3. EXCITATION MECHANISMS

PANEL DISCUSSION

C. H. Townes: Our intention is to discuss the various molecular excitation mechanisms, which are in all cases still uncertain and in many quite complex.

M. M. Litvak: The first figure gives the dimensions and densities that are compatible with various models for exciting the OH and the H_2O in dense clouds, perhaps in the process of forming a star. At the top left is shown the curve for rotational pumping, which requires diameters greater than 10^{17} cm, much larger objects than obtained by interferometric observations, which indicate that typical apparent sizes are of the order of tens of astronomical units, or about 3×10^{14} cm, while H_2O models require diameters somewhere near 10^{16} cm, but the apparent H_2O sizes are probably much smaller than for OH. Built into this figure is the supposition that there are about 10^{-7} OH molecules and 10^{-5} H_2O molecules per hydrogen atom. If there is a requirement for adjusting these numbers upward, it will generally just shift the scale, so that I will require fewer hydrogen atoms/cm^3. But the numbers indicated here are reasonable, I believe. I also have indicated with 3 lines slanting downwards, values of the hydrogen column density (per square centimeter); also there are 3 lines giving constant values of the mass contained in a cloud having that diameter and typical density. There is a shaded region which is unstable to gravitational collapse in the case of a transparent cloud which has a temperature between 10 and 100K. I have also shown a curve with the allowed values for vibrational excitation in H_2O by collisions. Also shown are a few of the chemical reactions that form vibrationally-excited OH, which finds itself eventually in the ground state, so that it hopefully might be in the maser condition (but calculations discourage this hope). The parameters of this diagram are not arbitrary. Rotational excitation is due to collisions with hydrogen, but the molecule has to de-excite mainly by radiating, in this case, in the far infra-red. If the radiation gets trapped, then the de-excitation by similar collisions will bring the molecule into thermal equilibrium. For maser action to occur, we must allow this radiation to escape, so high projected densities (going to the right in the first figure) will stop this rotational pumping. There is a similar effect for H_2O, having to do with the radiation resulting from rotational or vibrational excitation. There must also be adequate optical depth in the microwave region in order to reach the levels of brightness temperature that have been observed and enough excitation to account for the microwave luminosities that are typical for a source like W3 for OH and W49 for H_2O emission. This is why such high projected densities are necessary for each of the models.

Indicated by cross-hatching are regions of the diagram where one finds optical pumping either by ultra-violet or infra-red, assuming quite reasonably that they have comparable pumping efficiencies. This pumping is of course discouraged by too many

De Jager (ed.), Highlights of Astronomy, 447–459.

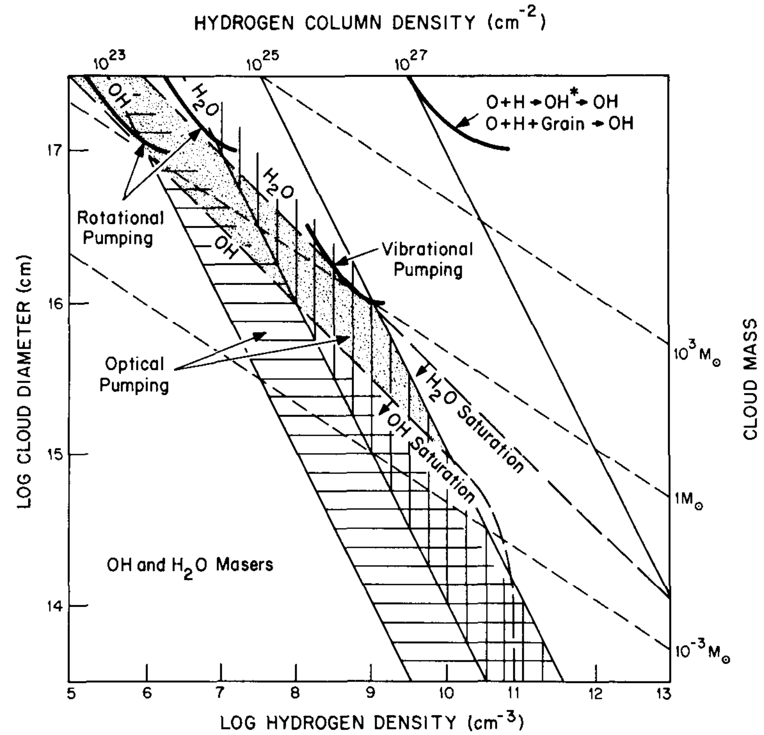

Fig. 1. Diameter of an OH or H_2O Maser Amplifier vs. Hydrogen Density as allowed by collisional or optical pumping mechanisms applicable to regions like W3 and W49. The assumptions used are:

(1) concentrations are in the ratios OH:H_2O:hydrogen $= 10^{-7}:10^{-5}:1$;

(2) rotational pumping occurs at ≈ 70K for OH and ≈ 120K for H_2O, and vibrational and chemical pumping at ≈ 1000K;

(3) the amplifier is roughly spherical;

(4) the *apparent* maser size is $\approx 3 \times 10^{14}$ cm for OH emission and ~ 100 times smaller for H_2O.

