Specific diagnostics of dust forming circumstellar environments

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Zusammenfassung: Wir schlagen spezifische SOFIA Beobachtungen von staubbildenden späten Riesen und R Coronae Borealis Sternen vor. Diese Beobachtungen zielen einerseits auf eine detaillierte Untersuchung der chemischen (Nichtgleichgewichts-) Struktur der inneren Bereiche zirkumstellarer Staubhüllen um pulsationsveränderliche Sterne ab, andererseits sollen die entscheidenden Schlüsselreaktionen und Moleküle diagnostiziert werden, welche aufgrund theoretischer Überlegungen entlang des chemischen Pfades, der die Bildung makroskopischer Staubteilchen aus kleinen Molekülen beschreibt, auftreten:

- Diagnostik von CO Linien in Verbindung mit einer zusätzlichen Analyse der H_2 Quadrupolstrahlung zur Bestimmung des CO/H_2 Verhältnisses in den Hüllen später Riesen,
- Untersuchung der Effektivität der C-Staubbildung über die Bestimmung des H/H_2 Verhältnisses,
- Aufklärung über die Art und Weise wie Kohlenstoffstaub astro-chemisch gebildet wird und Verifizierung theoretischer Reaktionspfade durch die Suche nach Emissionslinien von chemisch aktivierten intermediären Komplexen wie $C_6H_4^{\#}$ und $C_6H_5^{\#}$, sowie nach charakteristischen Torsionsmoden von Kohlenstoffringen in Absorption,
- Beobachtung spezifischer Linien vermuteter staubbildender Spezies in sauerstoffreichen Hüllen,
- Klärung der Frage inwieweit auch kohlenstoffhaltige Spezies in O-reichen Objekten vorkommen und wie sie radial verteilt sind,
- Einblick in die kosmische Biochemie durch Identifizierung einfacher Biomoleküle und ihrer molekularen Bausteine.

Abstract: We propose specific SOFIA observations generally focusing on the fundamental problem of the formation of solid structures in the shells of late-type giants and R Corona Borealis stars. These observations aim at a more detailed insight into the (non-equilibrium) chemical structure of the inner regions of circumstellar shells and at specific key reactions and molecules that are expected to occur along the theoretical astro-chemical pathways leading from the microscopic molecular domain to macroscopic dust particles. In particular the following important aspects are worth to be enlightened by a fruitful combination of IR-observations and theoretical modeling:

- diagnostic of CO lines, their temporal evolution and additional analyses of the H_2 quadrupole lines to determine the CO/H_2 ratio in the shells of pulsating AGB stars,
- determination of the H/H_2 ratio as an indicator for the efficiency of carbon grain formation,
- clarification about astro–chemical pathways to carbon dust by searching for the emission lines of chemically activated intermediates, especially $C_6H_4^{\#}$ and $C_6H_5^{\#}$ lines, and the carbon ring torsion modes in absorption,
- observations of characteristic lines of suspected dust forming species in O-rich shells,
- search for carbon bearing molecules in O-rich shells and their radial distribution,
- looking for the fingerprints of simple biomolecules and their precursors to gain more insight into cosmic biochemistry.

