	formylium	CH_3NH_2	methylamine	HNCO	isocyanic acid
OCS	carbonyl sulphide	NH_2CHO	formamide	HCOOH	formic acid
NH_2CN	cyanamide			$HCOOCH_3$	methyl formate

(*c*) *observed isotopes*

hydrogen	1	2 (DCO^+, HDO, DCN, DNC)
carbon	12	13 (CO, CS, HCO^+, HCN, HNC, H_2CO, HCCN)
nitrogen	14	15 (HCN, HNC)
oxygen	16	17 (OH, CO)
		18 (OH, CO, H_2O, HCO^+, H_2CO)
silicon	28	30 (SiO)
sulphur	32	33 (CS)
		34 (CS, SO)

TABLE 2. UNASSIGNED INTERSTELLAR TRANSITIONS (GIGAHERTZ)

8.188 83†	90.146	100.157
79.229	90.841	100.200
80.484	90.908	101.139
81.504	93.847	103.915
84.505	93.980	104.589
85.435	96.797	105.777
86.750		115.383

† In comet Kohoutek.

It seems very likely that as more telescopes come into use in the range up to 400 GHz a great problem of identification of lines will develop.

Very detailed analyses of certain molecular spectra have been made under the direction of the Office of Standard Reference Data of the National Bureau of Standards, and have been reported in a continuing series of publications, which are listed in the notes to table 3, which is primarily a list of the molecules that have been studied so far in the programme of the Office of Reference Data. Out of the 46 molecules detected in interstellar space, 24 have been analysed in the programme. In each case, the analysis has consisted in fitting a suitable expression for the energies of states to the frequencies of such transitions as had been measured and then calculating the frequencies of all possible transitions up to 300 GHz. A cursory glance at the reports of this work shows that most molecules have very many transitions in the range from 130 to 300 GHz where so far very few have been detected in astronomical observations, again calling attention to the likelihood of many more such observations being yet to be made. Very high accuracy is generally needed in laboratory measurements of frequencies of transitions, for many molecules occur in interstellar space and some of the transitions lie within 1 part in 10^6, so that secure identifications cannot be made unless frequencies are known to better than 1 part in 10^6.

TABLE 3. CRITICAL REVIEWS OF MOLECULAR TRANSITIONS

molecule	maximum frequency/GHz	isotopes	excited states	reference
OH	91	—	—	Beaudet & Poynter (1978)
SO	172	—	—	Tieman (1974)
SiO	43	yes	—	Lovas & Krupenie (1974)
SiS	53	yes	—	Tieman (1976)
H_2O	753	yes	—	de Lucia & Helminger (1974)
H_2S	689	yes	—	Helminger *et al.* (1973)
CO	807	yes	—	Lovas & Krupenie (1974)
CS	245	yes	—	Lovas & Krupenie (1974)
HCN	289	yes	1st vibrational	Maki (1974)
OCS	813	yes	1st vibrational	Maki (1974)
HCCCN	128	—	vibrational	Lafferty & Lovas (1978)
CH_3CN	239	—	1st vibrational	Boucher *et al.* (1980)
CH_3CHCN	183	—	—	Gerry *et al.* (1979)
CH_2	123	—	—	Kirchhoff *et al.* (1973)
NH_2CHO	84	—	—	Johnson *et al.* (1972)
$CH_3C{=}CH$	240	—	1st vibrational	Bauder *et al.* (1979)
HCHO	301	yes	—	Johnson *et al.* (1972)
HCHS	240	yes	—	Johnson *et al.* (1972)
CH_3OH	198	—	—	Lees *et al.* (1973)
CH_3CHO	119	—	A and E	Bauder *et al.* (1976)
CH_3OCH_3	116	—	torsional	Lovas *et al.* (1979*a*)
HNCO	220	yes	—	Winnewisser *et al.* (1976)
HCOOH	204	yes	$J_{max} = 56$	Willemot *et al.* (1980)
$HCOOCH_3$	55	—	A and E	Bauder (1979)

