Molecules in Bipolar Outflows

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Abstract. Bipolar outflows constitute some of the best laboratories to study shock chemistry in the interstellar medium. A number of molecular species have their abundance enhanced by several orders of magnitude in the outflow gas, likely as a combined result of dust mantle disruption and high temperature gas chemistry, and therefore become sensitive indicators of the physical changes taking place in the shock. Identifying these species and understanding their chemical behavior is therefore of high interest both to chemical studies and to our understanding of the star-formation process. Here we review some of the recent progress in the study of the molecular composition of bipolar outflows, with emphasis in the tracers most relevant for shock chemistry. As we discuss, there has been rapid progress both in characterizing the molecular composition of certain outflows as well as in modeling the chemical processes likely involved. However, a number of limitations still affect our understanding of outflow chemistry. These include a very limited statistical approach in the observations and a dependence of the models on plane-parallel shocks, which cannot reproduce the observed wing morphology of the lines. We finish our contribution by discussing the chemistry of the so-called extremely high velocity component, which seems different from the rest of the outflow and may originate in the wind from the very vicinity of the protostar.

Keywords. ISM: molecules, ISM: jets and outflows, stars: formation, radio lines: ISM

1. Introduction

Bipolar outflows are one of the most studied phenomena of the star-formation process. They result from the supersonic acceleration of gas in two opposite directions by a newly formed star, and were first identified more than three decades ago with radio observations (Snell, Loren, & Plambeck 1980). Since their discovery, bipolar outflows have been identified around protostars of nearly all masses, from below the brown dwarf limit to the precursors of the ultra-compact HII regions, and in environments as different as isolated globules and cluster-forming regions. This ubiquity of the outflow phenomenon suggest that bipolar outflow formation is a necessary element of the physics of star formation, likely associated to the need for the gas to lose angular momentum in its process of forming a highly compact object (see Arce *et al.* 2007 for a recent review).

Interest on the chemistry of bipolar outflows goes back in time as far as the interest on their physics. Outflow emission originates from ambient gas that has been accelerated by a supersonic wind, and therefore has been shock-processed. As a result, the study of outflow chemistry is unavoidably intertwined to the study of shock chemistry in the interstellar gas. Early questions on this chemistry were raised as soon as high velocity molecular gas was observed, and were related to the survival or shock-production of the CO molecules seen at velocities of tens of km s^{-1} in the wings of outflow spectra (Kwan & Scoville 1976) and the up to a hundred km s^{-1} velocities seen in some water masers

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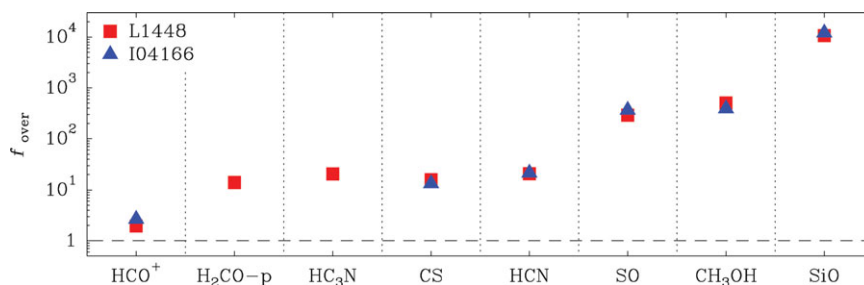
Figure 1. Overabundance factors with respect to dense core values for a number of molecules towards the outflows from L1448-mm and IRAS 04166+2706. Data from Tafalla *et al.* (2010).

(Morris 1976). Prompted by these observations, the first (and still relevant) models of molecule formation in shocks soon appeared (Hollenbach & McKee 1979).