1. Dust formation in the shells of pulsating AGB stars

Almost all Miras and most Long–Period Variables (LPVs) are highly evolved low and intermediate mass stars located on the Asymptotic Giant Branch (AGB). These objects are large amplitude pulsators with typical periods of the order of 1 yr, high luminosities $\approx 10^4 L_\odot$, low effective temperatures $< 3000K$ and high mass loss rates up to $10^{-4} M_\odot$ (e.g. Habing 1996). The outflows from these cool stars are sites of copious grain formation, which is sometimes so effective, that the circumstellar dust shell (CDS) totally obscures the central object.
In order to study the structure and dynamics of such CDS, the CO molecule is an especially well suited diagnostic probe. It is one of the most abundant species, both, in oxygen–rich and in carbon–rich objects. Due to its stability it forms already at high temperatures deep in the photosphere. In the subsequent outflow it remains relatively chemically inert out to large distances, thus, covering the whole range of physical conditions in the CDS. Its infrared and microwave spectrum is fairly simple, and line positions and oscillator strengths are well determined.
Based on dynamical models for circumstellar dust shells around long–period variable stars, which result from a consistent treatment of hydro- and thermodynamics, radiative transfer, chemistry and carbon grain formation (Fleischer *et al.* 1992, Winters *et al.* 1994)(see Fig. 6), non-LTE radiative transfer calculations for CO fundamental and $v = 2-0$ overtone lines have been performed. The resulting line profiles show dramatic temporal changes which are caused by the dynamical behaviour in the inner region of the circumstellar dust shell. Application of these calculations to the most prominent carbon-rich infrared object IRC+10216 clearly demonstrates, that these CO lines constitute a powerful diagnostic tool for probing the complex and dynamical behaviour of those time-dependent stellar outflows where the formation of grains occur

A comparison of synthetic CO line spectra with high resolution observations by SOFIA will also allow to obtain a more accurate determination of the shell densities and the resulting mass loss (see Fig. 5). Of particular importance for the shell diagnostics would be the CO fundamental and overtone line profiles (required resolution $\Delta\lambda/\lambda \approx 10^{-6}$) at 4.6$\mu$m, 2.3$\mu$m, 1.6$\mu$m, or the strength of the H_2 quadrupole lines (e.g. 1 - 0 S(1)) at 2.1 μm, in order to determine the CO/H_2 ratio. Additionally it is desirable to get long-term spectroscopic data to scan the temporal evolution of the CO lines as an indicator for the dynamical structure and the dust formation history throughout the circumstellar shell.

2. Routes to carbon dust formation

During the chemical processes leading from the known mixture of species in the photosphere to the dust grains in the stellar envelope a series of complex intermediates is produced. In the case of a carbon rich chemistry these species are mostly well determined by theory: The dominating acetylene polymerizes to polyacetylenic chains, which close to phenyl or benzyne, whereupon further growth successively leads to larger polyaromatic hydrocarbons (PAHs). Nevertheless, since the selfconsistent models up to now have failed to produce the observed amount of dust via those PAHs, the question remains, whether our concepts of the physical conditions in those shells (LTE, fluctuations…) and our data of the key molecules (which often is estimated by theory) are applicable. To clarify these questions, we propose to investigate the following processes:

The H to H_2 ratio

In circumstellar envelopes of C-stars the dangling bonds of carbon atoms on a grain surface are expected to be saturated by hydrogen atoms. Efficient grain growth, however, i.e. addition of carbon to the surface, will involve neutral-radical reactions of hydrocarbon species with the surface atoms. Thus, growth reactions preferably occur at temporary radical sites, where an H-atom has been abstracted (dehydrogenation, see Fig. 1).
Tracing a gas element in the stellar outflow, the predominating atomic hydrogen of the photosphere recombines to molecular hydrogen by three body collisions. Since the chemical timescale of the H_2-formation drops rapidly with at least p^{-2} and the expansion timescale increases with r/v, the H/H_2-ratio becomes frozen before effective nucleation starts. In order to determine the reactive fraction of the grain surface, the probability of a particular carbon surface site to have a free radical site, rather than being saturated by a free H-atom can be calculated by treating the following reaction scheme:

$$C-H \quad + \quad H \quad \rightleftharpoons \quad C\cdot \quad + \quad H_2 \tag{1}$$
$$C\cdot \quad + \quad H \quad \rightleftharpoons \quad C-H. \tag{2}$$

From Fig. 1 it can be seen, that for high temperatures and H/H_2 ratios hydrogen is abstracted more easily. For T$\leq$ 1600 K radical surface sites are predominantly formed at sp^3 surface sites. Therefore, the density of H-radicals determines the nucleation and growth rate of PAHs, and measurements of the H_2 quadrupole lines will help to support our ideas of the radial structure between photosphere and dust shell and the pathway to carbon dust.

