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ISO Observations of Gas and Dust Chemistry in Star-Forming Regions

E.F. van Dishoeck, F.P. Helmich¹, W.A. Schutte and P. Ehrenfreund Leiden Observatory, P.O. Box 9513, NL-2300 RA Leiden, The Netherlands

F. Lahuis²

ISO-Science Operations Centre, P.O. Box 50727, E-28080 Villafranca, Spain

A.C.A. Boogert, A.G.G.M. Tielens and Th. de Graauw

Kapteyn Astronomical Institute and SRON, P.O. Box 800, NL-9700 AV Groningen, The Netherlands

P.A. Gerakines and D.C.B. Whittet

Dept. of Physics, Applied Physics and Astronomy, Rensselaer Polytechnic Institute, Troy NY 12180, USA

Abstract. Recent results of searches for absorption lines of gas-phase molecules and solid-state species in the ISO spectra of embedded massive young stars are reviewed. The ISO-SWS is very well suited for the study of interstellar ices and provides an unbiased overview of their composition for the first time. Early highlights include observations of abundant, widespread solid CO₂, and the detection of solid CH₄ and HCOOH. Possible candidates for other weak features are discussed. In the gas-phase, ISO provides important information on the abundance of H₂O in warm regions, through observations of the vibration-rotation lines with the SWS and pure rotation lines with the LWS. Gas-phase CO₂ is also detected, but with a surprisingly low abundance. Recent data on gas-phase CH₄, C₂H₂ and HCN are presented as well. Gas/solid state ratios are determined, which give information on the importance of gas-grain chemistry, and on the evolutionary state of the object.

1. Introduction

The star-formation process is accompanied by enormous changes in the physical parameters of the immediate environment (Shu et al. 1993). Densities increase

¹Earth Observations Division, SRON, Sorbonnelaan 2, NL-3584 CA Utrecht, The Netherlands

²SRON, P.O. Box 800, NL-9700 AV Groningen, The Netherlands

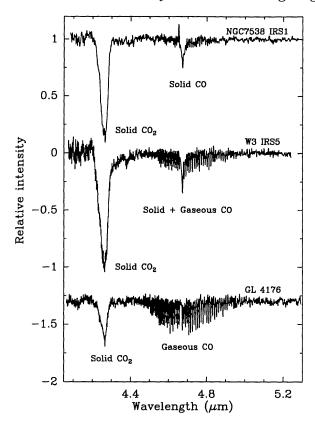


Figure 1. Normalized ISO–SWS spectra in the wavelength region of the CO_2 ν_3 and CO vibrational bands toward three embedded young stellar objects. The CO_2 is primarily in solid form, indicated by the broad line shape. Toward NGC 7538 IRS1, CO is also mostly in solid form, but toward W 3 IRS5 the ro–vibrational structure of gaseous CO is seen as well. Toward AFGL 4176, only gaseous CO is observed. The spectra have been shifted by 0.0, -1.0 and -2.25 for clarity (van Dishoeck et al., in preparation).

from 10⁴ cm⁻³ in the parental cloud to more than 10⁹ cm⁻³ in the circumstellar disk surrounding the young stellar object. Temperatures range from 10 K in the collapsing envelope to a few thousand K in gas shocked by the impact of the bipolar outflow. Although significant progress has been made in our understanding of the physical structure of young stellar objects from infrared and (sub-)millimeter observations, much is still unknown about the chemical composition. Observations with the *Infrared Space Observatory* are particularly powerful to address two major questions in the study of the chemical evolution of star-forming regions. First, what is the inventory of the chemical compounds containing the major elements (C, N, O, ...), both in the gas and on the grains? Second, how does the chemical composition change with evolution? Can we identify species whose abundances are particularly sensitive to the various evolutionary phases (e.g., collapse, outflow, radiation, ...)?