Lines of given hydrogen column density and cloud mass are shown. The shaded region corresponds to gravitational instability for uniform clouds of 10–100K. Regions of microwave saturation lie to the lower left of the dashed curves for OH and H_2O. The cross-hatched regions correspond to optical pumping by ultraviolet or infrared resonance radiation, assuming that continuum radiation is not intense enough, with the requisite number of pump photons sec^{-1}, about 10^{46} for pumping OH and 10^{48} for H_2O. Optical pumping beyond 10^{25} hydrogen cm^{-2} is neglected because of possible dust extinction. Each solid curve giving allowed conditions for collisional or chemical pumping terminates at larger hydrogen column density because ordinary collisions de-excite Λ-doublets or vibrational-rotational-levels instead of fluorescence, which has become trapped, thereby causing thermal equilibrium at the kinetic temperature.

thermalizing collisions, and so I show only regions where this radiation can compete with collisions, mainly those across the Λ-doublets in OH and across the two masering H_2O rotational levels. These optical pump regions cannot extend too far into high projected densities because presumably dust, even if some of it may have evaporated within the cloud, will prevent the penetration of optical radiation.

The ineffectiveness of the chemical processes is in part due to the fact that they take place at 10^{-7} OH's per hydrogen atom, a number obtained by balancing the formation rate with the destruction rate. Although this is a reasonable number based on the surveys you have heard about earlier, if the OH density should be a hundred times higher, the maser conditions approach those shown in the Figure for vibrational pumping of H_2O. However, this would imply molecular destruction rates that are hundreds of times slower than are to be expected. Also indicated in the figure are the regions where microwave saturation for H_2O and for OH exists. (By saturation is meant that situation for a given molecule where the rate of microwave stimulated emission competes with the rate at which the excitation is provided.) Thus it is likely that the OH is saturated while the H_2O is not very saturated, if rotational or optical pumping is occurring for the OH and most forms of pumping are occurring for H_2O. Vibrational or optical pumping seems likely to be occurring for H_2O masers, while vibrational pumping of OH (not explicitly shown in the figure) due to collisions is almost as unlikely as the chemical processes.

TABLE I

Galactic OH sources. Summary of prominent OH maser emitters, giving their estimated radial distance, observed microwave flux, dominant OH ground state frequency, and luminosity in photons sec^{-1} if isotropic. A comparison of optical pump sources, their effective surface temperature, their representative emitting diameters, the characteristic frequency pumped most strongly, and the available pump photons sec^{-1} from a single pump object, to be multiplied by a pump efficiency (~ 0.1). The protostar objects contain a converging shock front that emits ultraviolet or infrared resonance lines of OH or H_2O which pump the cooler molecules downstream.

Source	Dist. (kpc)	Flux ($\times 10^3$ phot./m^2 – sec)	Freq. (MHz)	Lum. ($\times 10^{43}$ phot./sec)
W3	3	20	1665	200
W49	14	30	1665	6000
W49	14	15	1667	3000
W51	5	4	1665	100
W51	5	1	1612	20
W51	5	4	1720	100
W28	4	10	1720	200
NGC 6334	1	20	1665	20
NGC 6334	1	15	1667	10
Orion	0.5	2	1665	0.6
NML Cyg	0.5?	150	1612	40
VY CMa	0.5?	150	1612	40

A comparison of optical pumps

Pump object	Temperature (K)	Size (AU)	Maser freq. (MHz)	Excitation ($\times 10^{43}$ phot./sec)
O5 star (UV emitter)	50000	0.3	1665, 1667	100
Protostar (UV shock)	4000	300	1665, 1667	1000
Near-infrared star	2000	10	1612	10
Protostar (IR shock)	1000	100	1612	100
Far-infrared nebula	100	10000	1720	1000

Table I summarizes some properties of the various microwave sources for OH, for the purpose of discussing the energy balance for the maser action. Note that each source is dominated by one or the other of the ground-state frequencies, indicating that there are different conditions of excitation associated with each of the astronomical objects. Also shown is an estimate of the total number of photons per second emitted in the microwave region, assuming isotropic emission. Now, any good pumping model must provide excitation that accounts for this number of microwave photons, and so I have compared various optical pumps: an O5 star, a near-infra-red star, and a far-infra-red nebula like that in Orion. I have also included a protostar with a shock front that is hot enough to have some degree of ionization so that electron collisions within the shock can excite ultraviolet resonance lines of OH, and