With time, additional chemical processes have been identified in the gas accelerated by outflows. Current interest includes the enhancement in the abundance of high-density gas tracers like SiO and CH_3OH, which is seen toward a number of outflow sources powered both by high and low-mass young stellar objects (Bachiller 1996). These abundance enhancements are believed to result from the erosion of dust grains via sputtering and grain-grain collisions, perhaps combined with a number of gas-phase chemical reactions favored by the temperature increase caused by the shock (see van Dishoeck & Blake 1998 for a review).

The amount of the abundance enhancement depends on the species under consideration, and typically ranges from factors of a few for species like HCO^+ to several orders of magnitude for species like CH_3OH and SiO (Fig. 1). Not all outflows show the same degree of molecular richness, however, and this apparent selectivity of outflow chemistry has lead to the creation of special category of outflows, the so-called "chemically active" outflows (Bachiller *et al.* 2001).

2. Chemically active outflows

Although easily distinguishable when observed in species like CH_3OH and SiO, the chemically active outflows do not stand apart from the rest when observed in CO (the standard outflow tracer), either by their line strength, velocity extent, or spatial collimation. It is well established that the chemically active phase corresponds to an early period in the outflow development, as the driving sources of this family of outflows tend to be Class 0 sources. The exact physical cause of the chemical richness is however unclear. One possibility is that the youngest outflows must encounter denser envelopes along their paths, and therefore must naturally give rise to stronger shocks. Another possibility is that early chemical activity is associated with the higher energy known to characterize the earliest outflow phases (Bontemps *et al.* 1996). In either way, the lack of chemical richness in the more evolved outflows indicates that chemical activity is highly transient, and that any signature of its presence must disappear quickly in the protostellar life (near the transition between Class 0 and Class I, Tafalla *et al.* 2000). Rapid depletion of the enhanced species via freeze out onto cold dust grains is the most likely cause of this effect (Bergin *et al.* 1998).

Among the group of chemically active outflows, the one in the L1157 dark cloud stands out for the strength of its lines in species like SiO and CH_3OH. As a result, it has been
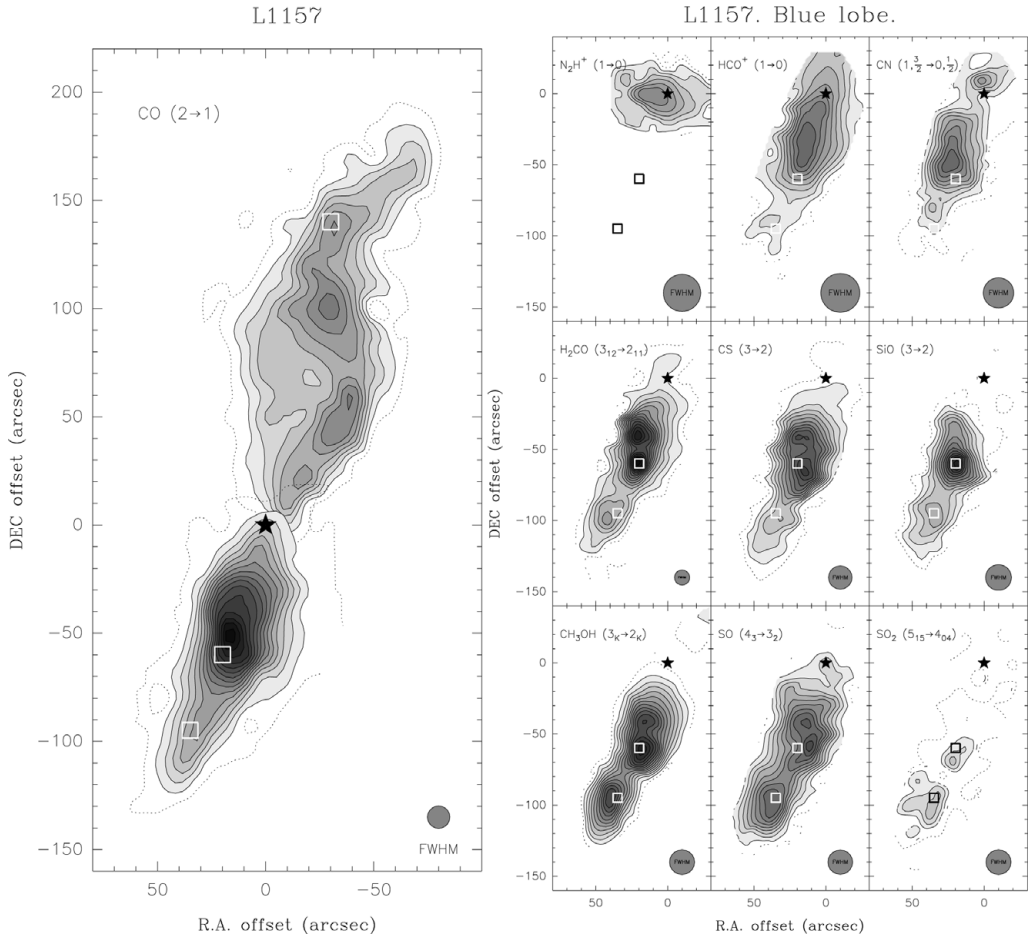
Figure 2. Left: map of CO(2-1) emission from the L1157 outflow. **Right:** maps of integrated intensity for different molecular species towards the blue (southern) lobe of the L1157 outflow. Note the different extension and peak position of each species. Figures from Bachiller *et al.* (2001).