In the last decade, a scenario has emerged for the interplay between the gas and dust in the earliest stages of star formation (see e.g., van Dishoeck et al. 1993, van Dishoeck & Blake 1995, Tielens & Whittet 1997, Tielens & Charnley 1997,

Hartquist et al. 1998 for reviews). During the cold collapse phase, the density increases to the point that most molecules accrete onto the grains. Here the chemistry can be actively modified by surface reactions (especially hydrogenation of O, C and N to H_2O , CH_4 and NH_3 and oxidation of CO to CO_2) and possibly through photoprocessing of ices. After the new star has formed, its radiation will heat up the surroundings and the molecules start to evaporate back into the gas phase, probably in a sequence according to their sublimation temperatures. In addition, the outflows create shocks when they interact with the surrounding envelope, which can drive high temperature chemical reactions (e.g., $O + H_2 \rightarrow OH \rightarrow H_2O$) and return icy mantles and more refractory material containing silicon to the gas phase (Martín–Pintado et al. 1992). These freshly evaporated molecules can then drive a rich and complex chemistry in the gas (called the "hot core" phase) for a period of $\sim 10^5$ yr (Charnley et al. 1992, 1995; Caselli et al. 1993). Finally, the chemistry returns to the quiescent phase dominated by ion–molecule reactions.

2. Infrared absorption vs. submillimeter emission observations

The chemical composition of the circumstellar environment can be probed by infrared and submillimeter techniques, which give very complementary information (Evans et al. 1991, Carr et al. 1995). Infrared observations probe the absorption of material along the line of sight to the embedded young star. This technique has the advantage that only a pencil-beam line of sight is sampled. Also, the population distribution over the energy levels can be directly constrained from a single infrared spectrum, whereas often different receivers or telescopes are needed to determine the excitation from submillimeter data. The excitation temperature gives information on the physical parameters of the gas where the molecule is located. In addition, molecules without a dipole moment such as CO₂, CH₄ and C₂H₂ have strong infrared vibration-rotation transitions, but negligible millimeter rotational emission. Finally, not only gas-phase molecules but also solid-state species can be detected at infrared wavelengths. A vibrational band of a molecule in the solid-phase can be clearly distinguished from that in the gas phase, because the former consists of a single broad spectral feature which lacks the characteristic ro-vibrational structure of the gas-phase spectrum and is slightly shifted in wavelength (see Figure 1).

The ISO-SWS grating spectrometer with a resolving power of $\lambda/\Delta\lambda\approx 2000$ is particularly well suited for observations of solid-state features. Not only information on abundances, but also on the ice environment can be obtained, since the shape and position of the bands are sensitive to the interactions of the molecules with their neighbors (e.g., Sandford et al. 1988, Ehrenfreund et al. 1997). For example, CO surrounded by a polar molecule (H₂O, CH₃OH, ...) has a broader line shape shifted to the red from that of CO embedded in a non-polar matrix (e.g., O₂, N₂). Such shifts have been observed and provide information on the chemical differentation along the line of sight (e.g., Tielens et al. 1991, Chiar et al. 1995).

On the other hand, submillimeter data have the advantage that they are not restricted to absorption toward the infrared source but can map the surroundings. Also, the spectral resolution is much higher $(R \ge 10^6 \text{ compared with } 10^6 \text{ compa$

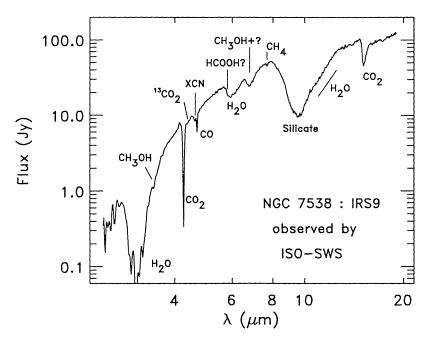


Figure 2. ISO-SWS spectrum toward the massive protostellar object NGC 7538 IRS9, showing numerous solid-state features along the line of sight (Whittet et al. 1996).

 \sim 2000 for ISO) so that the line profiles are resolved and provide information on the location of the molecule (e.g., outflow vs. envelope). Finally, molecules with much lower abundances can be detected with millimeter emission techniques, down to 10^{-11} with respect to hydrogen. For comparison, the ISO data probe abundances down to $\sim 10^{-7}-10^{-8}$ (Helmich 1996). Submillimeter spectral line surveys toward massive young stellar objects in e.g. the Orion (Blake et al. 1987, Schilke et al. 1997) and W 3 (Helmich & van Dishoeck 1997) GMCs have revealed a wide variety of species, ranging from simple diatomics to complex organic molecules. Clear differences in the chemical composition are observed, even between different YSO's within one GMC, which are likely related to their evolutionary state.

