SUBLIMATION MECHANISMS OF COMET NUCLEI

MARIA TERESA CAPRIA
CNR, IASF, Area di Ricerca di Tor Vergata, v. del Fosso del Cavaliere, 100 - 00133 Rome, Italy

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Abstract. In this paper the sublimation mechanisms of parent molecules from nuclei will be reviewed from the point of view of theoretical models, and the results of models will be compared with the results of the extensive observation campaign of C/1995 O1 Hale–Bopp. The simple model of a mixture of ices in which each gas sublimates independently from the others when the right temperature has been reached is in many cases inadequate to explain the observations. Many minor volatiles can be trapped in the amorphous water ice and released in a complex way when particular ranges of temperature are reached. The presence of sublimating icy grains in the inner coma of comets, suggested many years ago, seems now to be proven, at least for Hale–Bopp. From these grains a significant amount of water and other volatiles could contribute to the total flux measured in the coma. The unprecedented coverage of Hale–Bopp's gas production curve for such a long time and with so many instruments has offered to modellers a wonderful occasion to test and compare observation results with the predictions of sublimation models, demonstrating that current models are able to explain observed results.

Keywords: Comet, nucleus, sublimation

1. Introduction

In this review the models of sublimation of ice will be briefly reviewed from the point of view of theoretical nucleus models, and the typical results of these models will be compared with the results of the extensive observation campaign of C/1995 O1 Hale–Bopp.

All the species that we observe in the coma of a comet were once contained in the nucleus, and are called parent molecules, or are the product of a physical process that affected a parent molecule, and are called daughter molecules. Parent molecules found in the coma can have a direct or a distributed source. Parent species are said to have a direct source if they are sublimating from the nucleus, and are said to have a distributed source if they are coming from the inner coma, for example from grains. Two different sublimation mechanisms for a direct source will be described in the following: the first one, when the species is contained as an ice in the nucleus, and sublimates from the surface or the subsurface when the sublimation temperature is reached, and the second one when the species is contained in the nucleus as a gas trapped in amorphous water ice and is released during the phase change.

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A distributed production mechanism can be also defined as a production path that is not obviously a photolytic process (Festou, 1999). The evidence of a distributed source is obtained modelling the spatial distribution of coma species and studying the line profiles, that are different when a species is released directly from the nucleus.

The strong flux of supervolatiles such as CO observed in Hale–Bopp before the beginning of a significant emission of water suggests the possibility that grains containing ices can be ejected from the surface and can become, at their turn, a source of emission. This means that a parent (and many daughter) species can have also a distributed source, that is, it can be released in the inner coma from icy/refractory grains and large molecules (Lederer and Campins, 2002). The presence of sublimating icy grains in the inner coma of comets, suggested many years ago (Huebner and Weigert, 1996; Hanner, 1981), seems now to be proven at least in some cases. From these grains a significant contribution of water and other parent and daughter volatiles arrives to the coma. An extended source in the coma of Hale–Bopp contributed to nearly half of the CO production around the perihelion (Di Santi et al., 2001).

Yamamoto (1985) investigated the formation environment of comets in the primordial solar nebula and found a sublimation sequence of various ices which would have condensed on the grain surface in the parent interstellar clouds, by calculating the temperature of grains in the solar nebula. It was soon clear, anyway, that the simple model of a mixture of ices in which each gas sublimates independently from the others when the right temperature has been reached is in many cases clearly inadequate to explain the observations, and that it is not possible to achieve a direct correspondence between the heliocentric distance and the volatility of species defined by their sublimation temperature as pure ices. The sublimation mechanisms involved are more complex. From laboratory experiments we know that many minor volatiles can be trapped in amorphous water ice and released in a complex way when particular ranges of temperature are reached (Bar-Nun and Owen, 1998).

The understanding of sublimation mechanisms is important for answering two questions, fundamental for the study of the origin and evolution of the Solar System and of the comets in particular: how much are the ratios of components measured in the coma representative of those in the nucleus, and how much differentiated (pristine or not) is the interior of a nucleus. To answer the first question, it is necessary to know the storing and releasing mechanisms in the nucleus, and the production, destruction and transformation processings taking place in the coma. Nuclear chemical abundances can be compared to the abundances of interstellar ices, hot molecular clouds and bipolar flows around protostars, giving arguments to the models in which cometary volatiles formed in the interstellar medium and suffered little processing in the solar nebula. Chemical abundances measured in Hale–Bopp seem to support this theory (Bockelée-Morvan et al., 2000).

The recent passage of comet Hale–Bopp through the inner Solar System offered the astronomical community an unique opportunity to follow a comet for a long part of its orbit. The unprecedented coverage of Hale–Bopp's gas production curve for such a long time and with so many instruments has offered to modellers a wonderful occasion to test and compare observation results with the predictions of sublimation models. In this way it has been possible to refine these models and to better assess their initial parameters.