the subject of a very intense observing campaign, including the study using the Herschel Space Observatory presented by Lefloch (2011, this volume). The L1157 outflow was first identified by Umemoto *et al.* (1992) due to its strong CO lines. Its chemical activity was recognized very early on (Mikami *et al.* 1992), and has been characterized in great detail by Bachiller & Pérez-Gutiérrez (1997) and Bachiller *et al.* (2001). The chemical activity of L1157 is specially prominent towards several regions often denoted as B1 and B2 (for blue lobe) and R (for red lobe), and are most likely associated with regions where the ambient cloud is being strongly shocked by the outflow wind. Interferometric observations of these regions reveal a complex pattern of spatial distributions that indicate a very fragmented small-scale structure (Benedettini *et al.* 2007). As illustration of this chemical richness, we show in Fig. 2 (right panel) a series of maps of the southern lobe of the L1157 outflow in a number of molecules that are selectively enhanced in different parts of the outflow (especially B1 and B2).

3. Recent progress trancing outflow gas with molecules

It is not possible to review here with detail the rapid progress made in the study of molecules in outflows during the last few years. In this section we present a selection of studies that have been carried out since the last IAU Astrochemistry meeting in 2005. We concentrate on low-mass outflow studies and in molecules that seem specially relevant to our understanding of shock chemistry.

3.1. H_2O

Probably the most significant progress since the Asilomar meeting concerns the study of the H_2O molecule, thanks to the coming on line of a series of satellite observatories: the Submillimeter Wave Astronomy Observatory (SWAS), Odin, the Spitzer Space Telescope, and the Herschel Space Observatory.

Since the early discovery of its maser emission in outflows, water has been considered a sensitive outflow tracer. The maser emission is so bright that it can be easily detected across the galaxy, and the abundance of water required to produce the emission must have been significantly enhanced by shocks (Elitzur & de Jong 1978, Kaufman & Neufeld 1996, Cernicharo *et al.* 1996). The thermal emission of water, on the other hand, has taken longer to become a recognized tracer of outflow activity, especially in low-mass outflows. Early observations with the Infrared Space Observatory (ISO) revealed thermal water emission from a number of bipolar outflows (Liseau *et al.* 1996, Nisini *et al.* 1999, Giannini *et al.* 2001). These ISO spectra, however, did not resolve spectrally even the broadest outflow profiles, a fact that was later overcome by the SWAS and Odin telescopes, which observed the $H_2O(1_{10}-1_{01})$ transition with a resolution better than 1 km s^{-1}. These instruments, however, had a limited angular resolution, approximately 4 arcminutes for SWAS and half that size for Odin, that only allowed to study global averages of the water emission over the whole outflow, or at least over each of their lobes. Compilations of this work have been presented by Franklin *et al.* (2008) (SWAS) and Bjerkeli *et al.* (2009) (Odin).