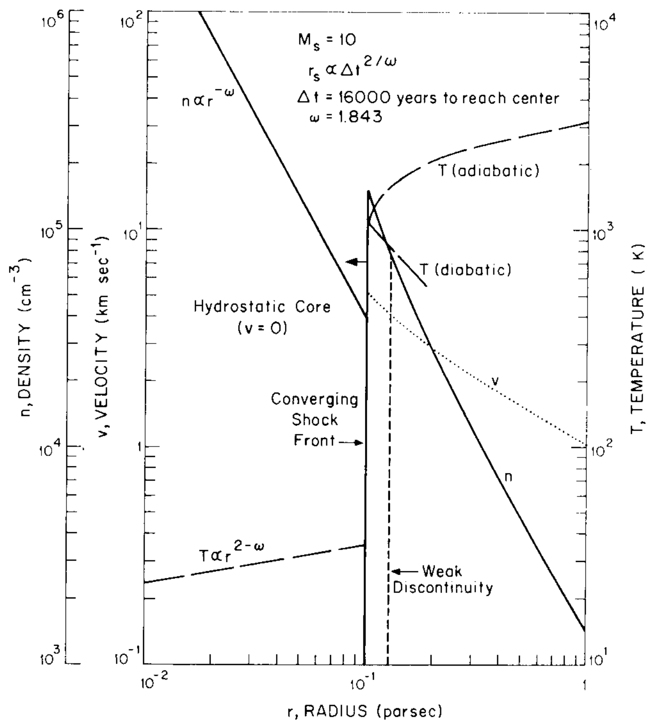

Fig. 2. Density, negative radial flow velocity, and temperature *vs.* radial distance from a center of spherical symmetry for a gravitationally unstable dark dust cloud. The shock at radius $r_s \sim 0.1$ pc heats a layer containing H_2CO and OH which emit infrared resonance lines that pump the molecules at larger radii, thereby causing H_2CO to anomalously absorb cm radiation from the cosmic background and OH to emit 1720 MHz with anomalous intensity compared to the other three ground state microwave lines. The adiabatic and diabatic temperature profiles refer to cases without and with radiation cooling, respectively. This unsteady flow contains a weak discontinuity (sonic point) where the velocity goes smoothly from subsonic to supersonic values relative to the shock front. Disturbances due to radiation cooling at larger radii than this cannot reach the shock front. The density profile being nearly inverse-square with radius is also found for isothermal gravitational collapse. The shock Mach number, M_s, is $\sim$ 10, and a constant of the motion. Δt is the time remaining for the shock front to reach the center.

these in turn can shine out and pump OH molecules still further away from the shock. Similarly, for infra-red resonance lines emitted by somewhat less hot OH (excited by hydrogen collisions), the shocked layer pumps cooler OH molecules further downstream. With the large area provided by this shock front, one obtains quite a large number of photons per second.

The next figure shows an application of a shock front for the excitation of formaldehyde in a dark cloud that is much less dense than the ones discussed before. You have heard that the 3 K blackbody background is absorbed by formaldehyde and that this is a non-thermal situation. A shock front might exist at some radius (taken to be 0.1 pc) from a center of symmetry (as in a spherical cloud) so there is a density profile having a sawtooth in it, superimposed on nearly a $1/r^2$ law. The temperature profile before and after the shock is shown for two cases, with and without radiation cooling. The shock Mach number may be high enough (the temperatures just behind the shock are around 1000°) that I can again have a situation where formaldehyde might even be formed in this shock front, while its infra-red resonance radiation reaches cold formaldehyde molecules at larger radii. (The details of this infrared pumping mechanism can be found in *Astrophys. J.* **160** (1970) L133.) The rates are reasonable for competition with collisions and with 3 K background as far as getting the formaldehyde to act as the required anti-maser.

