The Ice Survey Opportunity of ISO *

A review article

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Abstract. The instruments on board the Infrared Space Observatory have for the first time allowed a complete low (ISOPHOT, ISOCAM-CVF) to medium resolution (SWS) spectroscopic harvest, from 2.5 to 45μm, of interstellar dust. Amongst the detected solids, present in starless molecular clouds, surrounding recently born stellar and still embedded objects, or products of the chemistry in some mass loss envelopes, the so called "ice mantles" are of specific interest. They represent an interface between the very refractory carbonaceous and silicates materials that builded the first grains with the rich chemistry taking place in the gas phase. Molecules condense, react on ices, are subjected to UV and cosmic ray irradiation at low temperatures, participating efficiently to the evolution toward more complex molecules, being in constant interaction in an ice layer. They also play an important role in the radiative transfer of molecular clouds, and strongly affect the gas phase chemistry. ISO results shed light on many other species than H_2O ice. The detection of these van der Waals solids is mainly performed in absorption. Each ice feature observed by ISO spectrometer is an important species, with abundance in the 10^{-4}-10^{-7} range with respect to H_2. Such high abundances represent a substantial reservoir of matter that, once released later on, replenish the gas phase and feed the ladder of molecular complexity. Medium resolution spectroscopy also offers the opportunity to look at individual line profiles of the ice features, and therefore to progressively reveal the interactions taking place in the mantles.

This article will give an overview of selected results, in order to avoid to overlap with the numerous reviews the reader is invited to consult (e.g. van Dishoeck, 2004; Gibb, Whittet, Boogert, & Tielens, 2004).

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1. Ices everywhere

Interstellar ices have been observed with the SWS (de Graauw et al., 1996; Leech et al., 2003) instrument aboard ISO (Kessler et al., 1996; Kessler et al., 2003) in many different lines of sight among which the most common are :

OH-IR stars (and by extension, evolved stars circumstellar shells) which are oxygen rich post main sequence stars loosing mass at a high

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[*] Based on observations with ISO, an ESA project with instruments funded by ESA Member States (especially the PI countries: France, Germany, the Netherlands and the United Kingdom) and with the participation of ISAS and NASA.

rate. The dust and molecules formed in this mass loss ejecta feed a circumstellar shell, opaque to visible light and therefore reemitting in the infrared. In these lines of sight, H_2O is likely to be the only ice present on dust grains, generally in crystalline form (see Figure 1) as it was formed in the gas phase and then condensed at high temperature.
External galaxies (e.g. M82, Figure 2). In such lines of sight, the occurrence of ices is strongly dependent on geometrical effects. Not surprisingly, galaxies do contain large amounts of ices inside molecular clouds.
Field Stars are located behind molecular clouds (e.g. Elias 3−16, Figure 3) and by such allow one to use their infrared pencil to probe the foreground molecular cloud ice composition. They are crucial to understand ice evolution and chemistry during the earliest stage of starless clouds formation. The drawbacks are that they are statistically scarse and faint in the infrared. They are typically main sequence stars, often possessing intrinsinc photospheric absorptions one has to take into account to interpret the data.
Embedded protostellar objects (e.g. Figure 4) which constitute by far the most abundant and richest database of ice species, with an observational bias toward the brightest high mass sources. The drawback of these sources lines of sight is that the central object has generally started the interaction with the ice containing parental cloud, stimulating new processes but also complicating the analysis.

Such an extended panel of common line of sight, to which must be added the ones that to date escape detections such as optically thick disks, suggests ices are very common and abundant constituents in the lifecycle of dust in galaxies.

2. Inventory of the detected ice features

ISO has brought the number of ice features to more than twenty for clear detections, to which must be added a few ones to confirm. These features, the corresponding molecule, vibrational mode and integrated band strength are summarized in table I. The large wavelength coverage of the ISO spectrometers allowed to observe in the same spectra several modes of the same ice constituent.

Table I. Line list of ices absorptions observed by ISO.

Wavelength μm	Molecule[a]	Vibrational Mode	A 10^{-18}cm/molec	ref
2.70	$\mathrm{CO_2}$	Combination ($\nu 1+\nu 3$)	-	
2.78	$\mathrm{CO_2}$	Combination ($2\nu 2+\nu 3$)	-	
2.97	$\mathrm{NH_3}$	N-H stretch ($\nu 1$)	10-11	(1,2)
3.05	$\mathrm{H_2O}$	O-H stretch ($\nu 1$-$\nu 3$)	200	(1,3)
3.47	$\mathrm{NH_3..H_2O}$	Hydrate O-H stretch	$\sim$200	(4)
3.53	$\mathrm{CH_3OH}$	$\mathrm{CH_3}$ s-stretch ($\nu 3$)	5.3-7.6	(1,5)
3.84-3.95	$\mathrm{CH_3OH}$	Combination	2.6-3.2	(1,5)
4.27	$\mathrm{CO_2}$	Antisym. stretch ($\nu 3$)	76	(3)
4.38	$\mathrm{^{13}CO_2}$	Antisym. stretch ($\nu 3$)	78	(3)
4.55	$\mathrm{H_2O}$	Libration overt. ($3\nu_{\mathrm{L}}$)	$\sim$ 10	(3)
4.62	$\mathrm{OCN^-}$	C=N stretch ($\nu 3$)	40-80/(130 ?)	(1,6,7,8)/(9)
4.67	CO	CO stretch	11	(3)
4.78	$\mathrm{^{13}CO}$	CO stretch	13	(3)
4.90	OCS	CO stretch ($\nu 1$)	150-170	(5)
5.81	$\mathrm{H_2CO}$	CO stretch ($\nu 2$)	9.6	(10)
5.83	HCOOH	CO stretch ($\nu 3$)	67	(11)
5.85	$\mathit{CH_3CHO}$	CO stretch	13	(11)
6.02	$\mathrm{H_2O}$	O-H bend ($\nu 2$)	8.4-12	(1,3)
6.33	$\mathit{HCOO^-}$	CO stretch	100	(11)
6.85	$\mathit{NH_4^+}$	NH def ($\nu 4$)	40-44	(14)
7.25	HCOOH	C-H bend. ($\nu 4$)	2.6	(11)
7.25	$\mathit{HCOO^-}$	CO stretch	8	(11)
7.41	$\mathit{HCOO^-}$		17	(11)
7.41	$\mathit{CH_3CHO}$	CO stretch	1.5	(11)
7.7	$\mathrm{CH_4}$	CH def. ($\nu 4$)	6.4-7.3	(1,12)
8.85	$\mathrm{CH_3OH}$	$\mathrm{CH_3}$ rock ($\nu 7$)	1.3-1.8	(1,5)
9.35	$\mathrm{NH_3}$	Umbrella ($\nu 2$)	12-20	(2,13)
9.75	$\mathrm{CH_3OH}$	CO stretch ($\nu 8$)	18	(1,5)
11-14	$\mathrm{H_2O}$	Libration(ν_{L})	28-31	(1,5)
15.2	$\mathrm{CO_2}$	$\mathrm{CO_2}$ bending ($\nu 2$)	11	(3)