In the past two years, the Herschel Space Observatory (HSO) has started to provide water data with spatial resolution comparable to that of the large radio telescopes from the ground and, thanks to its Heterodyne Instrument for the Far Infrared (HIFI), also with velocity resolutions below 1 km s^{-1}. Two HSO Guaranteed Time Key Programmes have a strong component of low-mass outflow studies, the Chemical Herschel Surveys of Star Forming Regions (CHESS) and Water in Star-forming regions with Herschel (WISH, see van Dishoeck *et al.* 2011), while Herschel/HIFI Observations of EXtraOrdinary Sources (HEXOS) covers Orion. As a number of contributions in this volume by members of these teams detail the first results of these programs, here we will only present a brief description of the new exciting outflow science that the HSO is providing, and we refer the reader to the contributions by Bertrand Lefloch (CHESS), Lars Kristensen (WISH), and Nathan Crockett (HEXOS) for further details.

It is safe to say that we are still exploring the tip of the iceberg in our research of water emission from outflows. Much work still needs to be done to understand the excitation conditions of the H_2O emitting gas, and this understanding is critical to extract the full potential of the water data. Preliminary work on water excitation in outflows is presented in this meeting by the poster contributions of Vasta *et al.* and Santangelo *et al.*, which summarize the first results of a multi-transition analysis of water towards the very young outflows in L1157 and L1448. A more limited treatment in terms of water lines, but more extensive in terms of outflow sources, comes from the so-called "water outflow survey" carried out also as part of the WISH project, and illustrated in Fig. 3. This outflow survey
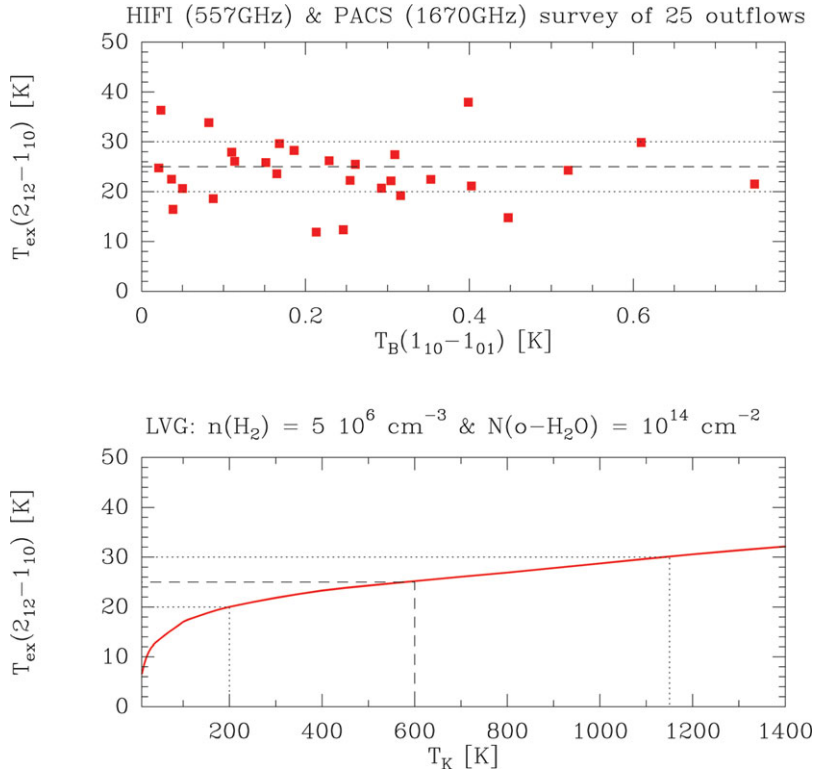
Figure 3. Top: excitation temperature between the first two excited levels of o-H_2O as a function of peak intensity in the 557 GHz H_2O line, as measured in a sample of 25 outflows within the WISH program. Note the constant value at a level of about 25 K (optically thin conditions have been assumed). **Bottom:** LVG radiative transfer results for representative physical conditions of the emitting gas ($n(H_2) = 5 \ 10^6$ cm^{-3} and $N(o\text{-}H_2O) = 10^{14}$ cm^{-2}). As can be seen, the excitation temperatures derived in the top panel require gas kinetic temperatures in the range 200-1100 K. From Tafalla *et al.* (2011), in preparation.