When discovered at a distance of 7 AU from the Sun the comet was already active. The early activity was attributed to the sublimation of CO (Jewitt et al., 1996; Biver et al., 1996). At 3–4 AU before the perihelion water production began to be higher than CO production. At perihelion, dust and gas production was enormous. Dello Russo et al. (2000) derived the following heliocentric dependence between 0.93 and 1.49 AU: $Q_{\mathrm{H_2O}} = (8.35 \pm 0.13) \times 10^{30}[R_h^{-1.88\pm0.18)}]$ molecules s^{-1}. For native CO, the following heliocentric dependence between 4.1 and 2.02 AU was found (Di Santi et al., 2001): $Q_{\mathrm{CO}} = (1.06 \pm 0.44) \times 10^{30}[R_h^{-1.76\pm0.26)}]$ molecules s^{-1}. A dust to ice mass ratio of 5.1 ± 1.2 was obtained (Dello Russo et al., 2000) within a heliocentric distance of 1.5 AU. The comet was still very active at 13 AU after perihelion, when it was imaged at La Silla Observatory in March 2001.

This review is devoted to the sublimation mechanisms of parent molecules. The modelling of the sublimation of a mixture of ices will be described in Section 2, followed by a comparison between the theoretical results and the results from observations of comet Hale–Bopp. In Section 3 the phase transition from amorphous to crystalline water ice will be discussed, along with the modelling of the release of trapped gases; a comparison between observations and theoretical calculations of the phenomenon will follow. A brief discussion on the possible presence of clathrate hydrates will be found in Section 3. Section 4 is devoted to the discussion of the contribution of the molecules from a distributed source to the inventory of parent molecules.

2. Direct Source I: Sublimation of Ice in the Nucleus

The idea that the sublimation of ice is the origin of gas flux in comets is old and dates back to Laplace (1813). The basis of nucleus modelling were laid down by Whipple (1950), who introduced the icy conglomerate model demonstrating that nuclei should be solid in order to explain the observed phenomena. Since the 1970's it became more and more evident that water is the major constituent of cometary ice. First nucleus model calculations, solving the heat conduction equation and giving temperature distributions and gas production rates, date back to the seventies (see for example Brin and Mendis, 1979; Horanyi et al., 1984; Fanale and Salvail, 1984, 1986; Weissman and Kieffer, 1981, 1984; Smoluchowski, 1982; Squyres et al., 1985).

If the water production rate Q_{H_2O} is known and if the average sublimation rate $\langle Z \rangle$ is estimated, it is possible to "measure" the active surface area S_n of the nucleus (Festou et al., 1993):

$$Q_{H_2O} = \langle Z \rangle \cdot S_n. \tag{1}$$

To estimate the sublimation rate which is a function of boundary conditions, a model of the nucleus is needed. The simplest model of ice sublimation considers a compact ice sphere sublimating directly from the surface (Festou et al., 1993). The water sublimation rate Z can be obtained from the heat balance equation between the solar input and the energy re-emitted in the infrared, conducted in the interior and used to sublimate surface ices:

$$\frac{S(1 - A_s)}{R_h^2} \cos\theta = \epsilon\sigma T_s^4 + K(T_s) \left.\frac{dT}{dr}\right|_{r=R_n} + Z(T_s) \cdot H(T_s), \tag{2}$$

where S is the solar constant, R_h the heliocentric distance of the comet, A_s the Bond bolometric albedo of the surface, and θ the solar zenith distance. On the right side of the equation, ϵ is the infrared emissivity of the surface, σ the Stefan-Boltzmann constant, T_s is the surface temperature, K is the thermal conductivity and H is the latent heat of sublimation. The simple solutions obtained assuming that the nucleus is an isotropic snowball and ignoring the conductivity term were rapidly proven to be inadequate, for example, to explain the high temperatures measured by the Vega and Giotto spacecrafts on the surface of comet Halley (Festou et al., 1993). Models in which conductive heat flow is considered and the heat diffusion equation is solved were soon introduced, and are the basis of the currently adopted models (see, for example, Prialnik, 2002; Tancredi et al., 1994; Prialnik et al., 1993; Benkhoff, 1999; Enzian et al., 1998; Capria et al., 2001). These models can be used to predict, on the basis of an assumed initial composition, the behaviour of comets, to test hypotheses on the nucleus composition and physical properties and to interpret the observations.

In the currently used nucleus models, heat diffusion and gas diffusion equations are solved in a porous medium, in which sublimating gas can flow through the pores. A boundary condition such as the equation described before is adopted. In more realistic models a mixture of ices and dust is considered, and the flux from surface and sub-surface regions is simulated for different gas and dust compositions and properties.