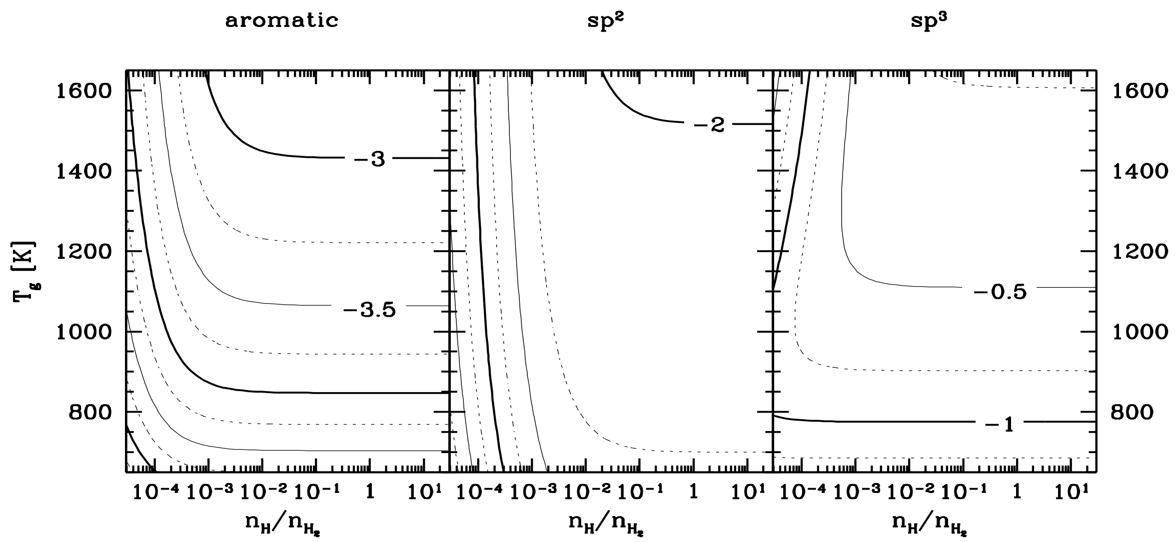

Figure 1: Contour plots of dehydrogenation probability log$w$ of a carbon surface site for different bonding configurations. Thick lines correspond to log$w$ = $-1, -2\ldots$; thin lines to log$w$ = $-0.5, -1.5\ldots$; dashed lines to log$w$ = $-0.25, -0.75\ldots$; in the upper right corner log$w \rightarrow 0$ (Krüger *et al.* 1996).

Activated precursor complexes

Some of the intermediates are formed as highly activated complexes, which relax by emission of vibrational transitions with a lifetime of about 10^{-1} sec rather than by fission or collisions. Especially the precursors of the first cyclic molecules, linear chains with a C_6-skeleton, are activated up to about 2400 K vibrational temperature within an environment

of about 1100 K kinetic temperature. Some of these chains, which do not undergo a ring closure spontaneously, for example $C_6H_4^\sharp$, are expected to show column densities up to $10^{17}cm^{-2}$. Other chain molecules, like 1, 5-hexadienynyl, within 10^{-8} sec close to a ring by dissociation of hydrogen, whereas the radical 1, 3-hexadienynyl cools down during repeatetly closing (see Fig. 2).
Consequently, the vibrational transitions of the non-closing chains should be detectable in emission (between ca. 500 and 20μ), whereas the quickly closing ones should be absent because of the short lifetime of the activated chain molecule (Goeres, 1993). Those chains which anneal radiatively should have typical features due to nonlinearities, and have to be measured in the laboratory prior to observation.