has explored about 25 different objects by observing in each of them two positions using two ortho-water lines, the 1_{10}–1_{01} at 557 GHz with HIFI and the 2_{12}–1_{01} at 1670 GHz with PACS. As seen in Fig. 3, the data from this survey shows a clear trend for the ratio of these two lines (when convolved to the same angular resolution) to be approximately constant independent on the intensity of the 557 GHz line. This ratio, assuming optically thin conditions (tested with an LVG code), is proportional to the excitation temperature between the first two excited levels of ortho-water ($T_{ex}(2_{12} - 1_{10})$), and as Fig. 3 (top panel) shows is approximately constant over the whole sample at a level of approximately 25 ± 5 K. Such a low level of scatter suggests that the bulk of the water emission we observe in outflows (at least from the lowest energy levels) arises from a rather narrow range of physical conditions.

Although a $T_{ex}(2_{12} - 1_{10})$ value of around 25 K may seem a relatively low temperature, it is important to remember that the large Einstein A coefficients of water make this molecule hard to become excited collisionally. To estimate the kinetic temperature of the gas responsible for this T_{ex} of 25 K, we need to estimate the balance between collisional excitation and radiative de-excitation (both spontaneous and induced). We have done this using the large velocity gradient (LVG) approximation together with the recently

calculated collision rates by Faure *et al.* (2007) (as provided by the LAMDA data base, Schöier *et al.* 2005), and assuming values for the gas volume density and H_2O column densities in line with those found by multi-transition analysis like those in the posters by Vasta *et al.* and Santangelo *et al.* As shown in Fig. 3 (bottom panel), $T_{ex}(2_{12} - 1_{10})$ values of around 25 K require relatively high gas temperatures, in the vicinity of 500 K. This result adds to existing evidence that the gas responsible for the observed water emission from outflows corresponds to a component warmer than that typically observed with low-J CO transitions.

3.2. H_2

H_2 emission from outflows has been observed widely since its discovery in Orion, and reveals the presence of gas heated to temperatures up to a few thousand Kelvin (Gautier *et al.* 1976). Most of the H_2 work has so far concentrated on the v=1–0 S(1) line at 2.12 μm, which is easily observable from the ground. A testimony of the widespread nature of this emission in outflows is its use to define the recently created category of Molecular Hydrogen emission-line Objects (MHOs), which are analogous to the optically-based Herbig-Haro objects but include more deeply embedded line-emitting regions thanks to its use of NIR wavelengths (Davis *et al.* 2010). At the time of writing this article, the MHO on-line catalog (`http://www.jach.hawaii.edu/UKIRT/MHCat/`) is growing steadily and contains more than 1200 entries.

Although some of the pure rotational transitions of H_2 are also observable from the ground (e.g., Burton *et al.* 1989), sampling the full H_2 spectrum, and therefore characterizing the population of its energy levels, requires the use of space-based telescopes. ISO observations in the late 1990's carried out the first complete observations of the H_2 spectrum in Orion, and revealed a distribution of excitation temperatures that ranged from about 600 K in the lowest levels to more than 3000 K in the highest levels (Rosenthal *et al.* 2000).