Energy and mass balance in the porous cometary matter can be described by the following pair of equations (Steiner et al., 1990), in which the first one expresses the heat diffusion and the second one the gas flow:

$$\rho c \frac{\partial T}{\partial t} = \nabla[K \cdot \nabla T] - c_g \Phi \nabla T + \sum_{i=1}^{n} Q_i, \tag{3}$$

$$\frac{\rho_g}{\partial t} = -\nabla\Phi + Q^*. \tag{4}$$

In the energy equation, T is the temperature, t is the time, K the heat conduction coefficient, ρ is the density of the solid matrix, c is the specific heat of comet material, c_g is the gas heat capacity, Φ is the gas flux, and the Q_i represent the energies gained or lost due to the sublimation and recondensation of the various ices. On the right side, the first term describes the heat conduction through the solid matrix, and the second term describes the energy transport by convection through the gas flow. It should be noted that the second term, i.e., gas advection, is several orders of magnitude smaller than the first one: in general heat transfer by advection is much smaller than the latent heat released by ice sublimation (Steiner et al., 1990).

In the gas equation, ρ_g is the gas density and Q^* is the gas source term due to sublimation-recondensation processes. Because of the low pressures that should exist within a comet nucleus, it can be assumed that gas density and pressure are related through the ideal gas law and that the flow of each gas does not influence the others: in this case the equation can be solved separately for each gas.

The temperature on the surface is obtained by a balance between the solar energy reaching the surface, the energy re-emitted in the infrared, the heat conducted to the interior and the energy used to sublimate surface ices. Due to the rising temperature, ices start to sublimate, beginning from the more volatile ones, and the initially homogeneous nucleus differentiates giving rise to a layered structure in which the boundary between different layers is a sublimation front. A refractory layer can form, quenching the sublimation from surface and sub-surface layers. At each passage in the inner Solar System, a varying amount of gases and refractories is lost giving rise to surface erosion, and the size of the nucleus is reduced.

A big problem in solving these equations is that many of the necessary input parameters are not or not well known. The composition of the nucleus and the dust-to-ice ratio are usually inferred from the observation of the coma, but the composition of the coma does not directly reflect the composition of the nucleus (Huebner and Benkhoff, 1997, 1999), due to the many processes taking place in the coma and due to the fact that sublimation processes in the nucleus are complicated and not directly linked to the temperature reached on the surface and in sub-surface layers. The parameters describing the comet matter, in particular key parameters such as porosity, thermal conductivity and pore size, are almost unknown and are usually deduced from laboratory experiments.

2.1. COMPARISON WITH OBSERVATIONS

At this point, let us compare the shape of the gas production curve that can be obtained from these models with the shape of the curve obtained from observations. A well tested model (Coradini et al., 1997a, b; Capria et al., 2000a, b, 2001, 2002; De Sanctis et al., 1999, 2000, 2001) of nucleus thermal evolution and differentiation will be used. Only a very short description of this nucleus model will be given in the following; for more details the reader is referred to the papers cited before.

The model is one-dimensional. The spherical nucleus, porous and initially homogeneous, is composed of ices (water and other volatiles) and a refractory component. The refractory material is described as spherical grains with given initial size distribution and physical properties. Up to two grain populations with different physical properties and size distributions can be considered in the model.

Energy and mass conservation is expressed by the following system of coupled equations, solved for the whole nucleus:

$$\rho c \frac{\partial T}{\partial t} = \nabla[K \cdot \nabla T] + \sum_{i=1}^{n} Q_i, \tag{5}$$

$$\frac{1}{RT}\frac{\partial P_i}{\partial t} = \nabla[G_i \cdot \nabla P_i] + Q\prime_i \quad i = 1, n, \tag{6}$$

where Q_i are the energies exchanged by the solid matrix in the sublimation and recondensation of the ices, R is the gas constant, P_i the partial pressure of component i, G_i its diffusion coefficient, and $Q\prime_i$ is the gas source term due to sublimation-recondensation processes.

Gas diffusion coefficients are computed on the basis of the mean free path of the molecules in the pore system; the model accounts for three different diffusion regimes: Knudsen, viscous and a transition one. Knudsen diffusion can be assumed for usual cases, i.e., each gas flow is independent from that of the others.

Nucleus rotation and seasonal effects can be taken into account. The model can be run both in the fast rotator approximation (the incoming energy can be assumed to be uniformly distributed along a thin belt at a given latitude), and in the slow rotator approximation (by allowing the variation of solar illumination due to the rotation of the nucleus).

When the ices near the surface of the nucleus begin to sublimate, the refractory particles become free and undergo the drag exerted by the escaping gas, so that they can be blown off or they can accumulate on the surface to form a dust mantle. To determine how many particles can be blown off and how many can be accumulated on the surface, the different forces acting on the single grain are compared, obtaining for each distribution a critical radius that represents the radius of the largest particle that can leave the comet. Surface erosion due to ice sublimation, particles ejection and dust mantle compaction is taken into account.