3. Interstellar ices

3.1. Solid CO_2 and CH_4

The availability of complete spectral coverage from 2–45 μ m with the ISO–SWS provides a landmark for the study of interstellar ices and allows for the first time an unbiased inventory (Whittet et al. 1996, d'Hendecourt et al. 1996). The spectrum toward the massive protostar NGC 7538 IRS9 is shown in Figure 2. Species such as solid H₂O, CO, CH₃OH, OCS and 'XCN'/OCN⁻ were already known from ground–based observations (see e.g. Whittet 1993, Allamandola et al. 1997 for reviews), but ISO has detected several additional species. A striking result is the presence of strong solid CO₂ absorption in the ν_3 stretching mode at 4.27 μ m and ν_2 bending mode at 15.2 μ m along all lines of sight to embedded young stellar objects (de Graauw et al. 1996, Gerakines et al. 1998). The overall

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 CO_2 abundance in ices is $\sim 15\%$ relative to H_2O , making it one of the most abundant solid-state molecules. This corresponds to an abundance with respect to gas-phase H₂ of $\sim 10^{-5}$.

Analysis of the profile shapes using data obtained in the Leiden Observatory Laboratory by Ehrenfreund et al. (1996, 1997) indicate the presence of grain mantles with distinct polar (H₂O-rich) and non-polar (CO, O₂ or CO₂rich) layers. The CO_2 bending mode at 15 μ m forms a particularly interesting diagnostic, since it shows a typical double-peaked structure in cold regions such as NGC 7538 IRS9. This line profile is characteristic of apolar, nearly-pure CO₂, and indicates the presence of a temperature zone far from the protostar at temperatures less than 45 K. The majority of the CO₂, however, appears to be embedded in H₂O ice. The laboratory data files, together with derived optical constants and extinction efficiency calculations for small grains, are available on the WWW at http://www.strw.leidenuniv.nl/~lab.

¹³CO₂ ice has also been detected in several sources at an abundance consistent with terrestrial and interstellar ¹²C/¹³C values. Its low optical depth facilitates the interpretation and comparison with laboratory data (Boogert et al. 1998).

Boogert et al. (1996, 1997a,b) detected an absorption feature near 7.67 μ m toward two deeply embedded objects (see Figure 3). Comparison with laboratory spectra shows that it can be identified with the ν_4 deformation mode of solid CH₄. Its abundance with respect to H₂O is $\sim 1 \%$ ($\sim 2 \times 10^{-6}$ with respect to H₂), indicating that C-H-bonds are less common than C-O-bonds in the ices. Interestingly, CH₄ appears embedded only in the polar, H₂O-rich ices. The lack of solid CH₄ in the non-polar component argues that methane is likely formed on grains by hydrogenation of accreted C.

Inventory of species and link with comets 3.2.

Using the deeply embedded sources NGC 7538 IRS9 and W 33A as templates, constraints on the abundances of various other species have been obtained. The spectrum toward NGC 7538 IRS9 is remarkably simple, and indicates that H₂O is indeed the dominant ice component, followed by CO₂ and CO. Other species such as CH₄, CH₃OH and 'XCN' are present at levels of a few percent.

The 6.0 and 6.8 μ m bands, previously discovered using the Kuiper Airborne Observatory (Tielens & Allamandola 1987), are among the strongest absorption features. Schutte et al. (1996) performed a detailed spectroscopic analysis of these features by means of comparison to various cryogenic solids produced in the laboratory. The high quality of the SWS spectra clearly demonstrates that the 6.0 μ m feature cannot be exclusively ascribed to H₂O ice, as was previously thought, but that additional components contribute to the red and blue wings. The excess blue absorption can be well reproduced by the C=O stretch vibration of an organic acid, in particular the most simple homologue, formic acid (HCOOH), at an abundance of ~ 3 % of H₂O ice. The red excess appears to reflect the presence of a feature at $\sim 6.2 \mu m$, possibly due to aromatic compounds (Schutte et al. 1997). Several candidates have been reviewed for the 6.8 μ m feature, e.g., CH₃OH, the NH₄⁺ ion and carbonates, but none of these appears to satisfy the observational constraints. Although CH₃OH contributes