P. Solomon: I would like to confine my direct remarks to the formaldehyde problem. By now it is quite evident that formaldehyde is refrigerated below the temperature of the background radiation in almost all locations. In other words that the temperature is below 3 K almost everywhere formaldehyde is found, and it seems to be seen in 80 or 90% of all dark clouds. Therefore some universal mechanism is required, and the mechanism which I propose as the result of joint work by myself and Thaddeus is pumping by the background non-blackbody radiation field. Formaldehyde is a perfect thermometer for microwave background radiation; the spacing between the levels corresponds to exactly the frequencies near the peak and just beyond the peak in the expected background radiation field. Of course, if there is nothing but this background field present, all the ratios of optical depths will reflect that 3 K, and of course if there is no other effect operating, there will also be no cooling of the ground state, and we will not observe formaldehyde in the dark clouds. However, if there is any deviation from a blackbody spectrum, then the rates of absorption in the transitions that couple the lower doublets to the upper doublets, which have different frequencies, are quite different. We have chosen two different distributions of the background to test the effect of deviations from the blackbody. One case just inserts a line or some feature in the background radiation which corresponds just to the frequency ν_{24}. The other case has a background radiation field which is 3 K at all centimeter frequencies and some other temperature, which we call T_{mm}, at all millimeter frequencies and at all shorter wavelengths. This would correspond to a background spectrum having a sharp break somewhere between 1 cm and 2 mm. The reason that cooling results is because the upward absorption rate due to absorption of the background radiation is frequency-dependent, and the frequencies are different by roughly 6%, so the Einstein A-coefficients are therefore different by 18%, and when the radiation temperature is increased there is preferential absorption out of level 2 to level 4, as opposed to absorption between levels 1 and 3. All permitted photon transitions are denoted by arrows, and all other transitions are forbidden. With an intense millimeter radiation field then, one preferentially takes molecules out of level 2 which is the upper level of the 6-cm transition (this is the level which is refrigerated) and dumps them back in level 1, which results in a cooling of levels 1 and 2.

Let us now consider the excitation state temperatures for a radiation field with one temperature for millimeter waves and $T = 2.7$ K at centimeter wavelengths. We see that the 2, 1 states are cool, about 1 K for millimeter radiation temperatures of about 7 or 8 K and a centimeter radiation field (which is the way it has been measured) of 3 K; we would always observe the 6-cm formaldehyde line cooled down to this temperature. The 2-cm transition would be between 2.7 and 3 K. The second case is the same except that now we insert just a sharp feature at one of the frequencies (assume that there is a real discontinuity between the two millimeter frequencies), and here one can get tremendous cooling even for a very small bump in the radiation field (only 10% in temperature); one can cool down to 1 K. Now there are other possible mechanisms for cooling formaldehyde which will be discussed by others, but I favor this one since formaldehyde is so ubiquitous and the refrigeration of formaldehyde is so ubiquitous that I think that a special mechanism involving, for example, something like shock fronts is unlikely. We must look for something which pervades all the interstellar clouds since in virtually all interstellar clouds, formaldehyde is cooled. I therefore suggest that there is something more universal like a discontinuity in the background radiation field.

I. S. Shklovsky: I would like to make a short remark in connection with the problem of the excitation of maser sources of OH and H_2O. I think that the observational situation today is not adequate for one to construct a good theory of the nature of the maser amplification, but I want to consider the following possibility. Let us suppose that in the millimeter or sub-millimeter region there are very strong maser emissions from H_2O; in this situation, I believe that it is necessary to take into account the interactions between the masers in H_2O and OH, although the problem will be extremely complicated. I wish also to remark that when such theories are constructed, it will be necessary to account for the polarization, since there are very interesting regularities in the polarization of different sources.

C. H. Townes: I would like to make a few general comments about this situation. I shall try not to specialize on the extreme cases of maser action or refrigeration. There are of course radiative and collisional interactions which are typical and of the most common types; yet each molecule observed shows its own peculiar variations. One question which is rather peculiar to the interstellar medium, and not uncommon there, is how quickly the para- and ortho-molecules come into equilibrium. I believe this rate is connected with the density of hydrogen atoms in many cases, because molecules of high symmetry frequently involve several hydrogen atoms, and a free hydrogen atom colliding with such molecules can undergo an exchange reaction and thus bring the ortho- and para-species into equilibrium. This is of some importance because unless that equilibrium occurs fairly rapidly, relative abundances of ortho- and para-species depend on the distant past of the cloud: estimates of equilibrium times are about 10^6 yr, a convenient time because that is the interval over which a cloud might change significantly. But if it is 10^8 yr or 10^4 yr instead, then we can be badly fooled. The relaxation time may depend on the hydrogen density, and hence is determinable.

Consider now the question of pumping more generally. Radiative processes certainly can give almost any desired pumping condition, in principle, but there are many possible types of radiative schemes, and much difficulty in knowing just what radiation is likely to be present and important. I tend to favor collision processes because we know collisions are present, and they generally demand less special requirements than do the radiative mechanisms. Furthermore, typical radiative processes require a trade of one fairly energetic quantum, like an infra-red or ultra-violet quantum, for a microwave quantum. Energetically, that's a poor trade and makes great demands on the total power. Collisions, on the other hand, generally have no such difficulties. Kinetic energy is quite abundant, collisions are abundant, and hence there is usually no problem from the energetic point of view.