More recently, the Infrared Spectrograph (IRS) on board of the Spitzer Space Telescope has covered the 5-33 μm wavelength range, and therefore has provided access to the lowest pure rotational lines of H_2. The high sensitivity of this instrument has allowed the systematic mapping of rotational emission from low mass outflows. Neufeld *et al.* (2006), for example, observed the S(0)-S(7) transitions towards the HH 7-11 and HH 54 outflows, and found that the ortho-to-para ratio is spatially variable, and presents values significantly below the expected equilibrium value of 3 for the observed gas temperature (which ranges between 400 and 1200 K). Such non-equilibrium ortho-to-para ratios can be understood as being a remnant of the gas pre-shock conditions, where the gas temperature was significantly lower (~ 50 K).

A more systematic study of the H_2 emission from low mass outflows using Spitzer observations comes from the series of papers by Neufeld *et al.* (2009) and Nisini *et al.* (2010), and the poster by Giannini *et al.* in this meeting, which concentrate on the outflows from L1157, L1448, BHR71, NGC 2071, and VLA 1623. Despite their differences in evolutionary stage and central source luminosity, all these outflows present a number of similar trends. One of them is the need for a multiplicity of temperatures to explain the H_2 emission, and which these authors fit with a distribution of mass with temperature that follows a power law T^{-b} with b in the range 2.3-3.3. In addition, the ortho-to-para ratio in all objects with the exception of L1448 is below the equilibrium value of 3, and suggest the presence of an activation energy in the para-to-ortho conversion. Similar results were obtained by Maret *et al.* (2009) in their study of the outflows in the NGC 1333 region.

3.3. *Complex Molecules*

There has also been substantial progress in the study of "complex molecules" in outflows over the last few years. These organic species are usually defined as containing 6 or more atoms, and are found in a number of different environments that range from the Orion hot core to the cold core of TMC-1 (see Herbst & van Dishoeck 2009 for a recent review).

In outflows, the most widely observed complex molecule is methanol (CH_3OH), whose abundance is often enhanced by several orders of magnitude, most likely due to its release from dust grain mantles (see Fig. 1). A recent result concerning methanol comes from the study of its high energy transitions by Codella *et al.* (2010), who used the Herschel Space Telescope to observe L1157-B1 as part of the CHESS project. These authors found that the excitation of the high-J lines (up to J=13) is characterized by a rotation temperature of 106 K, which is almost one order of magnitude higher than the rotation temperature of 12 K derived from the low-J lines (Bachiller *et al.* 1995). Given the excitation conditions of CH_3OH, a rotational temperature of more than 100 K implies a gas kinetic temperature of at least 200 K, and such a warm component represents a link between the low-excitation gas seen in most molecular tracers and the hotter gas traced by H_2 emission. (See also Nisini *et al.* 2007 for a similar result obtained from SiO observations.)

Molecules larger than CH_3OH have also been recently identified in L1157-B1. Arce *et al.* (2008) carried out deep integrations with the IRAM 30m telescope towards this position and detected for the first time in an outflow $HCOOCH_3$ (methyl formate), CH_3CN (methyl cyanide), $HCOOH$ (formic acid), and C_2H_5OH (ethanol). The detection of these molecules shows that outflow shocks can lead to a very rich chemistry, that in low-mass sources was previously restricted to the hot corino regions in the vicinity of some protostars like IRAS 16293-2422 (Cazaux *et al.* 2003).