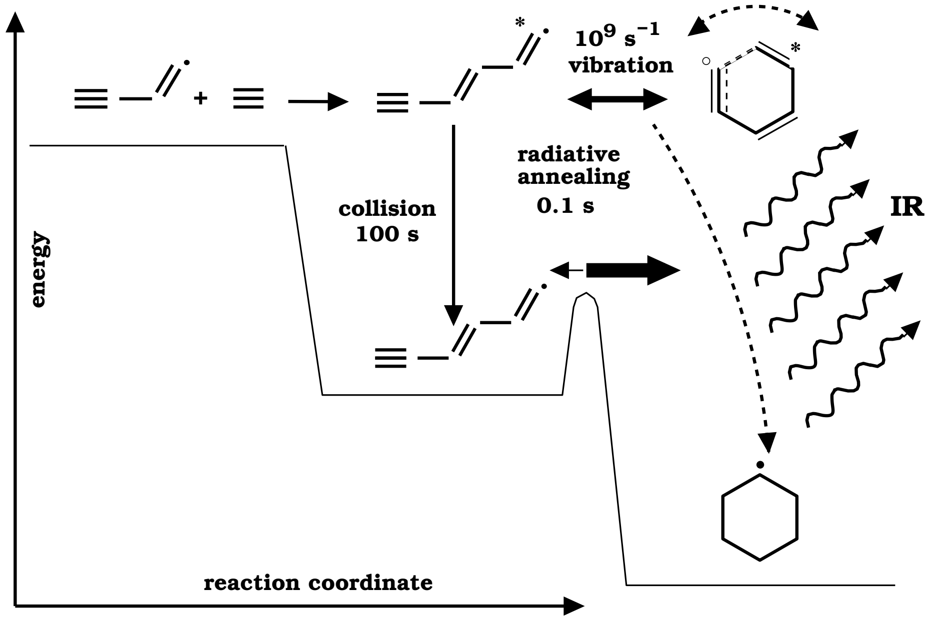

Figure 2: When $C_4H_3^\#$ reacts with acetylene, a highly activated complex $C_6H_5^\#$ is formed, which closes roughly 10^8 times to a ring and opens again, until it cools down by IR-emission. Since the collision time is typically larger than 100s, nearly all chains end up in phenyl-rings. The characteristic IR-radiation generated by this process should be detectable in emission.

Identification of key molecules

Along the chemical pathway to dust, the most stable intermediates are the smallest polyaromatic structures *benzene, naphthalene and acenaphthalene*. In the nucleation zone, these molecules have a temperature of about 750 K in radiative equilibrium and should be seen in absorption. The IR-spectra of these molecules are known up to 15μ. Of special interest are the ring torsion modes which are expected to occur in the range between 50 and 200μ.
In the hydrogen deficient case, the key structures are the monocyclic rings C_6 and C_{10}. The vibration frequencies between 7 and 21.8μ (resp. 8.9 and 54.3μ) are known from calculations only and should likewise be determined by laboratory measurements (Raghavachari and Binkley, 1987).

3. Grains in O-rich shells

In contrast to carbon–rich circumstellar shells forming carbonaceous dust grains, O–rich giants are observed to form silicate materials. Considering a cooling gas representing the outflow from an O–rich giant a clear equilibrium condensation sequence develops, where Aluminium compounds (e.g. Al_2O_3, $MgAl_2O_4$) are the first potential dust materials to become thermodynamically stable followed by Magnesiumsilicates (e.g. $MgSiO_3$, Mg_2SiO_4), and finally Ironoxides (e.g. Fe_2O_3, Fe_3O_4)(see Fig. 3). Therefore, a variety of solid materials of different composition can generally be stable under the physical conditions prevailing in oxygen–rich circumstellar environments, which means that the condensating grain does not neccessarily have to be of stoichiometric composition. Possibly, some kind of composite material will form resulting in dirty grains. In any case, grain growth in a cooling, expanding stellar outflow proceeds along a sequence of changing chemical conditions due to the consumption of condensable elements.