Figure 3 shows one kind of scheme which appears to be a rather potent mechanism where collisions produce something very different from thermal equilibrium. The figure represents a formaldehyde molecule. A neutral molecule moving in the plane

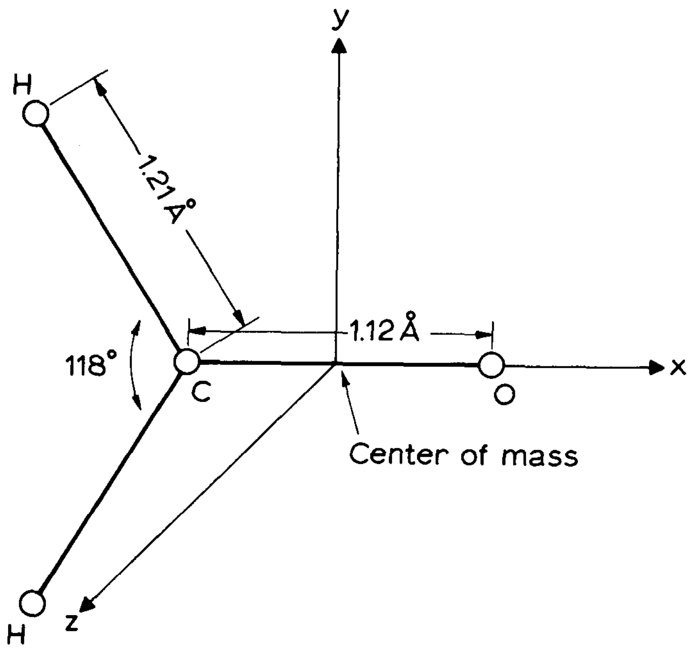

Fig. 3. Structure of the H_2CO molecule.

https://doi.org/10.1017/S1539299600000423 Published online by Cambridge University Press

of the figure and hitting the carbon atom would spin the molecule around an axis perpendicular to the paper, giving it angular momentum and energy. If it collided instead from a direction perpendicular to the paper, the molecule would spin around the other axis. Those two different motions correspond to the two different levels between which the microwave transition usually observed occurs. There is approximately equal probability of a collision from either direction. Suppose however, the approaching molecule hits one of the hydrogen atoms. A collision in the plane of the figure will spin the molecule perpendicular to the paper, but, a collision from the perpendicular direction would simply spin the hydrogen about the molecular axis, not producing any substantial angular rotation perpendicular to the axis. Hence, the two states involved in the microwave transition are not excited with equal probability. A classical calculation of the resulting pumping can be simply made, and it turns out that collisions between hydrogen molecules and formaldehyde would give approximately the cooling which is observed.

Which level such a mechanism favors, the upper or the lower, depends upon the correlation between the arms of the molecule which undergo collisions and the off-axis mass concentration. In the case of OH, the arm sticking out is a chemical bond, having one electron in it. So the arm in this case corresponds to the minimum of mass. The result is that this same process then populates the upper level and gives maser action. In the case of formaldehyde it populates the lower level and cools. On the other hand, if one allows molecular hydrogen to collide with OH, where there is no chemical interaction, then the situation is reversed. The largest interaction then is with the two electrons sticking out and in that case OH is cooled, which is presumably what occurs in the cool clouds. Such a mechanism seems rather attractive and of some generality. It would apply to a large class of slightly asymmetric molecules, but would not give any special pumping to linear molecules.

M. M. Litvak: My arguments for the shock wave in the case of formaldehyde was in response to the idea that the physical conditions are right for gravitational collapse, and in such a flow the process might occur. I do not think there is that strong evidence that the ubiquitous formaldehyde clouds in general are necessarily way out of equilibrium. In other words, absorption of the 3K background in some clouds does not prove that H_2CO is out of equilibrium everywhere else, since higher continuum temperatures than 3K are available for absorption.

P. Solomon: I do not follow that: it is observed against the background in absorption in 80% of all dark clouds.

M. M. Litvak: Dark clouds, yes. But there is a lot of formaldehyde in the Galaxy that has nothing to do with dark clouds. Those I would not say were necessarily out of equilibrium. However, there is nothing to prevent shock-wave and resonance line pumping to be present in other clouds, say, where anomalous OH, including masers, is present, too.