[a] detected molecules italicized are either tentative, need confirmations or their abundance are still subject to strong debate.

(1) Dhendecourt & Allamandola, 1986; (2) Sandford & Allamandola, 1993; (3) Gerakines, Schutte, Greenberg, & van Dishoeck, 1995; (4) Dartois & d'Hendecourt, 2001; (5) Hudgins, Sandford, Allamandola, & Tielens, 1993; (6) Grim & Greenberg, 1987; (7) Schutte & Greenberg, 1997; (8) Demyk et al., 1998; (9) van Broekhuizen, Keane, & Schutte, 2004 a value 3 σ above the other determinations; (10) Schutte et al., 1996a; (11) Schutte et al., 1999; (12) Boogert et al., 1997; (13) Kerkhof, Schutte, & Ehrenfreund, 1999; (14) Schutte & Khanna, 2003

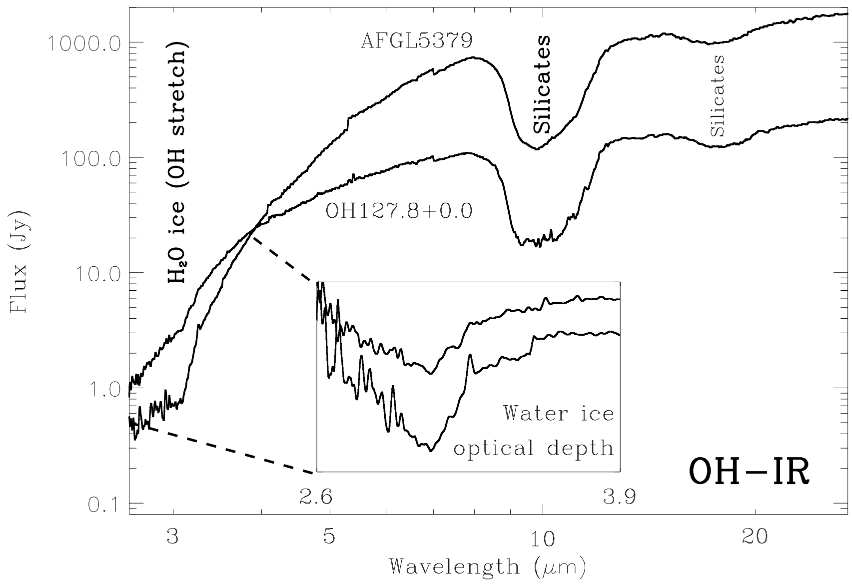

Figure 1. Short Wavelength Spectrometer (AOT01) observations of two OH-IR circumstellar shells, displaying silicates features and water ice signatures. The insert contains the continuum divided spectra in the 3 μm region of the spectrum, in order to show the OH stretching mode of crystalline water ice. Extracted from the ISO Data Archive (*http://www.iso.vilspa.esa.es/ida/*).

3. Molecule by molecule

H_2O : THE LORD OF THE ICES

One of the first but unsuccessful attempts to detect water ice was performed by Knacke, Cudaback, & Gaustad (1969) in the diffuse medium. Water ice was observed later on through its OH stretching mode at 3 μm, from the ground by Gillett & Forrest (1973). Since then, many line of sight were surveyed from the ground in this mode (e.g. Merrill, Russell, & Soifer, 1976; Léger et al., 1979; Willner et al., 1982; Whittet et al., 1983; Smith, Sellgren, & Tokunaga, 1989; Eiroa & Hodapp, 1989; Tanaka, Sato, Nagata, & Yamamoto, 1990; Sato, Nagata, Tanaka, & Yamamoto, 1990; Chen & Graham, 1993; Smith, Sellgren, & Brooke, 1993). After the discovery of the vibrational fundamental modes, phonon modes around 44 and 66 μm were found in emission by Omont et al. (1990) and followed by laboratory analysis (Moore & Hudson, 1992; Hudgins, Sandford, Allamandola, & Tielens, 1993; Smith, Robinson, Hyland, & Carpenter, 1994; Maldoni et al., 1999). So many others authors contributed to this search that a full list is