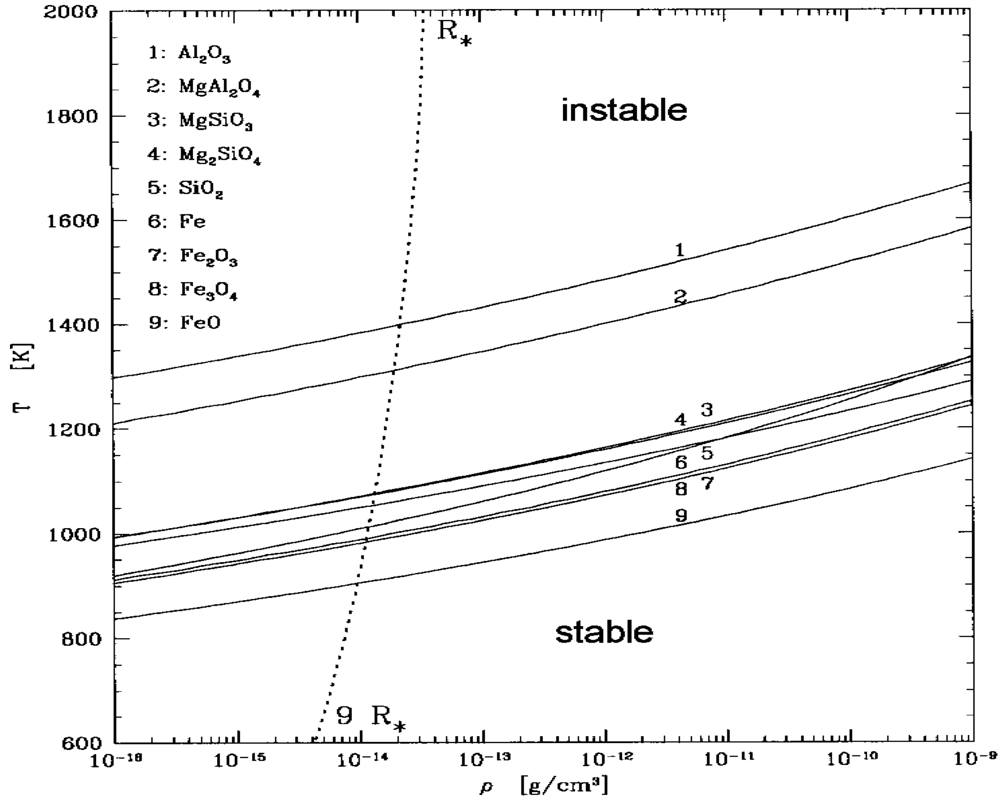

Figure 3: Equilibrium curves of stability of various dust materials supposed to be formed in oxygen–rich environments. The dashed line represent the trajectory of a representive M–star outflow (Breuer, 1996)

Consequently, a core–mantle grain like structure can be expected where each shell may consist of different pure or even composite material. However, which grain compositon and structure actually develops in a stellar outflow will strongly depend on physical and chemical conditions and the resulting availability of nucleation seeds.

One of the important points which have to be studied in detail for the understanding of astronomical silicate dust formation is the investigation of the gaseous molecular 'pre-cursors', because for most of the potential dust materials the corresponding monomer is absent from the gas phase. Therefore, IR observations ($\approx 4\mu$-30μ) of molecules involved in the grain formation process (e.g. SiO, FeO, AlO_2, ...) are undoubtedly necessary for a better understanding of the chemical processes leading to oxygen rich solid material.

4. Alien molecules

Infrared, millimeter, sub-mm and radio observations of the cool, massive envelopes of late-type giants have revealed unexpected high abundances of several C-bearing molecules in O-rich shells (Lindqvist *et al.* 1992, Nercessian *et al.* 1989). Theoretical considerations based on a detailed modeling of the non-equilibrium chemistry in O-rich environments (Beck *et al.* 1992) have shown that the validity of the general assumption of the role of the CO molecule concerning its blocking of either carbon or oxygen is restricted to the presence of chemical equilibrium conditions. Moderate outflow velocities as well as weak UV-fields lead to substantial deviations from the commonly assumed equilibrium situation, allowing both elements to participate in further chemical processes. Therefore new precursor molecules (HCN, HC_3N, HC_5N) might be created as a basis for the formation of solid particles. Thus one must strive for the identification of those "alien" molecules and their radial distribution. Typical molecules being observed are HCN and H_2CO (Lindqvist *et al.* 1992). Present calculations (Charnley *et al.* 1995) also point to the molecules CH_3OH, C_2H_2 and C_2H_4 as possible candidates for a detection in O-rich shells.