In this application the initial composition includes water ice, CO ice and only one distribution of dust grains; the ice is initially amorphous, but no gases are trapped inside the water ice. Dust-to-ice ratio is 1 and CO/H_2O has a value of 0.05. The comet was followed along the whole orbit. Here we will discuss only the gas curves obtained from the model; for more details on this application and a discussion of the internal stratigraphy and of the influence of input parameters see also Capria et al. (2000b, 2002b).

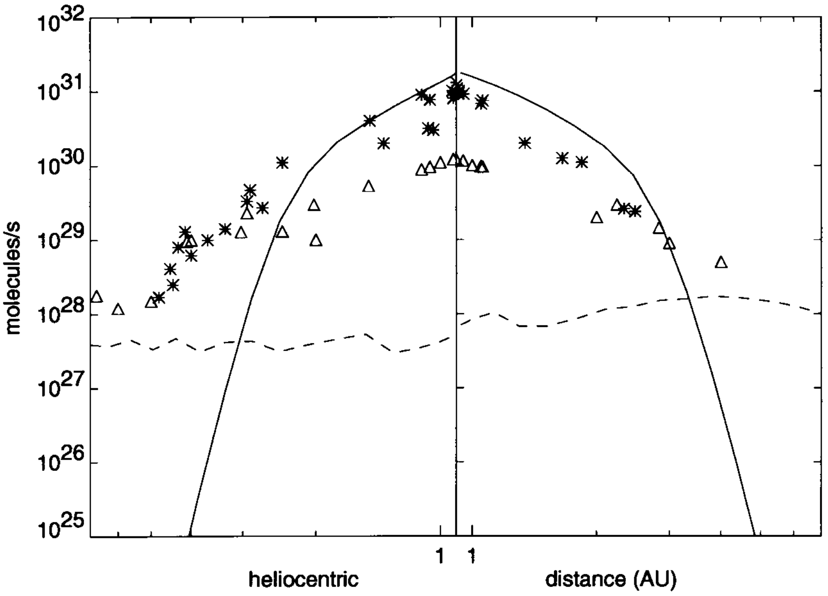

Figure 1. Gas production curve from observations (symbols) and model calculations (lines) in the range of 7 AU pre- and post-perihelion. Water: Asterisks and continuous line, CO: Triangles and dashed line.

In Figure 1 the gas production curve obtained from this model is plotted along with the one obtained from the observations of various authors (Bockelée-Morvan and Rickman, 1997; Di Santi et al., 2001). The CO production coming from a direct source (nucleus) is shown in the plot.

Looking to the symbols representing the observations, we can see that water emission seems to start beyond 4 AU pre-perihelion, when the surface temperature in the model is too low to allow water sublimation: the early beginning could be attributed to sublimating icy grains in the coma (see Section 4), although an alternative explanation was proposed by Kuehrt (1999). CO gas emission starts far from perihelion, and is the driver of the comet activity until it is substituted by water at 3–4 AU before perihelion. Between 3 and 4 AU post-perihelion water emission rapidly ceases, and CO starts dominating again. The maximum production rate of H_2O is around perihelion.

If we look to the curves obtained from the model explained above, we can notice that the curve for water production fits very well the observations except for distances of more than 4 AU pre-perihelion. This could be another indication of the existence of sublimating icy grains in the inner coma.

Looking to the theoretical curve representing the emission of CO, we see that the activity begins very far from perihelion due to the high volatility of this ice: at 20 AU pre-perihelion the CO flux is already of the order of 10^{27} molec/s (Capria et al., 2000b). There is no peak in the CO production at perihelion, since the ice sublimation front remains in a layer of quasi-constant (and very low) temperature (despite surface erosion). This subsurface layer is reached by the thermal wave with a delay depending on its depth. The CO emission curve tends to be flat over a long time span, i.e., it behaves completely different from that of the observational results. Changing in the model the initial amount of CO or the value of bulk conductivity or the differentiation state of the upper layers does not affect the shape of the curve, but only shifts it “up and down”: It is impossible to fit the observations of CO around perihelion without introducing a different sublimation mechanism.

3. Direct Source II: Release of Gases Trapped in Amorphous Ice

At low pressure and temperature (<120 K) water ice occurs in a metastable state called amorphous ice; this form can persist for time scales comparable to the lifetime of the Solar System, due to activation energy barriers preventing the transition from a state to another. When warmed to above 150 K, amorphous ice transforms into a cubic crystalline form and then, under confinement pressure and at temperatures of 195–223 K, into the stable hexagonal crystalline form. Amorphous water ice has physical properties (density, thermal conductivity etc.) which are very different from those of the crystalline state, and it has the ability to trap molecules with low sublimation temperatures that are expelled during the crystallization process.

What we know about the physical properties of amorphous ice and its thermal behaviour comes from laboratory experiments (Bar-Nun and Owen, 1988; Bar-Nun et al., 1985, 1988; Hudson and Donn, 1991; Jenniskens and Blake, 1994; Jenniskens et al., 1998).