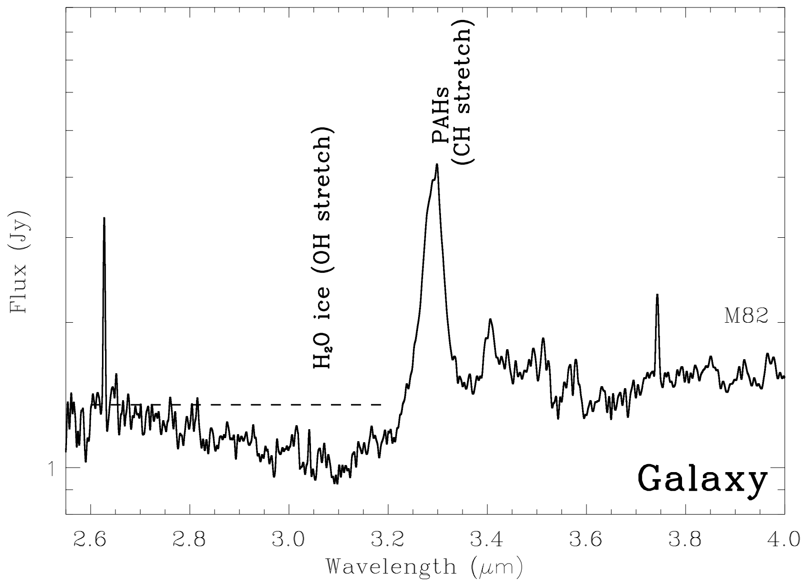

Figure 2. Short Wavelength Spectrometer (AOT01) observations of the Andromeda galaxy. The galactic continuum is absorbed by water ice present in the dense clouds of the galaxy. Extracted from the ISO Data Archive.

out of scope. In this context, the insight in a better understanding of water ice performed by ISO has first been to substantially extend the number of astrophysical lines of sight where water ice is observed and, more interestingly, to offer a complete and simultaneous coverage of the six principal modes/combinations occurring in the infrared : the OH stretch ($\sim$3.05 μm), the libration overtone ($\sim$4.5 μm), the OH bend ($\sim$6.0 μm), the libration ($\sim$11-13 μm), the longitudinal and transverse optical mode at $\sim$44 μm and $\sim$66 μm, respectively. The two latter modes are detected either in absorption (Dartois et al., 1998) or emission (Malfait et al., 1999; Molinari et al., 1999; Hoogzaad et al., 2002; Molster, Waters, & Tielens, 2002; Maldoni et al., 2003) betraying the radiative transfer effects at long wavelength. For the water ice seen in emission toward some lines of sight, care must however be taken to analyse the spectra, as silicates far infrared features (especially enstatite) contribute to the lines.

In addition to their detections, ISO has brought truly new spectroscopic constraints on the water ice modes. As an example, the OH bending mode profiles reveal the contribution of other features, unaccessible before (Keane et al., 2001), and whose identification will be discussed later on.

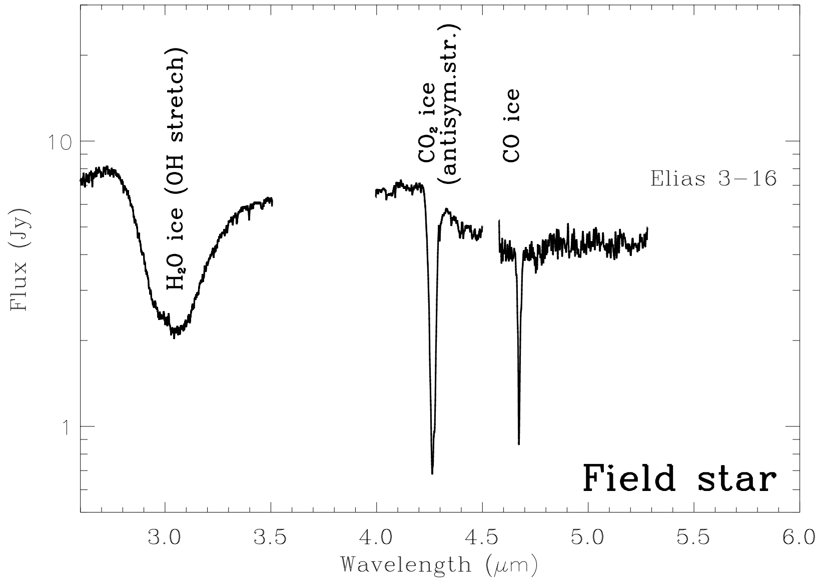

Figure 3. Short Wavelength Spectrometer (AOT06) observation of the Field star Elias 3-16, located behind the Taurus dark cloud. The infrared continuum of the star is absorbed selectively by the ice mantles located in the cloud. Extracted from the ISO Data Archive

Water ice is the dominant solid state frozen species and consequently the abundances of other ices are referred to this one on a relative scale (see table 6). On an absolute scale, in clouds with substantial visual extinction, water ice is the second most abundant species after H_2 ($[H_2O]/[H_2] \approx 10^{-4}$-$10^{-5}$), comparable to or even more abundant than gas phase CO.