5. Biomolecules

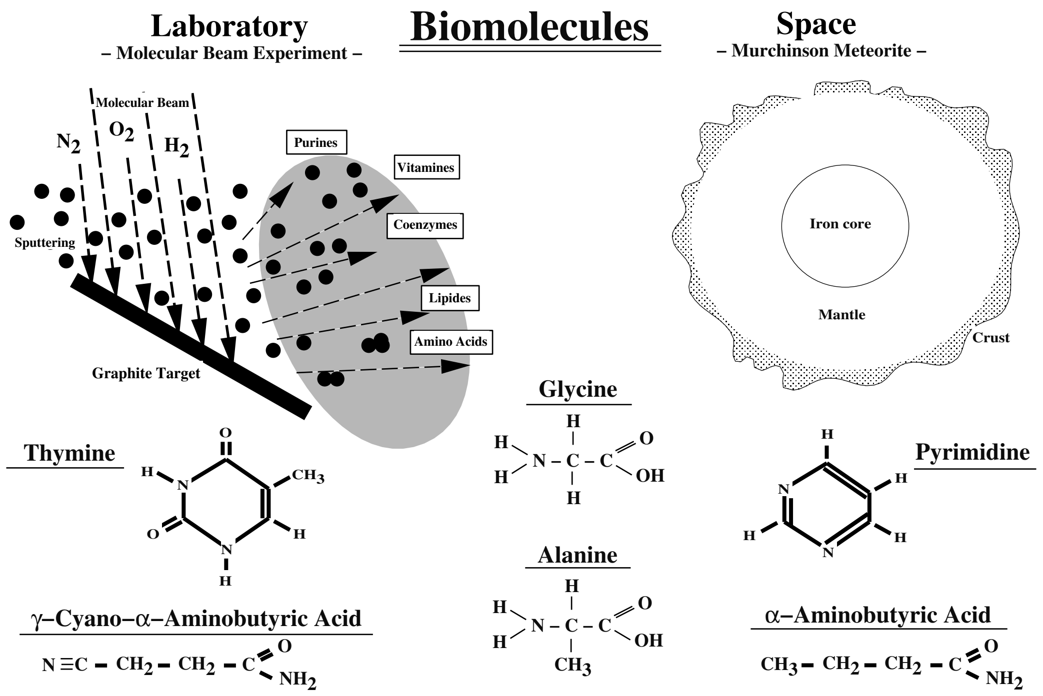

Figure 4: Biological relevant molecules have been identified in molecular beam experiments as well as by the analyses of meterotic material, thereby revealing the existence of similar and nearly identical compounds.

Glycine (NH_2CH_2COOH) is the simplest of the amino acids, which are the building blocks of proteins and therefore of central biological significance.
Regarding the present efforts for the spectroscopical detection of glycine in the astrophys-

ical environment by Combes *et al.* (1996) using the 30m IRAM telescope, the question arises, whether there exist more biological relevant molecular structures in space and if they are detectable. Further insight has been obtained by a comparison of molecular beam experiments (e. g. Devienne & Teissiere 1985; Devienne *et al.* 1994), which simulate the conditions in molecular clouds, and the chemical results from the analysis of the composition of the Murchison meteorite. In both cases a variety of very similar species have been identified, like glycine, alanine, thymine and γ-Cyano-α-aminobutyric-acid (labaratory) and glycine, alanine, pyrimidine and α-aminobutyric-acid in meteorites (see Fig. 4). Present analysis of the stable carbon isotope compositions of individual amino acids also support their extraterrestrial origin (Engel & Macko 1997). All this strengthens the need for an unambiguous identification of the most simple amino acids in interstellar space, like glycine (e.g. around 1,3mm, 200-220 GHz range) and their fragments like CH_3NH_2 and HCOOH.