Analyses like those carried out in the programme of the Office of Reference Data are essential for the identification of transitions found astronomically, for there are severe difficulties in the direct measurement of all possible transitions. Apart from the sheer number, not all transitions are equally readily observed, for on the one hand the strengths of transitions increase generally as the cube of the frequency, whereas, on the other, the radio techniques and frequency measurements are more difficult at 300 GHz than at 30 GHz. Many of the molecules detected in interstellar space, although stable, are highly reactive and so do not occur in normal laboratory conditions but must be produced as transient species in flowing gas systems, something often difficult to do. However, even in measurements on molecules that are not ordinarily reactive, molecular beams are frequently used. The principal limit to the precision of frequency measurements is commonly thermal Doppler broadening and there are four ways of reducing its effect (see de Lucia 1976). One is by saturated absorption, which has been shown to be possible in the millimetre region of the spectrum (Costain 1969; Winton & Gordy 1970; Winnewisser 1971). The beam of radiation, after passing once through the gas, is reflected back upon itself and the resulting absorption shows the Lamb dip corresponding to reduced absorption at the frequency corresponding to zero component of molecular velocity along the beam of radiation. The method is practicable because of the great strength of many transitions in the millimetre range.

Another method is to look for absorption in a gas moving at right angles to the direction of the microwave radiation, and in which the velocities in the direction of the radiation are reduced by careful collimation (see, for example, Huiszoon 1971). In such studies with the use of direct absorption, it is desirable to vary the transition frequency periodically, usually by the Stark effect, to obtain the derivative of the absorption with respect to frequency and so improve the identification of the centre frequency. In the apparatus of Huiszoon (1971) the molecular beam flows between plates across which the Stark voltage is applied.

The third way of reducing the effect of thermal motions is to operate a maser at the desired transition. In fact, the first maser to operate was on an inversion transition in ammonia, and it was briefly used as a frequency standard. Maser radiation has subsequently been obtained from many molecules, reactive as well as unreactive, and of course, the essential requirement is to find a way of separating molecules in the upper state of a transition from those in the lower state. The usual way is to pass a collimated beam of molecules through a quadrupole electric field. As a result of the Stark effect, molecules in the state of higher energy can be focused into a microwave resonator, while those in the state of lower energy fall outside the resonator. Much subsequent work is based on that of Thaddeus & Krisher (1961), and in particular Dymanus and his colleagues have applied masers to the measurements of transitions in water (Bluyssen *et al.* 1967; Verhoeven *et al.* 1968) and hydroxyl (ter Meulen & Dymanus 1972).

The fourth technique is molecular beam electric resonance spectroscopy, by which molecules in a beam pass through a state selector in the form of an electric quadrupole lens and then through parallel plates across which an oscillating electric field is maintained at the frequency of the transition being studied. Molecules in which transitions have occurred are selected by a second quadrupole lens and fall upon a suitable dector. HF and HCl have been studied by this means (de Leeuw & Dymanus 1973) and so have OH, OD, SH and SD (Meerts & Dymanus 1975).

Double resonance methods have also been applied to microwave molecular transitions but in so far as they employ optical or far intrared transitions from the ground state, they depend on a laser source being available with a frequency coincident with a molecular transition. The coincidence between the 3.39 μm line of the helium–neon laser and a methane line has allowed transitions in that molecule to be studied (Oka 1976).

A difficulty with simple absorption measurements is that the signal:noise ratio is poorest at the central frequency. Acoustic detection of absorption can do better. The principle is that the absorption of radiation heats the gas and leads to an increase of pressure in an enclosed volume. If the radiation is switched on and off at a low frequency (about 100 Hz in general), the pressure will also fluctuate at that frequency and can be recorded with a suitable microphone. Acoustic detection has proved to be a powerful technique over a wide range of applications (Pao 1977), but so far only little use has been made of it in microwave spectroscopy (Krupnov & Buremin 1976). Acoustic detection can of course be coupled with Stark modulation at a different frequency.

Of the nearly 50 molecules so far detected in interstellar space, 24 have appeared in the series of 'Microwave spectra of molecules of astrophysical interest', although other diatomic molecules are listed by Lovas & Tieman (1974), who give data for 83 molecules in all. It is clear that as astronomers bring more telescopes into use that will operate up to 300 GHz, so there will continue to be a pressing need for laboratory measurements of transition frequencies.