In these experiments, a mixture of water vapour and other gases such as CO are frozen at low temperatures, obtaining amorphous ice; once the gas is trapped (the more the lower the deposition temperature), its release depends only on changes in the ice structure related to temperature changes. A major release occurs when ice transforms into cubic structure ($\sim$145 K). Guest molecules such as CO and Ar can be trapped up to temperatures higher than the sublimation temperature of the species in pure ice form. The amount of trapped molecules depends in a complicated way on the initial ice composition, thus it is impossible to determine uniquely the trapped amount of guest molecules. In the experiments, trapped gases are emitted during the transition from the amorphous to the crystalline phase of water ice. Moreover, it seems that some of this gas is held so tightly that it is released only at the moment of water ice sublimation.

The phenomenon of gas trapping and release is very important in interpreting the activity of comets, and it was taken into account in sublimation models since many years: Herman and Podolak (1985) and Podolak and Herman (1985) introduced the effect of the phase transition from amorphous to crystalline ice, using the results of Klinger (1981). All the modern nucleus models consider this process. The trigger for outbursts by the propagation of a heat wave in the amorphous ice was proposed to explain, for example, activity at large distance from the Sun, namely the outburst of comet Halley at 14 AU (Prialnik and Bar-Nun, 1992) and the irregular activity of comet Schwassmann-Wachmann 1 (Cabot et al., 1996).

3.1. CLATHRATE HYDRATES

Another physical phenomenon that can result in the release of gas is the formation of clathrate hydrates. Clathrate hydrates constitute a class of solids in which the guest molecules occupy, fully or partially, cages in host structures made up of H-bonded water molecules. The usually unstable empty clathrate is stabilised by inclusion of the guest species. Clathrates are believed to occur in large quantities on some outer planets binding gas at fairly high temperatures (Kargel and Lunine, 1998). Two distinct structure types exist, both with cubic symmetry (type I with SG Pm3n and type II with SG Fd3m). For each structure type, the ubiquitously important filling factor is calculated using models all based on the van der Waals–Platteeuw theory of solid solution.

Very few experimental data on the filling factor exist. The main reason for this shortage of experimental data is the moderate stability of many clathrates under near-ambient conditions and the slow to very slow formation kinetics at lower temperatures. Stability is increased at higher partial pressures of the guest species, yet it is difficult to establish the composition of the clathrate under such conditions. Only in-situ crystallographic work (at gas pressures of up to a few kbars only possible with neutrons or very hard X-rays) may answer the question.

Warming-up impure amorphous ice can lead to clathrate hydrates formation. They are typically produced and are stable under an enclosing gas pressure, but can also be formed in low-pressure environments. The formation of clathrate hydrates under solar nebula conditions was demonstrated only for methanol (Blake et al., 1991) and hydrogen sulfide (Richardson et al., 1985). Gas trapping by clathrate hydrate formation in low temperature cometary water ice has been quoted repeatedly and was introduced in the earlier nucleus evolution models, see for example Houpis et al. (1985). The idea that nuclei can contain clathrate hydrates was proposed by Delsemme and Swings (1952) to explain the simultaneous degassing of different ices, but was later on questioned (Klinger, 1981) on the basis of thermodynamical considerations. Recently a model of the activity of Hale–Bopp was published that considers clathrate hydrates in the initial composition (Flammer et al., 1998).

Methanol clathrate hydrate formation and the trapping and release of other gases were recently experimentally studied by Notesco and Bar-Nun (2000). They concluded that (1) clathrate-hydrate formation with methanol does not alter the trapping of gases that do not form clathrate-hydrates. However, it changes somewhat their release from the ice when warmed up, not modifying the temperature range of the major gas release when the ice itself sublimates. (2) When the gas is released, even a thin layer is able to drive some of the gas inward, while releasing a large fraction outward. This could change considerably the original gas/water mixture in the coma from the original ratio in the nucleus. (3) Structural changes