P. Solomon: I would suggest that all the formaldehyde in the Galaxy *is* in dark clouds. If extensive surveys are performed in large regions, one sees it in absorption even where there is a very weak continuum.

M. M. Litvak: I would not exactly call, say W3, a dark cloud in the same sense as Heiles' clouds. Surely there is considerable excitation hidden just behind the dust in W3.

P. Solomon: I think what we mean by a dark cloud is one that is near enough that it shows up optically as dark.

I. S. Shklovsky: Dr Litvak, do you differentiate between OH sources of Types I and II? These are quite different phenomena.

M. M. Litvak: Yes, I address myself mainly to the first type which would be the strong collapsing variety, where there are real problems of energy balance; that is, one has to find a strong source of pumping. This however could include one or two of the special infra-red stars like VY CMa and NML Cygnus, in which the ordinary infra-red continuum does not seem to be quite adequate for accounting for the microwave emission. However, there is enough uncertainty about the nature of those objects that perhaps there are some more similarities than we think to the Class I objects. However, there are many cases where the continuum radiation in the infra-red would be adequate for explaining the OH emission and so there is no need for gravitational collapse or a shock wave or anything of that sort.

I. S. Shklovsky: I think there is a very deep difference between the two types of OH sources, from the spectroscopic point of view from the nature of the sources themselves, for many reasons. Possibly the mechanisms will turn out to be completely different.

M. M. Litvak: The various infra-red stars usually emit 1612 MHz, and that is what I predict for infra-red pumping, although there is not enough infra-red continuum from the special stars that I mentioned, and yet they emit strongly at 1612 MHz.

C. H. Townes: It seems to me that for the bright infra-red sources where 1612 MHz occurs strongly, one has a very reasonable case for infra-red pumping, but in other cases the pumping is probably quite different.

M. M. Litvak: I agree. As you know, I have advocated ultraviolet pumping via continuum radiation and resonance lines for the other cases.

P. Solomon: I would like to report the results of some work by Thaddeus. He has done calculations on the mechanism suggested by Townes and Cheung. These are quantum calculations which use basically the same assumptions, namely that the molecule is standing still as in the classical calculations. He has done a sudden approximation calculation with *S*-wave scattering, and the results of these calculations (which have been done both numerically and analytically) by Thaddeus give some very interesting results for the collisional excitation of formaldehyde by neutral molecules. The significant quantity is T_{21}, the temperature of the ground-state 6 cm transition. When it cools below 2.7°, then there is agreement with observation. The dashed line corresponds to negative temperatures or maser action – not anti-masers but masers – and one finds that for low kinetic temperatures, below about 30°, that the collision of neutrals with formaldehyde instead of cooling the formaldehyde gives a maser process. This is analogous to the effect in electron collisions. In other words,

https://doi.org/10.1017/S1539299600000423 Published online by Cambridge University Press

when all the collision rates are approximately equal, there is a heating of the lower state. Thaddeus' calculations show that for kinetic temperatures below 35°, one would not observe the refrigeration of formaldehyde but maser action, which is definitely not found. For temperatures higher than 35°, T_{21} decreases and goes into the regime of the classical calculations of Townes and Cheung. This would predict that if the formaldehyde were at temperatures above 35° or 40°, cooling due to collisions with neutrals would be expected, but heating at the lower temperatures. Now, I believe interstellar clouds to be below 40° almost certainly, so Thaddeus' prediction is not supported by observation. My way out of this – I do not know if it is Thaddeus' – is to say that probably the temperature in the clouds is so low, maybe less than 10°, that this calculation then becomes invalid. And in fact the collisions will then have very little effect, so we do not really know what will happen at below 10K. Collisions may have very little effect, either to cool or heat, in which case the cooling would be due to the radiation.

I. S. Shklovski: What is the situation with respect to the excitation of OH in the ordinary interstellar clouds? Is it collisional or not?

B. E. Turner: The observations simply show that the satellite lines are distinctly out of thermal equilibrium in the dust clouds while the two main lines appear to be probably in thermal equilibrium. The satellite anomaly is in the direction of the 1720 MHz line being enhanced while 1612 is reduced. All four lines are in emission. The 1720 line is as much as half as strong as 1667, whereas it should be only $\frac{1}{9}$ as strong in LTE. The 1612 line is in one case not detected at all and must therefore be very close to 3° excitation temperature, and is in other cases very weak.

C. H. Townes: These are new observations, and interesting in that they show that in these clouds also as in the localized OH maser sources, the hyperfine levels are not normally populated.

M. M. Litvak: It seems to me however, that if collisions are the dominant means for getting this non-equilibrium in normal clouds, then you might not expect the hyperfine populations to be so far out of their LTE ratios, because collisions are too impulsive to effect the distribution in hyperfine states, especially if the far infrared optical depth is small.