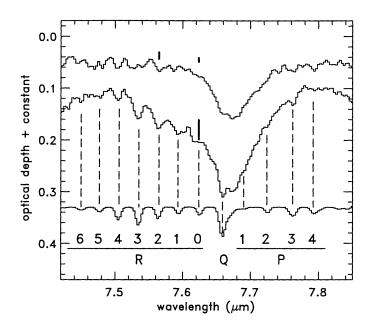


Figure 3. ISO-SWS spectrum toward the massive protostellar objects NGC 7538 IRS9 (top) and W33A (middle), showing the detection of solid CH₄ (broad feature) with gas-phase CH₄ lines superposed. The lower figure is a model gas-phase CH₄ spectrum for $N=10^{17}$ cm⁻² and $T_{\rm ex}=100$ K (Boogert et al. 1997b).

to a fraction of the absorption, the main carrier of this strong feature remains one of the biggest puzzles.

The ISO spectra of W 33A and NGC 7538 IRS9 also show two weak absorption features at 7.24 and 7.40 μm for the first time. Since these fall in the X-H bending region of organic molecules (X = C, O, N), a great number of molecules may be responsible. By comparison to infrared catalogues of room temperature spectra, most possibilities can be excluded. For the remaining species spectra were obtained in the laboratory embedded in astrophysical ice matrix analogs by Schutte et al. (1998). The 7.24 μm band is well matched by formic acid (HCOOH), consistent with the above result from matching the 6.0 μm absorption band. For the 7.40 μm feature two candidates remain, acetaldehyde (CH₃HCO) and the HCOO⁻ ion. This latter species can, as shown in the laboratory, be efficiently produced by activationless acid–base reactions following the production of HCOOH by grain surface reactions. The abundances of these species are 0.5–3% with respect to H₂O, well in excess of theoretical predictions.

The abundances of most detected molecules in ices are similar to those found in comets such as Halley, Hyakutake and Hale-Bopp, supporting the model that comets are largely made of unaltered interstellar dust (Bockelée-Morvan 1997). Does this similarity also extend to more complex species? Ethane has been observed in surprisingly large abundances in the coma of comets (Mumma et al. 1996). Although ethanol has not yet been detected in comets, it is found in high abundances in interstellar hot core regions, probably due to evaporation of grain mantles (e.g., Millar et al. 1994). Theoretical models also suggest that these species may have formed on interstellar grains (Charnley et al. 1995).

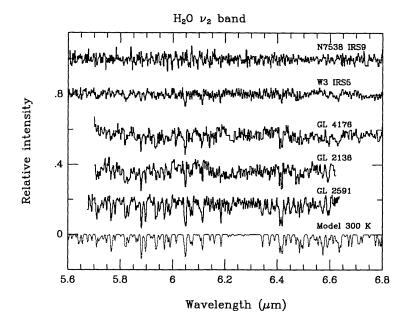


Figure 4. ISO-SWS normalized spectra of five massive protostellar sources, showing absorption by hot, abundant H_2O in at least 3 sources. A model H_2O spectrum for a column density of 2×10^{18} cm⁻², $T_{\rm ex}$ =300 K and Doppler parameter b=5 km s⁻¹ is shown for comparison (van Dishoeck & Helmich 1996, van Dishoeck et al., in preparation).

Boudin et al. (1997) have made a comparison of laboratory data of several molecules with ISO and ground-based spectra, and have put significant upper limits on the abundances of C_2H_6 and CH_3CH_2OH toward NGC 7538 IRS9 of 0.4 and 0.7 % relative to solid H_2O , respectively. This indicates that these species are considerably less abundant than their more simple homologues, CH_4 and CH_3OH , by factors of more than 4 and 5, respectively. The CH_4/C_2H_6 ratio in the ices is at least a factor of two larger than observed in comets, but additional observational data are needed to investigate whether this difference is significant. No strong constraints can be obtained on the abundance of interstellar solid C_2H_2 , which has been detected in comet Hyakutake at an abundance of 0.3–0.9% relative to solid H_2O (Brooke et al. 1996).