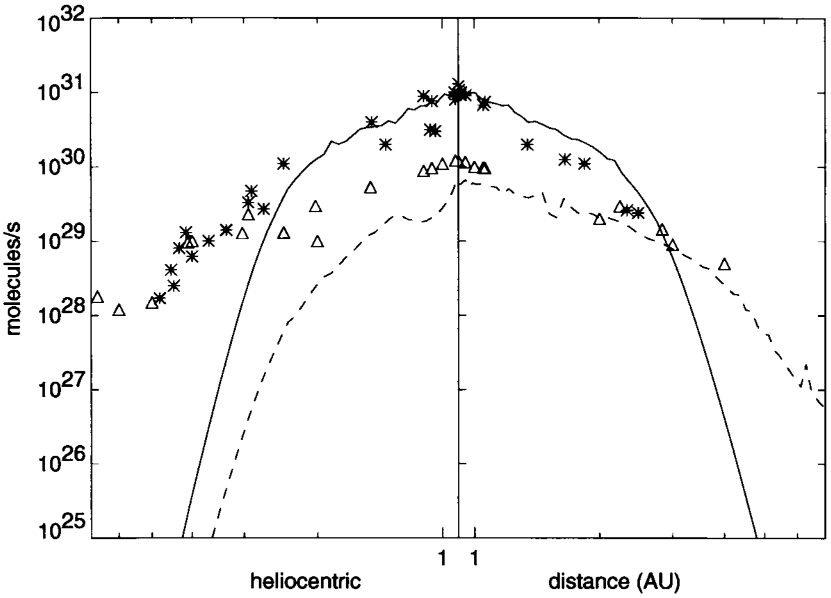

Figure 2. Gas production curve from observations (symbols) and model calculations (lines) in the range of 7 AU pre- and post-perihelion. Water: Asterisks and continuous line, CO: Triangles and dashed line.

in the ice are sluggish, but are aided by the presence of trapped gas which prevents the formation of well bound tight structures.

3.2. COMPARISON WITH OBSERVATIONS

In all nucleus models published recently, the phase transition from amorphous to crystalline ice is considered. In the model described in the Section 2.1 a term Q_{am-cr}, describing the heat released during the transition of water ice from amorphous to crystalline form, is added to the heat equation, and the gas source term due to the release of trapped CO, $Q_{CO_{tr}}$, is added to the CO diffusion equation. The phase transition from amorphous to crystalline ice is exothermic, as the heat released during the transformation is 1620 J mol^{-1} (Ghormley, 1968).

Figure 2 shows results from the theoretical model described in the Section 2.1. Here it is assumed that all the CO initially present in the nucleus is contained as trapped gas in amorphous ice, and is released during the transition to the crystalline phase. All the other assumptions are the same as those described in that section. The points obtained from observations are shown for comparison.

The shape of the emission curve of CO is completely different from that in Figure 1. This time we have a peak around perihelion, because the phase transition is occurring in layers with a temperature (130–145 K) much higher than the CO ice sublimation temperature, and consequently the gas is coming from layers much closer to the surface. The CO gas production is concentrated around perihelion: if

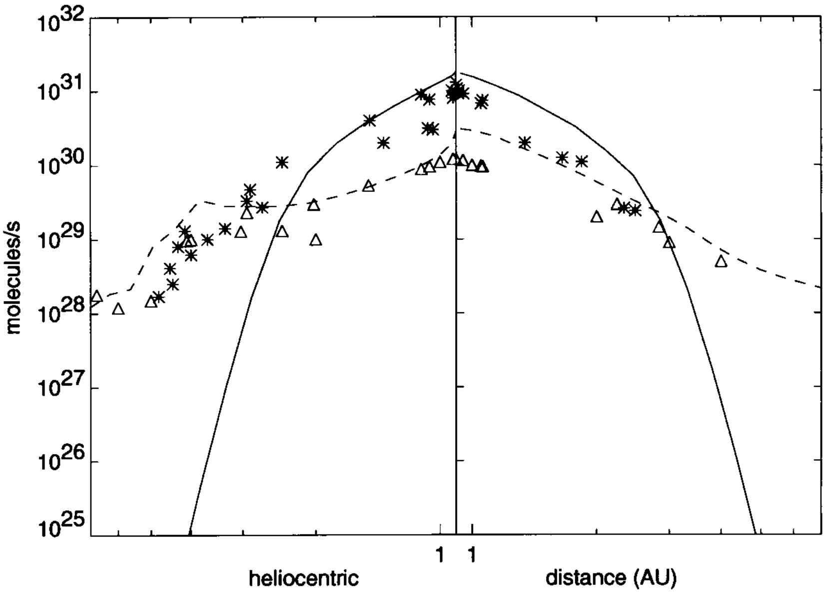

Figure 3. Gas production curve from observations (symbols) and model (lines) in the range of 7 AU before and post the perihelion. Water: Asterisks and continuous line, CO: Triangles and dashed line.

we assume that all the CO is contained in the nucleus as a trapped gas, we cannot explain any kind of activity far from the Sun, when internal temperatures do not allow phase transition and the related release of gas. Moreover, the general shape of this curve is not affected by lower internal conductivity, by changing initial temperature, latent heat budget of phase transition or gas diffusivity.

At this point, it seems obvious that, in order to explain the observations of Hale–Bopp with our theoretical model, we can assume that initially the CO gas is contained partly as pure ice in the nucleus and partly it is contained as a trapped gas in the amorphous ice. The trapped gas is released during the transition to the crystalline phase. Figure 3 shows the results obtained under these assumptions: now, the agreement between the observational data and the model results is quite good.