3. TRANSITION FREQUENCIES ABOVE 300 GHz

The identification and mapping of molecules in interstellar space depends on knowing transition frequencies below 300 GHz, but the interpretation of astrophysical results will often require a knowledge of other parts of the spectrum of a molecule. Many molecules are detected in regions of space where the infrared or far ultraviolet radiation field is intense because they are close to infrared sources or to O or B stars, and consequently it may be desirable to have a good knowledge of the spectra of molecules in those ranges of frequency, something which may be especially significant in understanding maser sources. Unfortunately, far infrared and vacuum ultraviolet spectra are often poorly known. Technically the far infrared and vacuum ultraviolet are difficult ranges in which to work. In the former, photon energies are comparable with thermal energies at room temperatures and consequently noise from apparatus is a major limitation to sensitivity and precision. Things would be very much simpler if powerful laser sources, tunable over appreciable ranges, were available, as dye lasers are in the visible, but although a great many molecules will produce laser radiation in the far infrared, none so far tunes over more than a narrow range set by pressure or thermal broadening of the energy levels in the molecule. An alternative is to mix signals at a higher frequency to produce radiation at a lower frequency: the relative range of tuning at the lower frequency will be greater than that at the higher frequency in the inverse ratio of the two frequencies (Oka, this symposium). Here again, no widely usable source is available in the far infrared.

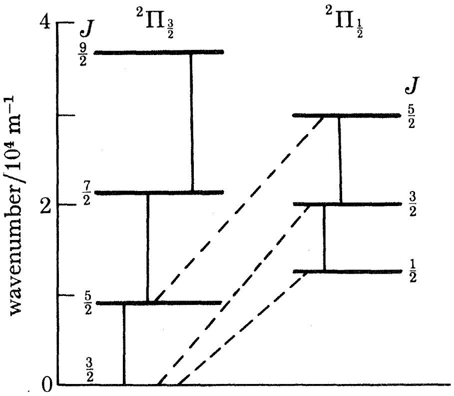

FIGURE 2. Far infrared rotational transitions in hydroxyl observed by Viney (1979): ——, strong transitions; – – – – –, weak transitions.

An alternative to spectroscopy with tunable sources of high power is to study emission spectra with a Fourier transform spectrometer; of course, great care must be taken to cool the detector and any part of the apparatus seen by it, yet even so the signal:noise ratio will be poor, and it will be necessary to superpose many scans if reliable observations are to be made, especially of reactive species produced only transiently in a flowing gas system. Such observations, while difficult, can be valuable and informative. Thus Viney (1979), using a Fourier transform spectrometer at the National Physical Laboratory, was able to detect a number of the pure rotational transitions in hydroxyl (figure 2), as a result of which he was able to resolve doubts about the angular momentum coupling scheme in hydroxyl, which cannot be of Hund's type (*a*) (see Gwinn *et al.* 1973), and is most likely intermediate between types (*a*) and (*b*).

The far ultraviolet spectra of many non-reactive molecules have long been known in great detail, but some of astrophysical importance, especially those of reactive molecules, remain very poorly known. Hydroxyl, again, is an important example. The existence of a C level with possible transitions to the ground state in the neighbourhood of 121 nm (close to Ly α) has been known for some time, from transitions to the B level, but the transitions to the ground state have not been detected certainly. Douglas (1974), using the 10 m spectrograph at the National Research Council in Ottawa, found transitions at a slightly longer wavelength (122.117, 122.207, 122.252 nm) which he attributed to a D level (Σ^+) that is a Rydberg state.

An evident difficulty in observing the far ultraviolet spectrum of hydroxyl is that water is always present in any hydroxyl source and so the spectrum of hydroxyl has to be searched for in the presence of the strong ultraviolet transitions of water. Viney (1980) has used a synchrotron source at Bonn and an associated spectrograph to photograph ten broad features between 85.5 and 95.6 nm that it seems highly probable are to be ascribed to OH (and OD). The features are very broad and so far no systematic relation between them (save for the isotope shift) has been found, and consequently they cannot be interpreted. In this they stand in contrast to lines in the spectrum of SiO in about the same range of frequency which Viney (1979) has shown form a Rydberg series converging on the same ionization energy as found from photoelectron spectroscopy (figure 3).

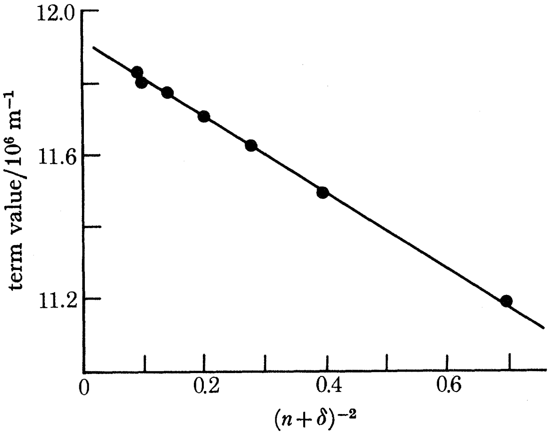

FIGURE 3. Term values and ionization limit of the Rydberg series of SiO (Viney 1979).