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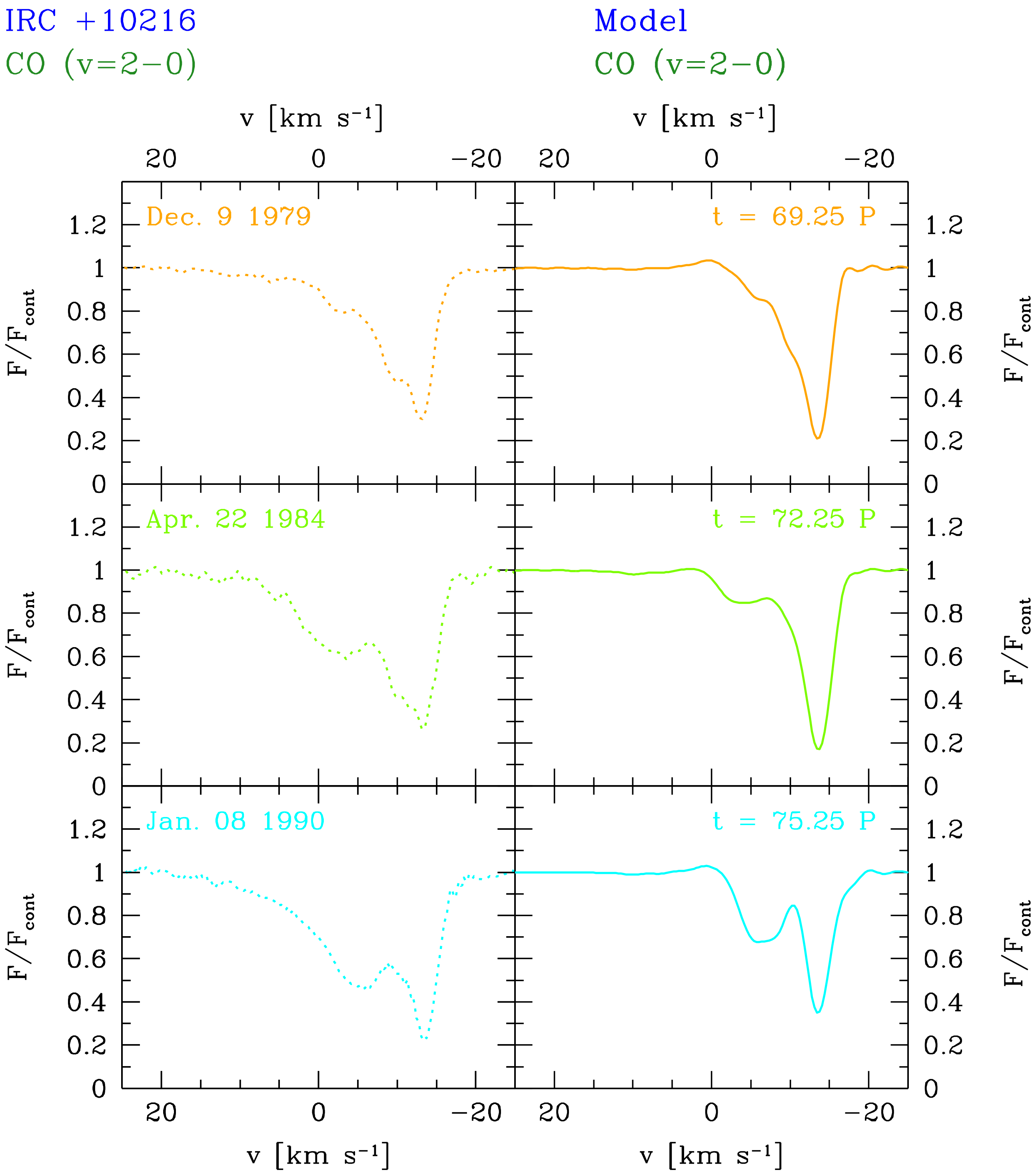

Figure 5: Temporal variation of low excitation CO 1st. overtone lines. Observed profiles of IRC +10216 (Sada 1993) (l.h.s.) and calculated profiles (Winters *et al.* 1997b (r.h.s.)).