4. Distributed Source: Sublimation from Grains in the Inner Coma

A distributed source can be defined as any emission source not located in the nucleus or, following Festou (1999), a source of non-photolytic origin. This source can be, for example, ice containing grains that are ejected by the strong flux of supervolatiles in Hale–Bopp (Wooden, 2002), or large molecules present in the inner coma.

The existence of a distributed source is suggested by the spatial profile of the emission in the coma: the profile for central plus distributed source is much broader compared to that of a species directly emitted from the nucleus. This evidence can be obtained by comparing the apparent spherical production rate of a given species as a function of line-of-sight distance from the nucleus with that from a representative stellar profile (Di Santi et al., 2001; Dello Russo et al., 2000; Magee-Sauer et al., 1999). The spherical production rate is derived from the intensity measured at a specific location with the assumption of uniform spherical outflow from the nucleus. Spherical production rate curves are generated by stepping a 1×1 arcsecond aperture along the emission profile and extracting the production rate at one arcsecond intervals. Production rates obtained in this way increase from a minimum at the nucleus to a steady-state (terminal) value at some distance from the nucleus. This terminal value is reached quickly for the species having only a direct source and farther from the nucleus when a distributed source is present (Di Santi et al., 2001). This does not mean, anyway, that all the spatial profiles not looking similar to those obtained from a direct source should be automatically interpreted as hinting to the presence of a contributed source: other processes could give this particular appearance to the profiles (Festou, 1999).

Other observational evidences for extended sources are the steep heliocentric evolution of the gas production curve and the profiles of the radio lines which trace the velocity field of the molecules (Bockelée-Morvan and Crovisier, 2002).

Various parent molecules were found to have also a distributed source contributing to the total gas production measured in the coma (Bockelée-Morvan and Crovisier, 2002): CO, H_2O, OCS, H_2CO, and HNC. Distribution sources were found in Hale–Bopp for OCS (observations in the infrared, Dello Russo et al., 2000) and H_2CO (Di Santi et al., 2001; Wink et al., 1999). The distributed sources for water and CO will be briefly discussed in the following.

The contribution of distributed sources to the total gas production cannot be derived, obviously, by a nucleus model, because usually these models deal only with the phenomena occurring in the nucleus and on its surface.

4.1. H_2O FROM ICY GRAINS

It is highly probable that icy or icy/refractory grains can be ejected by the gas flux along with dust particles, and that these grains can sublimate in the inner coma giving a contribution to the total flux measured from ground observations.

The existence of a halo of icy grains around the nuclei of comets was suggested many years ago: see, for example, the pioneering work of Huebner and Weigert (1966) and of Delsemme and Miller (1970, 1971), who described in their comet nucleus models the formation and the properties of this water ice grains halo. This halo has been searched for without success for many years (for a review of the early detection attempts see Campins, 1985), until the arrival of Hale–Bopp. Hanner (1981) explained in her paper, on the basis of theoretical considerations, why it is difficult to detect icy grains in the coma of comets, if they exist: while grains of pure ice would have a long lifetime even at 1 AU, because they absorb little solar radiation and remain very cold, the presence of a very small amount of absorbing material drastically lowers the albedo and increases the temperature. At large heliocentric distances, where the energy going into sublimation is low, dirty ice grains can exceed black-body temperature: owing to the efficiency at radiating heat, these grains can become warmer than the surface of the nucleus and sublimate. The characteristic sublimation timescale (lifetime) of an icy grain depends on its optical properties: the admixture of absorbing material can reduce the lifetime to hours or minutes. In the case of icy mantled dust grains, a very specific ratio of mantle size/core size would be required in order for the grains to be at such a temperature to evaporate over the distance scale of the observable coma.

In comet C/1996 B2 (Hyakutake) an interaction arc or crescent-shaped feature was seen in images of OH (Harris et al., 1997), and this seems to indicate that large icy particles were ejected from the nucleus becoming secondary sources of gas at distances of the order of at least 1000 km down the tail. The interaction of the secondary source with the nearly spherical outflow of gas from the nucleus is the origin of the crescent-shaped feature. Harris et al. (1997) suggested also that the large gas production rate measured in this comet and the nearly spherical production of gas from the region around the nucleus could be due to a halo of icy grains similar to that in the secondary source in the tail.

In the spectra of comet Hale–Bopp taken at 7 AU from the Sun in the range 1.4–2.5 μm (Davies et al., 1997), the authors found broad absorption features that they attributed to an admixture of water ice, probably amorphous, and low albedo materials. These grains were still present at 3 AU, as confirmed by ISO spectra (Leech et al., 1999), and it is possible that the early beginning of water emission at 3.5 AU can be attributed to the evaporation of these grains (Bockelée-Morvan and Rickman, 1997).