UNRAVELLING THE UBIQUITOUS CO_2

Before the launch of ISO, the carbon dioxide existence in ice mantles was founded on very few astrophysical data. Its inference was indirect and based on the possible influence of CO_2 interacting with other molecules on their line profiles (Sandford, Allamandola, Tielens, & Valero, 1988; Kerr, Adamson, & Whittet, 1991; Tielens, Tokunaga, Geballe, & Baas, 1991). Indeed, besides an infrared oscillator strength amongst the strongest of ISM solid molecules, the atmospheric carbon dioxide prevents any ground based or airborne observations detection of its space parent. The very first direct detection was performed in 1989, on unresolved CO_2 bending mode profiles, using IRAS Low Resolution Spectrometer spectra (d'Hendecourt & Jourdain de Muizon, 1989). The

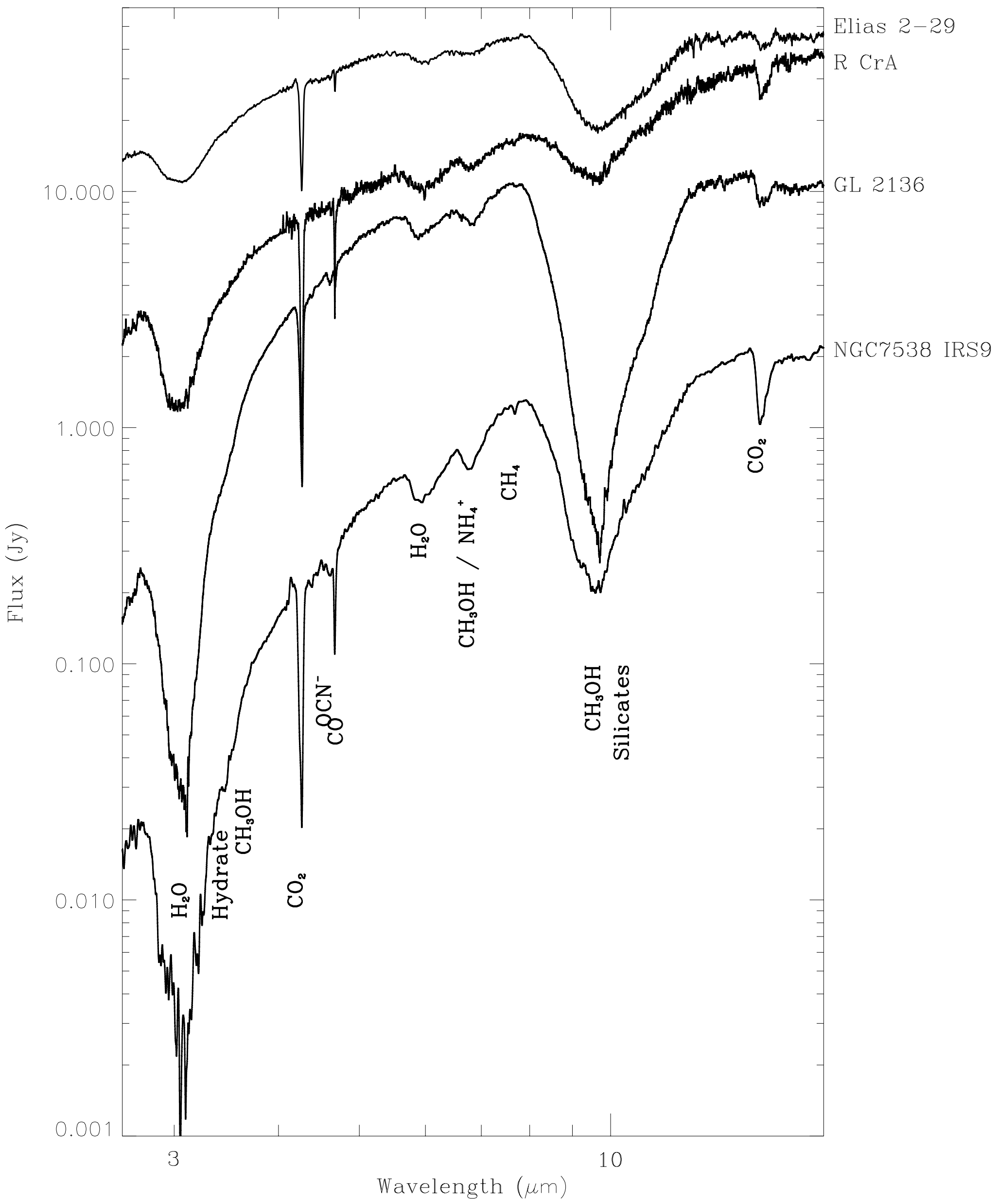

Figure 4. Short Wavelength Spectrometer (AOT06) observations of the rich ice spectrum of embedded intermediate to high mass protostars. From top to bottom : Elias 2-29, RCRA, GL2136, NGC7538 IRS9. Spectra have been shifted in flux by arbitrary constants for better clarity. The more common identified features are labelled below the spectra. Extracted from the ISO Data Archive

ubiquitous nature of carbon dioxide was revealed and firmly assessed with ISO spectrometers (Guertler et al., 1996; Gerakines et al., 1999; Alexander et al., 2003; de Graauw et al., 1996). CO_2 then appears as the most abundant molecule after H_2O in ice mantles, with a mean CO_2/H_2O ratio ranging generally from 10 to 50% in protostellar environments with a mean around 15-20%.

The $^{13}CO_2$ stretching mode was detected, and its line profile analysed by Boogert et al. (2000). This is a valuable information, because being about 60 times less abundant than the main molecule, this isotopomer is experiencing and therefore tracing the ice matrix environment field. It allows to a certain point to distinguish between different thermal processing having affected in the past the ice mantles.

Some combination modes (symmetric + antisymmetric stretching and twice the bending + symmetric stretching modes) have also been detected in S140 IRS1 (Keane et al., 2001), being the first detection of solid state identified combinations in space ice mantles. The position and profiles of these combinations implies that the carbon dioxide is mixed in roughly equal proportions with methanol and water ice. The ability to observe combination modes, with low integrated absorption cross sections further demonstrate these ices are abundant components of molecular clouds.