4. Gas-phase molecules

4.1. Hot, abundant gas-phase water

In spite of its low spectral resolution, the ISO-SWS is a useful instrument for searches for gas-phase molecules which cannot be readily observed from the ground. Particularly important examples are $\rm H_2O$ and $\rm CO_2$, which are among the dominant oxygen- and carbon-containing molecules. Helmich et al. (1996) and van Dishoeck & Helmich (1996) presented the first detection of infrared absorption lines within the bending vibration of water at 6.3 μ m toward a number of massive young stars which cover a range in physical parameters (Figure 4). Comparison with model spectra indicates high excitation temperatures

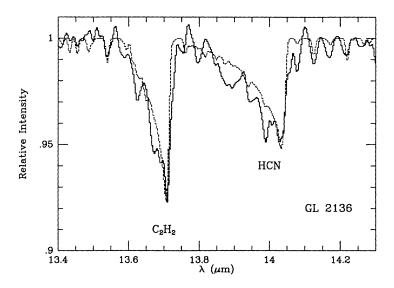


Figure 5. ISO–SWS normalized spectra of GL 2136, showing the detection of C_2H_2 and HCN absorption. The thin dashed line indicates the best fitting single component model spectra for $N(C_2H_2)=2\times10^{16}$ cm⁻², $T_{\rm ex}(C_2H_2)=1000$ K and $N({\rm HCN})=6.5\times10^{16}$ cm⁻², $T_{\rm ex}({\rm HCN})=1500$ K (Lahuis, van Dishoeck & Helmich 1998).

 $(T_{\rm ex} > 200 \text{ K})$ and surprisingly high abundances of $(2-6) \times 10^{-5}$ with respect to H₂, suggesting that a significant fraction (>5%) of the available oxygen is tied up in H₂O.

Observations of abundant gas-phase H₂O in star-forming regions have also been made by observations of the pure rotational lines with the ISO-LWS, e.g. by Liseau et al. (1996), Cernicharo et al. (1997) and Ceccarelli et al. (this conference).

4.2. Gas-phase CO_2 and CH_4

Searches for gas-phase CO_2 have been made in the ν_3 and ν_2 bands at 4.3 and 15 μ m. As Figure 1 shows, the 4.26 μ m band is dominated by the strong solid CO_2 feature and no hint of the ro-vibrational P- and R-branch structure of gas-phase CO_2 is seen. The 15.2 μ m solid CO_2 band is less saturated, and a weak, sharp absorption band due to the Q-branch of gas-phase CO_2 at 14.98 μ m has been detected by ISO (van Dishoeck et al. 1996). The inferred abundance is surprisingly low, at most 2×10^{-7} with respect to H_2 .

Gas-phase CH₄ was identified by Lacy et al. (1991), but the quality of the ground-based data is severely hindered by the Earth's atmosphere. Although the ISO-SWS has lower spectral resolution, careful data reduction of the 7–8 μ m region reveals the presence of gas-phase CH₄ toward several sources (Boogert et al. 1998, Dartois et al. 1998) (see Figure 3). Comparison with simulated spectra indicates that the CH₄ gas is warm, with an excitation temperature of 100 ± 30 K. Its abundance with respect to H₂ is $\sim 10^{-6}$.

4.3. Gas-phase C_2H_2 and HCN

The ISO spectra have also been used to search for the presence of a number of less abundant molecules, including C_2H_2 and HCN. Lines of these species have been detected from the ground by Lacy et al. (1989), Evans et al. (1991) and Carr et al. (1995), but only for a few sources. In contrast with CH_4 , C_2H_2 is thought to be formed primarily in the gas phase, and then passively accreted onto grains.

Lahuis et al. (1998) have found clear detections of the C_2H_2 ν_5 band at 13.7 μm and the HCN ν_2 band at 14.0 μm in the ISO spectra of several sources (see Figure 5). The inferred excitation temperatures are again high, at least a few hundred K up to 1000 K, and typical abundances with respect to H_2 are $\sim 10^{-7}$. For HCN, these abundances are more than an order of magnitude larger than obtained from submillimeter data, providing important constraints on the source structure.