Absorption spectroscopy of molecules in the far ultraviolet with the aid of a synchrotron source is difficult, because at wavelengths shorter than 130 nm, all materials absorb strongly and so windows cannot be placed between the synchrotron and the cell containing the molecules. The synchrotron and cell must be isolated by a series of narrow slits separated by chambers with differential pumping, and the performance of the system has to be rigorously specified and maintained to prevent molecules from entering the synchrotron and degrading its performance. That is especially critical if the synchrotron incorporates an electron storage ring. Furthermore, the contrast of absorption spectra and signal:noise ratios are poor (as in Viney's work on hydroxyl) if the concentration of a reactive species is low in a flowing system. It is for these reasons that C. M. Foale, in the Cavendish Laboratory, has been investigating the possibility of using acoustic detection in a flowing system. His theoretical analysis shows that it should be quite possible, and it has the advantage that only a small volume of gas is needed (the increase of pressure is independent of the length of the absorption path through the gas). Unfortunately the power from the synchrotron sources so far available to us is insufficient to study hydroxyl in low concentrations, but we hope that in time it will be possible to use the Daresbury synchrotron for such studies.

Magnetic fields in clouds of molecules in space can be estimated if Zeeman splitting can be observed in any transitions, and so it is important to measure Zeeman effects in low fields for those molecules that show appreciable splitting. Hydroxyl gives relatively large splitting in its Λ-doublet levels and the dependence of frequency on magnetic field for many of the magnetic substates is well established. It may be noted that if a transition shows an appreciable Zeeman effect, it is important in measuring the unperturbed frequency to shield the molecules from the Earth's field, for that is much stronger than interstellar fields and so could give rise to errors that are astrophysically significant (see ter Meulen & Dymanus 1972).

4. RADIATION AND COLLISIONAL PROCESSES

If the conditions in molecular clouds are to be inferred from observations of molecular radiation, then the lifetimes of excited states, the rates of radiative excitation and the cross sections of collisional processes must all be known. For example, the populations of molecules in specific states can be derived from the strengths of absorption by those states only if the radiative transition probabilities are known. If molecules were in thermodynamic equilibrium in some region, a few well chosen observations would enable the conditions there to be derived, but it is usually the case, and maser radiation is but the most striking instance, that molecules are frequently not in thermodynamic equilibrium in the clouds in interstellar space; consequently many observations are needed to characterize the conditions in a cloud and it is necessary to know not only radiative transition probabilities but cross sections for collisional excitations and for radiative and collisional dissociation and ionization, and to know the states in which molecules are formed by dissociation or ionization. Further, because molecules may end up in states that can be examined by microwave observations as a result of a set of transitions from more highly excited states, the radiative processes of interest may extend to those in the infrared and ultraviolet, especially since many molecular clouds are associated with strong infrared sources or with hot O or, as already pointed out, B stars. Nor must it be forgotten that absorption of ultraviolet light from the nearer stars has been measured in instruments carried by satellites, particularly *Copernicus*. Strong absorption by H_2 and HD has been observed (Morton 1975) but CO, though detected, is apparently depleted in the solar neighbourhood, while absorption by other molecules has not been found. If such observations are to be used to set limits to, for example, the abundance of OH in the solar neighbourhood (Jenkins *et al.* 1973), clearly the strength of the ultraviolet transitions (above 122 nm) must be known.

There are essentially three ways of determining transition probabilities of atoms or molecules: the direct measurements of lifetimes, the measurement of the strengths of absorption lines and the measurement of emission intensities. The last is notoriously uncertain because it is difficult to know the population of atoms or molecules in the upper state of a transition. Absorption measurement is applicable only if the lower state is the ground state, or close to it in energy, so that populations can be reliably estimated from the pressure of the gas and its temperature; and high resolution is needed since the line shape must be accurately delineated.

Direct measurements of lifetimes would also require high-resolution spectroscopy so that individual lines of a band could be isolated, and that would often reduce the intensity too greatly; lifetime measurements are much more straightforward in atoms, which do not have the complexity of band structure. In any case, the slower vibration–rotation transitions of molecules would be greatly perturbed by collisions. Measurements on transient species suffer the additional disadvantage that the density of molecules is low and not well known.