Dello Russo et al. (2000), in their high-resolution infrared spectroscopy study of the heliocentric dependence of water with direct detection of water itself, concluded that most of the water was released directly from the nucleus at heliocentric distances less than 1.5 AU, but at larger heliocentric distances, when CO and other supervolatiles are controlling the comet's activity, water is likely released primarily from a distributed source of icy grains.

4.2. THE DISTRIBUTED SOURCE OF CO

CO is the most abundant molecule in comets, after H_2O, and is one of the first species that leaves the nucleus, due to the low sublimation temperature. This molecule can have also a distributed source in the coma, as was found during the *in-situ* Giotto and Vega spacecrafts observations of comet Halley. Following Eberhardt et al. (1987) and Eberhardt (1999), two thirds of the total CO production come from a distributed source in the coma. (An alternative view exists in which the spacecraft flew through a gas jet, see Greenberg and Li (1998)). The production mechanism of this distributed source of CO was uncertain, and many possibilities were suggested. Huntress et al. (1991) suggested that carbon suboxide could be the responsible for the distributed source of CO, because this species, obtained in laboratory by ion irradiation by Brucato et al. (1997), is readily decomposed after being released from the nucleus. Meier et al. (1993) proposed the photolysis of monomeric formaldehyde (H_2CO), released from CHON particles (Kissel et al., 1986), as a significant source for the production of CO in the coma.

Cometary CO was observed for the first time in the infrared in comet C/1996 B2 (Hyakutake), where probably a distributed source was concurring to the total CO flux detected (Mumma et al., 1996). Millimetre-wavelength spectra were obtained of CO, HCN, H_2CO, and CH_3OH in comet C/1996 B2 (Hyakutake) with the NRAO 12 m telescope on March 21 in 1996. The emissions of CO, H_2CO, and HCN were mapped in the coma, providing a detailed look at the behaviour of these species in the inner coma. Millimetre-wavelength spectra of CO, between other molecules, were obtained by Womack et al. (1997) with the NRAO telescope when comet Hyakutake was at nearly 0.16 AU from the Earth: in order to study the near nucleus behaviour of these molecules, the emissions were mapped in the coma. The authors concluded that, while the main source of CO was the nucleus, the gas was coming also from a distributed source. CO was also detected in the comet C/1996 B2 (Hyakutake) during a molecular radio lines monitoring by Biver et al. (1999): in this case the authors concluded that the extended CO source was absent or much weaker than the nuclear source. Anyway, such kind of observations are insensitive to extended sources of CO with large scale lengths, such as those coming, for example, from the dissociation of long-lifetime molecules (CO_2 and CH_3OH).

An extended study at infrared wavelengths, by means of high resolution spectroscopy, of the evolution of CO production in comet Hale–Bopp was conducted by Di Santi et al. (2001). The results of the detailed study of line-by-line excitation support a dual-source nature for CO production, as already found in comet Halley: half of the observed CO was initially contained in the nuclear ice, and half was produced in the coma. The onset of distributed CO production occurred between 2.02 and 1.49 AU from the Sun pre-perihelion, and was ceased at 2.24 AU post-perihelion. Following the authors, the abrupt onset of the distributed production seems to suggest a thermal threshold rather than some photochemical process: for example, the thermal destruction of a precursor material (small grains?) is consistent with the data.

5. Conclusion

After the passage in the inner Solar System of comets Hyakutake and Hale–Bopp, like after the spacecraft missions to comet Halley, the cometary science did a leap forward. The inventory of the parent and daughter species detected in comets is considerably longer (Bockelée-Morvan and Crovisier, 2002) and the picture of the nucleus and of the coma is now clearer.

From the point of view of theoretical nucleus models, the unprecedented coverage of Hale–Bopp activity has confirmed some physical phenomena that were proposed years ago: long-distance activity triggered by CO and the presence of sublimating grains in the inner coma.

The ability of the CO and other supervolatiles to produce and sustain a dusty coma and drive comet's activity was demonstrated. Hale–Bopp still had an enormous coma and a broad, fan-shaped tail at nearly 13 AU from the Sun, a distance midway between the orbits of Saturn and Uranus. This could explain how some of the Centaurs show traces of activity.

In her fundamental paper on the detection of icy grains in the coma of comets, Hanner (1981) concluded that "The problem at larger heliocentric distances is how to maintain a sufficient gas flux to strip grains larger than micron size from the nucleus". After Hale–Bopp and its huge supervolatiles flux, this is no more a problem. A part of the volatiles in the coma was sublimating from grains, and this is probably true for most comets. It is important to understand exactly the mechanisms and the production paths of these volatiles and quantify their relative contribution: probably, to do this, we need to wait for in-situ studies.

But, more important for modellers, it confirmed that existing models are able to reproduce many of the observed effects: just put the right input parameters, such as the enormous size. This can be viewed as an indirect confirmation to the fact that the wonderful behaviour of Hale–Bopp was due only to the uncommon size and not to strange unknown characteristics. It was, at the end, only bigger than others.

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