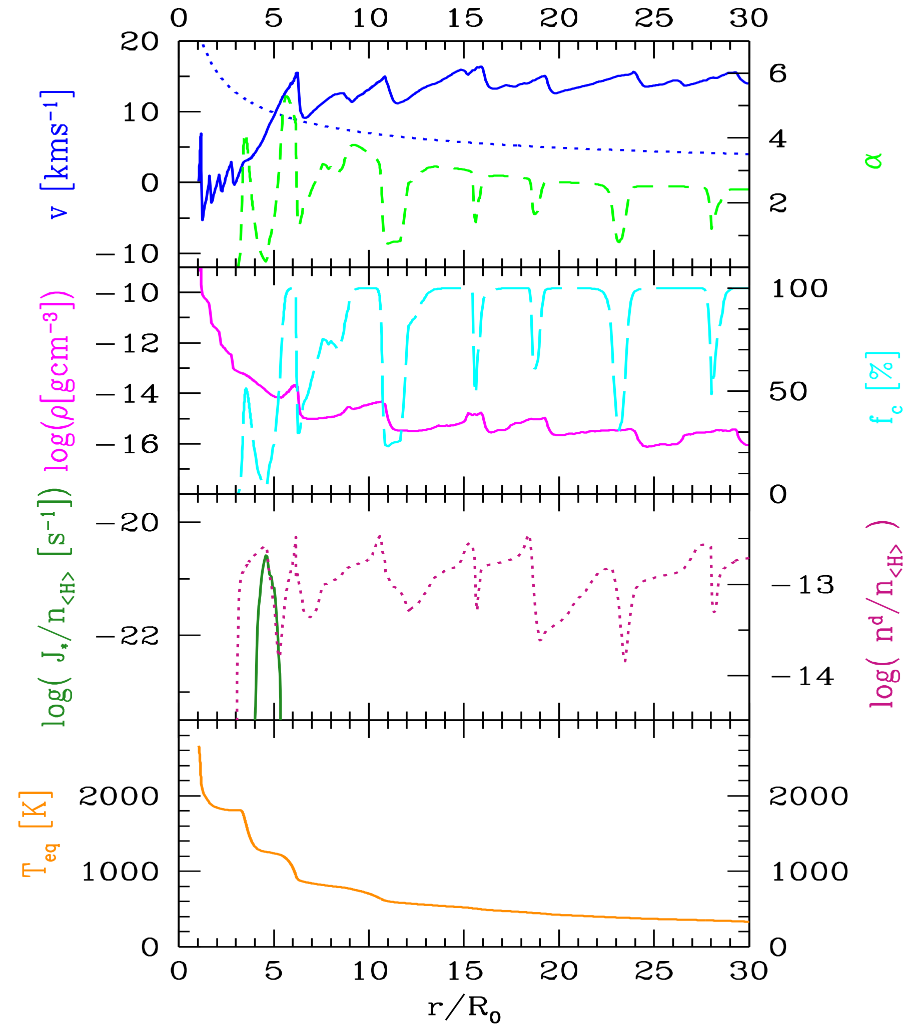

Figure 6: Snapshot of a typical radial structure of a dust shell model (from Winters et al. 1997a). **upper diagram:** velocity u (solid line), escape velocity (dotted line), and radiative acceleration in units of the local gravitational deceleration α (dashed line), **2**nd **diagram:** density ρ (solid line) and degree of condensation f_c (i.e. the fraction of condensible carbon actually condensed into grains) (dashed line), **3**rd **diagram:** nucleation rate $J_\star$, i.e. the number of dust particles formed per second and H-atom (solid line) and number of dust particles per H–atom $n_{\rm d}/n_{<\rm H>}$ (dotted line), **lower diagram:** equilibrium temperature $T_{\rm eq}$. The normalization radius R_0 is the stellar radius of the hydrostatic initial model ($R_0 = 5.5\,10^{13}\,$cm).