Because of these problems it is scarcely surprising that the number of measured radiative transitions probabilities is very small compared with that for atoms. Thus in contrast to the great number of atomic transition probabilities already listed in the *Journal of physical and chemical reference data*, there are none for molecules. Of course, the strengths of rotational transitions are calculable if the dipole moment is known, as it is for a great many molecules (see, for example, Burdyuzka & Varshalovich 1977), and most of the observed microwave transitions are pure rotational transitions; none the less, there are many transitions at other frequencies relevant to the interpretation of the microwave observations. A catalogue of infrared line strengths of many molecules, some of them of astrophysical importance, has been compiled by Pugh & Rao (1976).

Collision cross sections are even more difficult to determine experimentally than are radiative probabilities. Although Oka (1968) has shown how double resonance methods may be used to study transitions between rotational levels of ammonia produced by collisions with rare gases, it is usually necessary to study collisions by the scattering of a beam of one type of molecule upon a second beam of the other type. Two collisional processes of particular importance are, first, that of H_2 and CO because that is the process that is believed to excite CO in the general galactic disc, and knowledge of the cross section enables the distribution of H_2 to be inferred from that of CO; and, secondly, the collisions of e^- or H or H_2 on OH because it has often been proposed that they might populate the upper of the Λ-doublet levels of OH and so give rise to the maser action (see, for example, Kaplan & Shapiro 1979). Collisions of H on CO have been studied by Carracuolo *et al.* (1979); hydrogen atoms were generated by a radio-frequency discharge in a stream of hydrogen, while the carbon monoxide beam came from supersonic discharge through a nozzle.

Such experiments can give the equivalent spherical potential of the molecule, which may be used in theoretical calculations of scattering but are not suited for more refined studies (as of the H on OH process) because of the high energies of the beams (equivalent to 870 K in the CO experiments): if realistic results are to be obtained for the more sensitive processes, beams of lower energy are needed, but are very difficult to produce, whether they be neutral or charged. Thus it is that there are very few experimental results from direct measurements of scattering on molecules at low energies.

Many molecules may well be produced by the dissociation of other species and studies of both radiative and collisional processes are important, especially since it has frequently been suggested that hydroxyl produced by the dissociation of water may show inversions in the populations of the Λ-doublet levels (see Gwinn *et al.* 1973) and also that radiative dissociation of water may lead to inversions and maser action in water itself (Oka 1973). The study of such processes gains added interest from the fact that hydroxyl produced in chemical reactions may show inversions of the Λ-doublet levels (ter Meulen *et al.* 1976), although the particular reactions themselves, especially $H + NO_2 \rightarrow OH + NO$, are unlikely to occur in the interstellar gas. It seems that it will be very difficult to study the results of collisions of electrons or atomic or molecular hydrogen on water because insufficient hydroxyl molecules would be produced in a practical experiment, but C. Javanaud has pointed out that a photodissociation experiment may be practicable. As usual with so many experiments on molecular processes, the problem is how to overcome the competing thermalizing effects of collisions when the density of molecules is sufficient to give observable radiation. If a pulse of ultraviolet radiation lasting for, say, 1 ns is delivered from a laser into water contained in a microwave resonator tuned to a Λ-doublet transition of hydroxyl, it should be possible to observe the strength of that transition within a microsecond or so before collisions take effect. Javanaud is at present developing the experiment.

The possible importance of predissociation in astrophysics has long been emphasized by Herzberg, and as mentioned above, Oka (1973) has suggested that rotational predissociation might be important in exciting water masers. The possible significance of predissociation is further emphasized as it becomes possible to extend measurements into the vacuum ultraviolet with synchrotron sources and to observe lines that lie not only above the dissociation continuum but also above the ionization continuum, as Viney (1979, 1980) appears to have found for SiO and OH. Predissociation line profiles have recently been discussed by Child (1974).

A final type of collision is that in which isotope exchange occurs. It is well known that some isotope ratios determined in molecular clouds appear anomalous and while the problems involved in comparing absorption in optically thick and optically thin lines account for some of the discrepancies, some ratios do seem to depart from terrestrial or cosmic abundancies. Watson *et al.* (1976) have used ion cyclotron resonance to study certain reactions, but recently, as reported elsewhere in this symposium, D. Smith has used the ion-flow technique developed at Birmingham to make very detailed studies of a number of reactions important in processes in molecular clouds.