5. Gas/solid state abundance ratios

In Table 1, the gas/solid state ratios derived from the ISO data for the major species CO, CO₂, H₂O and CH₄ are summarized. The temperatures listed in the last column refer to those derived from the CO excitation by Mitchell et al (1990). In all 5 sources, CO is principally in the gas phase, although the gas/solid ratio still increases for the warmer sources (see Figure 1). In contrast, CO₂ is primarily in the solid phase, even in the warmest regions. The gas/solid H₂O ratio varies from less than 5% for NGC 7538 IRS9 and W 33A to more than unity for GL 2591 and GL 4176. The gas/solid CH₄ ratio of 0.5 derived for the cold sources is considerably higher than that of H₂O and CO₂, but lower than that of CO. Since solid C₂H₂ does not have any strong absorption bands, no stringent limit on its gas/solid ratio can be obtained.

Table 1.	Gasz	'solid	state	abund	lance	$ratios^a$

Object	СО	CO_2	H ₂ O	CH ₄	T_{warm} (K)
NGC 7538 IRS9 W33 A GL 2136 GL 2591 GL 4176	15 100 200 >400 >400	0.01 0.01 0.02 0.04 0.04	<0.04 0.02 0.4 ~ 1 ~ 2	0.5 0.5 >1 >1	180 120 580 200–1000 200–1000

^a See van Dishoeck et al. (1996) and Boogert et al. (1997b) for references to data

What do these ratios imply for the source structure and evolution? As the young star evolves, its radiation heats up the surrounding gas and dust, leading to enhanced evaporation of the ices and an increased gas/dust ratio. The sublimation temperatures of pure CO, CO_2 , CH_4 and H_2O —ice under interstellar conditions are 20 K, 45 K, 20 K and 90 K respectively (Sandford & Allamandola 1988). For traces (<5%) of CH_4 and CO_2 embedded in an H_2O —matrix, these temperatures increase to \sim 90 K. The observed trends for the gas/solid H_2O

and CH₄ indicate that some outgassing of the icy mantles likely plays a role. However, part of the observed abundant gas-phase H₂O could also be formed by high-temperature gas-phase chemistry initiated by the O + H₂ reaction. This path starts to become significant at temperatures greater than 200 K (Ceccarelli et al. 1996, Charnley 1997), which could be reached either by shocks associated with the outflow or by radiative heating close to the star. Indeed, the available data on gas-phase H₂O in a dozen sources, combined with the lack of abundant gas-phase CO₂, suggest that in the hottest sources, gas-phase chemistry plays a role as well.

It should be recalled that the observed gas/solid ratios are averaged along the line of sight to the star. In reality, strong gradients in the abundances of these species likely exist, both in the gas and on the grains (e.g. Tielens & Whittet 1997, Ceccarelli et al. 1996, Doty & Neufeld 1997). For example, the presence of apolar CO or CO₂ ices indicates an (outer) region with temperatures less than 20 K and 45 K, respectively. On the other hand, the presence of hot H₂O, CH₄ and C₂H₂ gas suggests an (inner) 'hot core' zone with temperatures of at least a few hundred K. Indeed, the gas-phase H₂O abundance could be as high as a few $\times 10^{-4}$ in this inner region, decreasing to $< 10^{-7}$ in the outer cold part, resulting in an averaged abundance of a few $\times 10^{-5}$ along the line of sight. The data suggest that for the more evolved objects, the outer region has been heated to temperatures of 20-40 K so that the CO ice has disappeared. At the same time, the fraction of gas in the inner 'hot core' region has increased, resulting in more prominent lines of hot gas-phase H₂O, CH₄ and C₂H₂. Release of CH₃OH in this warm region can lead to other, more complex species in the gas. More detailed modeling is required to assess whether this scenario can quantitatively reproduce the observed gas-phase and solid-state abundances from both infrared and submillimeter observations.

In summary, the results illustrate that ISO can provide important new insights into the chemical and physical evolution of star–forming regions, and can put significant constraints on the role of gas–grain interactions.

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