Another results of ISO medium resolution spectra is the first detection of interstellar molecular complexes implying the interaction of a carbon atom of the carbon dioxide with the lone electron pairs of the methanol oxygen (Ehrenfreund et al., 1999; Dartois, Demyk, d'Hendecourt, & Ehrenfreund, 1999; Klotz, Ward, & Dartois, 2004). This interaction deforms the CO_2 molecule in such a way that the degenerescence of the bending mode is broken, giving rise to two individual absorption components around 15.2 μm (see Figure 5, right panel), whereas the stretching mode is only slightly affected. The combination of this complexation with the thermal evolution of ice mantles gives rise to characteristic substructures, possessing from one to three subpeaks (Figure 5, left panel, Dartois, Demyk, d'Hendecourt, & Ehrenfreund, 1999) in the bending mode regions of carbon dioxide infrared spectra. Such a spectroscopic constraint is of major importance for the understanding of the structure in which are organised here the carbon dioxide and methanol ices. These structures are not fortuitous, require a specific stœchiometry, and the premice of better understanding of their formation history.

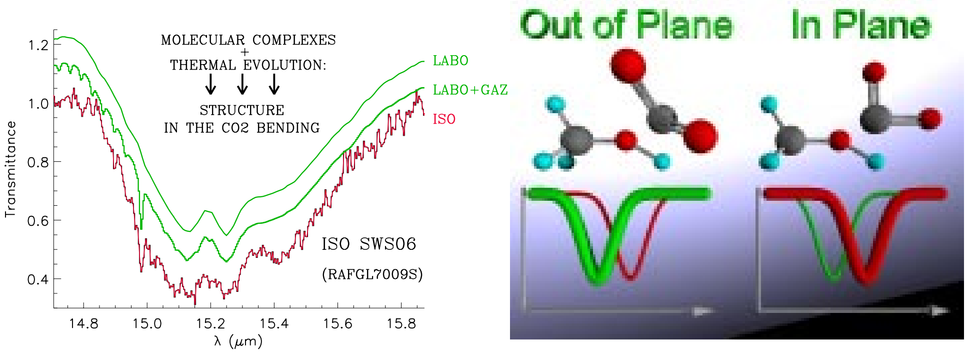

Figure 5. Left : SWS06 absorption spectrum of RAFGL7009 in the CO_2 bending mode region displaying a triple substructure, compared with laboratory ice spectrum + gas phase model. Right : This structure partly arises due to the break of degeneracy of the in-plane and out-of-plane CO_2 bending mode (see text for details).

CO

Solid CO is a molecule observed almost routinely from ground based telescopes and recently its principal isotopomer ^{13}CO was reported (Boogert, Blake, & Tielens, 2002). Ground based observations allow to study the carbon monoxide line profiles (Pontoppidan et al., 2003) with unprecedented spectral resolution. The reader is referred to the huge literature on the subject, notably on the various profiles induced by the polar or apolar environment of this molecule.

One of the results of ISO was to allow a comparison with the same infrared pencil beam of gas-to-solid state CO ratio (Dartois et al., 1998; van Dishoeck et al., 1996), showing that even if it is an abundant component of ice mantles (typically 3%-20%), it resides principally in the gas phase in the general case.

OCS AND SULFUR CONTAINING MOLECULES

Sulfur is an abundant element of interstellar medium and one expects therefore to observe it in ices. Geballe, Baas, Greenberg, & Schutte (1985) detect toward W33 A two absorptions at 3.9 μm and 4.9 μm, respectively attributed by these authors to H_2S and another sulfur containing molecule produced in laboratory experiments. The 3.9 μm feature will be attributed later on to solid methanol combination modes, the only really containing sulfur molecule giving rise to the feature at 4.9 μm.

Smith (1991) discuss the search for H_2S in six objects and put an upper limit of about 1% on its presence.

Palumbo, Geballe, & Tielens (1997) and Palumbo, Tielens, & Tokunaga (1995) observe the 4.9 μm feature, identify it with carbonyl sulfide and discuss its abundance toward various lines of sight. The line profile is best reproduced when OCS is mixed with methanol. In fact there is an overlap of the second overtone $2\nu_8$ of methanol with this line.

With ISO, OCS has been evaluated in many lines of sights (see references in Gibb, Whittet, Boogert, & Tielens, 2004), but most of the time without evaluating the methanol overtone contribution, especially towards RAFGL 7009 and W33 A.

The CO stretch of OCS is one of the more intense infrared bands and therefore OCS is the molecule detected with the lowest abundance with respect to H_2O, of about 0.05-0.15%. This can be considered as the limit of detection of ices.

CH_4

The ground based very difficult detections of methane were started by Lacy et al. (1991). With ISO, the methane molecule was detected in several sources via its deformation mode at 7.67 μm mode, with abundances up to 4% with respect to H_2O (d'Hendecourt et al., 1996), but more generally at the 1-2% level (Boogert et al., 1996). The gas-to-solid methane ratio in such lines of sight is less than unity, favouring a formation of this hydride by hydrogenation of atomic carbon directly on the surface of grains. The actual abundance of methane does not reflect its initial abundance in the solid phase as it is one of the easiest molecule to dissociate upon UV secondary photons photolysis or ion irradiation, typical of dark clouds.

H_2CO

Most of the molecules containing a carbonyl group strongly absorb in the 5.7-6 μm region of the spectrum, the simplest of them being the formaldehyde (e.g. Schutte, Allamandola, & Sandford, 1993). The first attempt to detect it was made by Schutte et al. (1996a) in GL 2136 but the abundance controversed due to a mixing of formaldehyde modes with methanol ones, also present in large amount in the same line of sight. An estimate was also given for W33 A by Brooke, Sellgren, & Geballe (1999). These "pre-ISO" estimates were based on C-H stretching modes rather difficult to disentangle from the methanol CH stretchs present in the spectra.