5. THEORY

In view of the general difficulties in the way of making the sorts of measurements of radiative and collisional processes needed to interpret astrophysical observations, it is not surprising that considerable attention has been given in recent years to theoretical calculations of molecular properties and processes. With the ever-increasing power of programmes for calculations of wave functions, *ab initio* calculations of energies of excited states and hence of transition frequencies are used more and more in attempts to identify unknown lines (see, for example, Hammersley & Richards (1977) for calculations on Λ-doublets), but the main aims of calculations have been to determine the nature and rates of collisional processes.

Green and his colleagues (Green & Thaddeus 1976; Green & Chapman 1978; Green & Truckler 1979; Green *et al.* 1978) have made extensive series of calculations of the rotational excitation of CO, CS, OCS, HC_3N, H_2 and formaldehyde by collisions with H, He and H_2. They use the close coupling method, but need to adopt an empirically determined potential for the interaction: it may be taken from scattering experiments at high energy. Two problems are of particular interest. As already mentioned, the distribution of H_2 in the galactic disc has been estimated from the intensity of the $J = 1$ to $J = 0$ line in the spectrum of CO, for which a knowledge of the cross section for excitation of CO into the $J = 1$ level by collisions with H_2 is required. The other problem is that of the anomalous absorption by formaldehyde at wavelengths of 2 mm and 6 mm, which Townes & Cheung (1969) suggested could be explained by collisional redistribution of populations of levels in formaldehyde. Collisional excitation of formaldehyde has also been studied by Evans (1975) with the use of close-coupling methods.

The theory of these calculations is reasonably well established and their development requires essentially greater computing power but also, and more importantly, better intermolecular potentials which at present are for the most part empirical and spherically averaged.

The means by which the populations in the Λ-doublet levels of hydroxyl may be inverted in interstellar clouds continues to be a problem and, in addition to experimental work mentioned earlier, there have been theoretical studies of possible processes. Two in particular should be mentioned. It may be that inelastic collisions of various partners on hydroxyl itself would lead to changes in populations of the hydroxyl. Kaplan & Shapiro (1979) concluded from a numerical study that collisions of hydrogen atoms on hydroxyl would lead to inversions, and Dixon & Field (1979) have confirmed that result by an alternative treatment that they have applied to CH as well as to OH. Dixon & Field extended their calculations to collisions of H_2, He, H^+ and H_3^+ on hydroxyl, OD and CH, they find that rotationally inelastic collisions would invert Λ-doublet populations and have drawn some conclusions about details of maser excitation in interstellar clouds. Gold *et al.* (1980) have studied inversion by collisions with hydrogen molecules by an approximate method in which alteration of populations depends on the formation of a partial chemical bond between the collision partners (see Gwinn *et al.* 1973; Hammersley 1976; Elitzur 1977). Gold *et al.* agree with Hammersley (1976) and Elitzur (1977) that collisions of H_2 on OH and CH would invert Λ-doublet populations in those molecules (Gwinn *et al.* (1973) predicted anti-inversion for CH) and they further predict inversion in Λ-doublets of NH^+, HF^+, SH and HCl^+ and suggest that some of those molecules might show maser action in interstellar clouds.

Gwinn *et al.* (1973) also examined the collisional dissociation of water and suggested that it could lead to inversion of Λ-doublet populations in the resulting hydroxyl.

The possible importance of far ultraviolet radiative processes in the neighbourhood of O and B stars and the increasing interest in spectroscopic studies of reactive species in that range of wavelengths show that there is a need for more theoretical studies of the properties of Rydberg series (Johns 1974) and of pre-dissociation (Child 1974). A problem that is posed by some observations in the far ultraviolet is that the energies of observed transitions may exceed not only the dissociation energy but also the ionization energy, so that some interactions will occur not only between discrete states and a single continuum (Fano 1961) but between discrete states and two continua.

6. Conclusion

Two things will, I hope, be clear from this brief review. In the first place there continues to be a need for measurements of microwave transition frequencies of many molecules, especially of species that are transient in the laboratory, and along with that is the need to continue to search for sources of unidentified transitions. In the second place, the study of molecules hitherto little observed, together with the need to understand processes in interstellar sources, increasingly leads to experimental and theoretical investigations of more complex aspects of molecular structure and molecular processes. There is still plenty to do!

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