C. H. Townes: Let me comment on that first and then I would like to say something about Thaddeus' calculations. Litvak has emphasized the importance of the infrared particularly in changing relative populations of the hyperfine levels, and I think that is an important observation. It does not rule out collisions, however, because normally one expects the collisions to excite a rotational state, which would then emit an infrared photon which is trapped and then produces the redistribution within the hyperfine structure.

M. M. Litvak: Yes, but then I do not think you will get the 1720 line. The key point is that you are affecting the whole Λ-doublet.

C. H. Townes: I disagree there. The collision process basically emphasizes the upper member of the Λ-doublet. Then when the infrared quantum from the rotational excitation is emitted and trapped it can, I believe, emphasize the 1720 line.

M. M. Litvak: It could be in that direction, but because of the stronger line strengths of the main lines at 1667 and 1665 MHz, the effect would be more for emission at 1667 in excess of the 9:5 ratio to 1665 (an effect not observed) than your imbalance on these satellite lines at 1720 and 1612 MHz. Also, I think the kinetic temperature over most of a dark cloud is too low for fast enough pumping by collisionally-exciting the nearest rotational state (84 cm^{-1} high) compared to the collisions that thermalize the Λ-doublet states.

C. H. Townes: I think that simply depends on the particular constants, of the amounts of trapping and the conditions that one assumes. I believe this really reduces to something very similar to the process you have been talking about, once the infra-red quanta are generated. My supposition is that the infra-red is simply generated by collisions. One other comment I would have on Thaddeus' calculation, which he has kindly sent me. I have not had time to understand it fully, in particular why it reverses sign. However, Thaddeus mades the sudden approximation in which the molecules are not supposed to move. The transitions he considers are separated by about 5 wave numbers and he considers temperatures of about 40°. The actual energy corresponds to only about 7° in temperature. But the time required for the molecule to rotate one radian if the rotational frequency is 5 cm^{-1} is comparable with the collision time for temperatures of about 100°. Hence it appears that at 40° the approximation may have broken down and give erroneous results. Cheung and Evans at Berkeley have made a quantum mechanical calculation also, using the first Born approximation. It has similar difficulties because this approximation breaks down when there is a large fractional exchange of energy. While this calculation gives strong pumping, I believe neither one of the quantum mechanical calculations so far made give adequately clear answers for the cases of interest.

L. E. Snyder: I think an observational result should be emphasized here, namely that in the dark clouds the OH is seen only in emission and the formaldehyde only in absorption, which leads quite naturally to two questions. In the case of the collisional pump, it seems as though we are given some boundary conditions that we do not normally have in interstellar clouds, and it seems as though we might be able to give some unique information in cases where we do see formaldehyde in absorption and OH in emission. For example, can we solve the pumping problem and at the same time obtain good densities for the colliding particles? In the case of the radiative pump, is the inferred information for formaldehyde consistent with what one expects for the OH emission, and *vice versa*?

M. M. Litvak: In reply to that last question, the heated OH in the shock wave that I spoke of would pump cooler OH nearby to emit 1720 MHz, which is the observed frequency, if the OH was not too thick optically. So it does fit nicely.

P. Solomon: The microwave background does not affect the OH temperature pumping. In formaldehyde, pumping is through the rotational transitions, which are at 5 or 10 cm^{-1}. Rotational transitions in OH are at 100 cm^{-1} roughly, so the microwave background just does not affect OH.

B. E. Turner: I think there is general agreement among theoretical workers as to the origins of the anomalies in the satellite lines, namely infra-red effects. It is when we come to the most powerful OH masers which affect only the main lines that there is controversy. I would like to point out one feature in one source that might provide a clue to the phenomenon: the line 43.6 km/sec in W 3. The point about this transition is that it demonstrates that the bottom three rotational states, which are the only ones thus far observed in the $^2\Pi_{3/2}$ ladder, definitely have inverted populations in the Λ-doublets, and that the bottom three states in $^2\Pi_{1/2}$ have anti-inverted (or at least not inverted) populations. One must conclude that the exciting mechanism in OH orients the electron orbitals with respect to the rotation axis in a unique way. There are collisional theories which in fact predict just this sort of excitation. Dr Townes has alluded to one, while the other involves chemical reactions of H_2O. I think any pumping theory, however, ought to consider the fact that most of the strong mainline emission sources demand a process that orients the electron orbitals with respect to the rotational axis.

C. H. Townes: That can be done, I think, by a collision mechanism; in the infra-red picture something a little more complicated is required.