Formaldehyde ice strongest modes fall at 5.8 and 6.68 μm, both inaccessible from the ground. ISO therefore allowed the search of these reliable modes for the first time, even if protostellar sources do possess strong absorptions in the same wavelength region due to the H_2O bending mode and the so-called 6.85 μm feature. Formaldehyde abundance in ISO spectra was estimated in five high mass protostellar envelopes (W33 A, AFGL7009, GL2136, GL989, NGC7538 IRS9) to range between 1 and 3% (see Keane et al., 2001 Table 3, Dartois, Demyk, Gerin, & d'Hendecourt, 1999; Gibb et al., 2000, and references therein).

CH_3OH

CH_3OH is mainly detected from ground based observations of its ν_3 mode around 3.53 μm . It was early detected through this mode (Baas et al., 1988; Grim et al., 1991; Allamandola, Sandford, Tielens, & Herbst, 1992) in massive protostars lines of sight. The presence of the methanol-carbon dioxide complex, discussed above in the CO_2 section, raised a new interest for its search (e.g. Dartois et al., 1999). Only recently and from the ground, it was shown by Pontoppidan et al. (2003) that methanol is also present around some low mass protostars. Methanol is a key molecule in ices, as it sometimes represent up to several tenth of the water ice abundance. Its formation route is under a controversial debate. Some authors think it is formed directly from grain surface hydrogenation of CO, but to date laboratory experiments performed give contradictory answers to the hypothesis (Hiraoka et al., 2002; Watanabe, Shiraki, & Kouchi, 2003).

Others think that it can be created by energetic processes (UV or cosmic rays) (Hudson & Moore, 1999; Moore & Hudson, 1998), eventually followed by selective desorption enhancement effects, methanol being a rather refractive ice.

Nitrogen bearing species

N_2

Nitrogen is an abundant cosmic element and N_2 is a stable molecule, its presence would therefore be logical. In practice, this homonuclear molecule is, due to its symmetry, inactive in the infrared. However, when embedded in an ice matrix, the crystal field breaks this symmetry and an infrared transition is activated around 4.295 μm. This weakly intense transition, with an integrated absorption cross section of 10^{-6} to 10^{-4} the OH stretching one of water ice in the best activated mixtures (Sandford et al., 2001; Ehrenfreund & van Dishoeck, 1998 and references therein), is a challenge to detection limits. In addition, this feature falls in the red wing of the strong CO_2 antistretch absorption, both in the solid and gas phase. To date, the only few upper limits derived for the presence of N_2 when embedded into water ices, and using ISO SWS data (see above cited references), are not sufficiently low to provide strong constraints. Only very (too ?) specific ice mantles compositions (such as pure N_2:CO_2 ice mixtures) could lead to push down this limit by enhancing the activation of the otherwise inactive N_2 stretching mode, which remains to be proved in an ice mantle dominated by water ice.

NH_3

After N_2, the most abundant nitrogen bearing molecule is certainly ammonia. Knacke et al. (1982) were among the firsts to claim for an identification of NH_3 in interstellar grains from an infrared absorption at 2.97 μm (NH stretching mode), a detection refuted later on cite1987AJ.....94..972K. Hagen et al. (1983) show that the H_2O stretching mode profile is best reproduced with an ice containing a significant fraction of ammonia. Since then, many authors entered into the still opened debate of ammonia ice abundance in grain mantles.
Ammonia possess three main modes at 2.97 μm(NH stretch), 6.2 μm (NH bend) and 9 μm (umbrella mode, which shifts to longer wavelength if pure ammonia). Importantly, and often underestimated, when mixed with H_2O, the major ice mantle constituent, ammonia forms an hydrate that gives rise to a large and intense band around 3.47 μm(with an integrated absorption cross section similar to the water OH stretch). All modes, except for the hydrate one, fall in spectroscopic regions overlapping with the dominant water ice or silicate features, which renders the detection task difficult. In addition, toward lines of sight where methanol is present, the CH_3 rock can contribute significantly to the ammonia umbrella mode. Detecting the relatively intense 9 μm umbrella mode in the wing of the strongly absorbed silicates features has always led to high overestimates of the true ammonia contents.

A school case to support this view comes from the well studied W33 A line of sight. The methanol contribution at 8.9-9 μm, inferred from other modes, should provide an optical depth around $\sim$0.1. To show consistency in interpreting spectra of this source, and before any ammonia search, this CH_3OH mode must be evidenced and subtracted to the data. Based on ISOPHOT-S (Lemke et al., 1996; Laureijs et al., 2003) and SWS spectra around 9 μm, various authors derive quite different column densities of NH_3, namely 1.7×10^{18}cm^{-2} (Gibb, Whittet, & Chiar, 2001), 1.2-2.2×10^{18}cm^{-2} (Gürtler et al., 2002), representing a high percentage (11-20%) as compared to water ice. These numbers were in fact all contradicted by the recent ground based upper limit toward this source by Taban, Schutte, Pontoppidan, & van Dishoeck (2003), which lies about two to three times lower.

In the analysis presented in Dartois & d'Hendecourt (2001) and Gibb, Whittet, & Chiar (2001), on 20 different sources lines of sight (mainly massive YSOs), only in three of the Gibb's article are claimed NH_3 detections. For these three sources : (i) W33 A detection was later on rejected by Taban, Schutte, Pontoppidan, & van Dishoeck (2003); (ii) NGC7538 IRS9 possess a considerable uncertainty on ammonia abundance given the scatter in the derived NH_3/H_2O ratios of 10% (Lacy, Faraji, Sandford, & Allamandola, 1998), 15% (Gibb, Whittet, & Chiar, 2001), $< 5\%$ with ISOPHOT and $\sim$8% with SWS (Gürtler et al., 2002); (iii) GL989 possess at most 5% of ammonia (Dartois & d'Hendecourt, 2001; Gibb, Whittet, & Chiar, 2001).

Based on the absence of the 2.97 μm NH stretching mode and the maximum contribution of the ammonia hydrate at 3.47 μm, Dartois & d'Hendecourt (2001) deduced that a conservative upper limit of 5% ammonia relative to water ice can be hidden in the ice mantles.

ISO has allowed to cover the full range of main ammonia modes and this is a great advantage when searching for a molecule with several infrared active modes. A detection should therefore be compatible with the complete spectrum as discussed thoroughly in Dartois et al. (2002). The uncertainties and scatter in the determination of ammonia column densities using only its umbrella mode evidence this mode is not reliable when extracted on a deep silicate stretching mode absorption.

OCN^-

A special nitrogen molecule in interstellar ices is represented by the cyanate anion which possess its strongest infrared active mode around 4.62 μm, aside to the CO feature. Falling in an atmospheric window, it has been seen early by McGregor et al. (1982); Lacy et al. (1984) and assigned then to a nitrile bond (-C≡N) although it was present but unresolved (i.e. mixed with solid CO) in the observations of W33 A by Soifer et al. (1979). It was then first assigned by Grim & Greenberg (1987) to the OCN^- cyanate anion, by photolysis of CO/N_3 ice mixtures and using ^{13}C and ^{15}N isotopic labelling. Such species was confirmed by further experiments using ^{18}O substitution (Schutte & Greenberg, 1997). Many others authors have pursued the "XC≡N" in

the laboratory through isotopes substitutions, proton and UV irradiations of ices, etc..., among which one can cite the non exhaustive list of Novozamsky, Schutte, & Keane (2001); Hudson, Moore, & Gerakines (2001); Hudson & Moore (2000); Bernstein, Sandford, & Allamandola (2000); Palumbo, Pendleton, & Strazzulla (2000); Pendleton, Tielens, Tokunaga, & Bernstein (1999); Demyk et al. (1998).
The observation of OCN^- was long thought to be very important because it was the molecule giving evidence of the ultraviolet field present inside dense clouds. However, recently, the debate about its formation mechanism has been relaunched as several laboratory investigations gave an alternative route via a direct proton transfer from HOCN (or HNCO) to NH_3, leading to the formation of $OCN^-NH_4^+$ (Demyk et al., 1998; Raunier et al., 2004; van Broekhuizen, Keane, & Schutte, 2004; Raunier et al., 2004). Such a proton transfer could be so efficient, even at low temperature, that it would be impossible to see the HNCO precursor.

The abundance of OCN^- relies on the adopted integrated cross Section A, which varies from about 4×10^{-17} to 1.3×10^{-16} using different approaches to estimate it (Dhendecourt, Allamandola, Grim, & Greenberg, 1986; Grim & Greenberg, 1987; Demyk et al., 1998; van Broekhuizen, Keane, & Schutte, 2004), but favouring the lower value for A. From the ISO observational point of view, the exact abundance or upper limits reported on various ISO lines of sights (e.g. Gibb, Whittet, Boogert, & Tielens, 2004), completed by ground based recent VLT ones (von Broekhuizen, private communication) of OCN^- represent at most a few percent of the water ice content, up to 4% for the highest column density found, for W33A.

NH_4^+

To preserve the global neutrality of the ices, and as a consequence of the processes proposed for the existence of the OCN^- anion, the counterion NH_4^+ has been proposed years ago (Grim, Greenberg, Schutte, & Schmitt, 1989; Grim et al., 1989). Such an assignment was compatible with the early detection of a band at around 6.85 μm(Russell, Soifer, & Puetter, 1977), therefore associated with the ν_4 mode of this cation.

The first medium resolution spectra of this band were obtained by ISO (e.g. Schutte et al., 1996b; Demyk et al., 1998). A rather complete analysis of the various hypothesis to explain this 6.85 μm absorption was performed by Keane et al. (2001), on lines of sight with different environmental conditions. They conclude that this band is composed of two components, related through thermal processing.

In the laboratory, after many years of laboratory experiments with ammonia containing ice mixtures or thermal processing of NH_3 with acids (formic acid, cyanic acid, isocyanic acid), it could be said that NH_4^+ should explain a part, if not all, of the 6.85 μm feature (Schutte & Khanna, 2003 and references therein for a view of laboratory work), and other counterions than OCN^- would be present in the ices, forming an infrared absorption continuum that is hardly detectable.

O_2

Like N_2, the homonuclear oxygen molecule O_2 is infrared inactive, except when embedded in an ice matrix, where it is slightly activated (Ehrenfreund, 1992; Ehrenfreund & van Dishoeck, 1998) and gives rise to an absorption around 6.45 μm. Considerable laboratory work was dedicated to infer the presence of O_2 by studying its influence on other modes, among which Ehrenfreund et al. (1997); Strazzulla, Brucato, Palumbo, & Satorre (1997); Elsila, Allamandola, & Sandford (1997); Ehrenfreund et al. (1996). With ISO, the upper limits found by Vandenbussche et al. (1999) are not sufficiently low to give any constraint on the ice mantles oxygen content, but still tell us that no more than about 6% of the oxygen cosmic budget can be hidden in this particular component. Molecular oxygen seems not extremely abundant in ice mantles. Additional indirect evidence for that might come from the absence of detection of its photoproducts like CO_3 or O_3. A high abundance of molecular oxygen would also influence drastically the ice mantles spectra observed by creating a lot of new radicals that can be seen in all the relevant irradiated mixtures found in the references of this review.