M. M. Litvak: There are a variety of conditions that affect the excited states. It is not proven that the whole $^2\Pi_{3/2}$ ladder is inverted. Only the three lowest states have been observed, and there are many ways in which far infra-red effects could produce inversion in these Λ-doublets, and not restricted to satellite line emission, without invoking inversion by collisions for the whole $^2\Pi_{3/2}$ ladder.

B. E. Turner: But could they explain the effects in the other ladder as well?

M. M. Litvak: It is generally satisfactory for the lowest levels of the $^2\Pi_{1/2}$ ladder for which we have data. Calculations are underway in which we are investigating other pumping effects by far infra-red on levels higher in the ladder. One difficulty with the model involving H_2O mentioned by Turner is that it requires very high temperatures (~ 10000 K) because of the high activation energy for $H + H_2O \rightarrow OH + + 2H$, and as a consequence, the suggestion was made that it occurred at the foot of a very strong shock front. There are very serious problems in getting pumping strengths adequate to account for the strong sources (cf. Litvak, Zuckerman, and Dickinson 1969, *Astrophys. J.* **156**, 875).

B. E. Turner: However, while that may be a difficulty, it also provides the energy required to pump H_2O, which is dissociated. It is the only theory which before the discovery rather than after, predicted a close association of Type I OH masers with H_2O. I think that some of the technical difficulties with H_2O sources may explain the lack of an even closer correlation.

C. H. Townes: You are referring to Gwinn's idea of tearing up H_2O to make OH in the excited state. I want to make one comment which represents a kind of melting of two different ideas. Solomon has raised the question whether the so-called black-body radiation deviated enough from Planckian to give this pumping. We have tried very hard to examine that along with the general question of what this background radiation is by looking at excited states of formaldehyde. Evans and Sloanaker have just completed another study in which they find excited states in rather weak sources.

This seems to indicate again, if one is not in too much trouble with optical thickness, that the blackbody temperature may well be higher than 3° at 2 mm. There are other indications that it is rather high below 1 mm, so there are strange indications about the isotropic radiation in this region. It is important to get well into the millimeter region and study a number of molecular states there.

Pimentel: Chemical processes are commonly known to give product molecules in vibrational, rotational, and, in the case of the iodine atom, electronic disequilibrium. If molecules, such as formaldehyde, are present in steady state, formed in chemical reaction and, lost through some other process, such as photolytic decomposition, they may not have enough collisional opportunities to relax completely. Is it not possible that the energy level disequilibrium associated with the chemical formation of these interstellar molecules contributes to the population inversions observed for some molecules or to the anomalously low temperatures observed for others?

P. Solomon: I suggested one chemical pumping mechanism for OH several years ago, but this involves the formation of OH in an excited state through direct radiative excitation from the ground state. I was not able to make detailed calculations of this process simply because we do not have accurate information on fine-structure states. The process may be important enough to account for the formation of OH in dense, neutral sources. It is very difficult to make good calculations in the absence of an accurate potential curve for the upper state.

M. M. Litvak: There is one fundamental difficulty. These observations of departures from thermal equilibrium refer to the ground rotational and vibrational state. Chemical reactions occur only with a relatively small probability compared to all other possible collisions, such as hydrogen collisions that rapidly equilibrate the populations in a given Λ-doublet. This produces thermal equilibrium in the ground-state, especially at low temperatures. So chemical pumping is basically inefficient: even if vibrational and electronic states are excited in the process, this cascading population inversion in the Λ-doublets of OH, e.g. is easily thermalized.

G. C. Pimentel: I do not understand your answer at all. All the molecules are formed in dis-equilibrium. In what sense is that inefficient?

M. M. Litvak: Excitation cascades to the ground state but very little non-equilibrium between the two closely-spaced Λ-doublet energy levels is carried to the ground state because, simultaneously, there are very rapid collisions with hydrogen that quickly bring those two states, and the other higher doublets, into thermal equilibrium at the kinetic temperature, regardless of all the details of what happened in the high-lying rotation-vibration states. Thus the efficiency of forming more of one ground state of a Λ-doublet over the other is multiplied by a small factor: the ratio of chemical rate per molecule to the rate of collision-induced transitions between the states of the Λ-doublet. This point about thermalizing collisions argues especially against Solomon's suggested chemical process (cf. Litvak, M. M.: 1969, *Science* **165**, 855 and Litvak, Zuckerman, and Dickinson: 1969, *Astrophys. J.* **156**, 875.)

[Figure 2 is reprinted with permission of the Astrophysical Journal, see Litvak, M. M.: 1970, *Astrophys. J. Letters* **160**, L133].