The fact that the SWAS satellite also demonstrated O_2 is not abundant in the gas phase tends to demonstrate the oxygen atom assume other forms. In particular, in dense clouds, carbon monoxide and dioxide (gas and solid), water ice and silicates already consume a large part of the total oxygen budget.

RELATIVE ABUNDANCES

A schematic diagram showing the typical relative abundances of species with respect to the main H_2O ice, based on ISO references of this review, is presented in Figure 6. Grey histogram implies the values can be lower than typical, especially for sources lines of sight where a warming of the mantle has begun (e.g. S140). The ammonia case is specific, as no truly reliable column densities are generally available

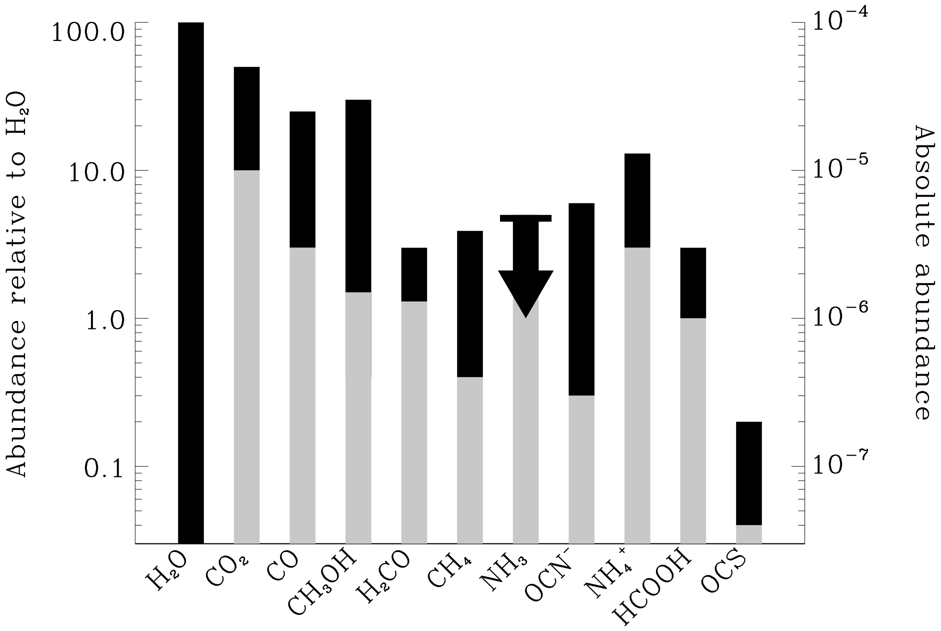

Figure 6. Schematic diagram of solid species typical abundances, normalized to water ice. The grey line are here to represent the selective disappearance of species from the solid phase by e.g. selective thermal desorption. Approximate absolute abundances are given on the right scale. See text for explanation.

(see corresponding section), but its occurrence is however certain. On the right side, an approximate absolute abundance is given, assuming that about 10-15% of total cosmic oxygen is locked into water ice. Such a reference is based on typical correlation found in dark clouds between visual extinction and H_2O ice (e.g. Murakawa, Tamura, & Nagata, 2000 and references in the H_2O section).

4. Tentative detections, requested confirmations

Other species, with low fractional abundances have been proposed/suggested to explain some minor features in ISO ice mantles spectra. The presence of most of them requires however confirmations to assess their role in ices. In this list one can find $HCOO^-$, CH_3CHO, $HCONH_2$ (Schutte et al., 1999) and $(NH_2)_2CO$ (Raunier et al., 2004).

A feature still under debate is the 6.85 μm one. It falls in a wavelength range which is an infrared spectroscopic accumulation point. In fact, many molecules absorb in this range and if it is due to the superposition of many distinct species, it will be difficult to sort out which ones. This feature can then also be considered as needing further confirmations for the contributing species.

Conclusions

ISO has opened a new era of ice mantles compositional determination, by providing for the first time a complete coverage of the vibrational spectrum of interstellar ices. The analysis is now based on a laboratory simultaneous match of all the modes of a species to be able to claim an identification, which from the ground is simply impossible.

ISO showed that ices are a truly ubiquitous dense medium component, serving as interface between gas and solid state. It also provided insight into the initial conditions from which such dense media evolve to protoplanetary systems, and therefore the ice compositions to be explored by laboratory photo-thermo and/or cosmic rays processing of grain mantles.

Typical abundances of ices summarized in Figure 6 tells us that the detection limit for ices by direct absorption spectroscopy against infrared sources continuum is about $10^{-7} - 10^{-8}$ with respect to H_2. This fact contrasts with radio astronomy detection of gas phase molecules that can push down this value by more than five orders of magnitude. One must keep in mind this observational bias and remember that it does show that every detected ice with ISO is a major element of the astrochemical evolution of clouds.

In addition to a complete view on relative abundances of ice components, ISO showed that medium resolution spectra are the prerequisite to understand physically the behavior and interactions inside interstellar ice mantles. Without such a resolution, astrophysicists would have been unable to detect the CO_2 combinations and overtones, to decipher the formation of CH_3OH-CO_2 intermolecular complexes, the NH_3-H_2O hydrate, to understand the gas-to-solid state ratios probed in the same lines of sight, to cite few of them.

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