Additional detection of complex molecules in the L1157-B1 region comes from a 3mm spectral line survey being carried out with the Nobeyama 45m telescope, and whose first results have been presented by Sugimura *et al.* (2011). This survey has already produced new detections of complex molecules in this chemically active outflow: CH_3CHO (acetaldehyde) and the mono-deuterated variety of methanol CH_2DOH. From the first analysis of the line survey, Sugimura *et al.* (2011) find that the relative abundance of the complex molecules with respect to methanol is significantly lower in L1157 than in the prototype hot corino IRAS 16293-2422. These authors suggest that such a difference reveals a difference in the chemical processing of the dust in the cloud regions sampled by the outflow shock compared to the vicinity of the protostar sampled in the hot corino phase. Detection of more complex molecules is possible given the on-going nature of the survey.

Another recent detection towards the L1157-B1 position is that of HNCO (isocyanic acid) by Rodríguez-Fernández *et al.* (2010). Although not a complex molecule, HNCO is a well-known organic tracer of warm environments, like hot cores, the Galactic center, and even extragalactic sources, and the good correlation of its distribution with that of methanol in IC 342 had led to the suggestion that this species is shock-sensitive (Meier & Turner 2005). The detection of HNCO in L1157-B1 by Rodríguez-Fernández *et al.* (2010) not only reinforces this suggestion, but illustrates the important role of relatively simple regions like L1157-B1, which is far enough from the YSO to be considered a "pure shock" region (without stellar heating), and therefore provides a clean template to recognize shock chemistry in more complex environments.
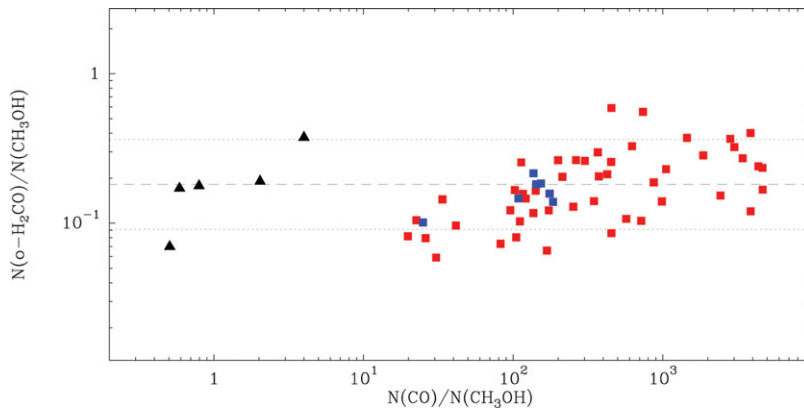
Figure 4. Abundance ratio between H_2CO and CH_3OH in the outflow gas phase (squares) and in the ices of dust grains (triangles). The red squares represent values for a sample of low-mass outflows from Santiago-García *et al.* (in preparation), and the blue squares are values towards high-mass star forming regions from Bisschop *et al.* 2007. The black triangles are ice values from Gibb *et al.* (2004). The good match between gas-phase and solid-phase values reinforces the idea that the abundance enhancement of H_2CO and CH_3OH in outflows results from the release of these molecules from the mantles.

4. Do we understand outflow chemistry?

A meeting like this one is an appropriate occasion to look critically at the state of our understanding of outflow chemistry in a more global way than usually done in research papers. A look of the literature reveals a generalized consensus in the belief that shock chemistry can explain most (or all) abundance anomalies observed in the outflow gas (apart from the EHV component discussed in the following section). This consensus, however, seems based more on the lack of observational counter-examples and alternative models than in the existence of a quantitative proof that a single shock chemistry model can explain simultaneously the set of abundances observed in an object like L1157-B1.

This incomplete state of affairs mostly results from a too-focused approach in outflow-chemistry work. From the observational point of view, and this paper testifies it, most of this work has been dedicated to a single object, the L1157 outflow, and more exactly, to the B1 position of this outflow. Although L1157 is sometimes called "prototypical" in terms of outflow chemistry, the lack of objects with comparable chemical richness and complexity suggest that L1157 is probably extreme, if not for its abundances, at least for the column densities responsible for its very bright lines.

Clearly, more general studies of outflow chemistry are needed, not only to understand how typical L1157 is, but to reconstruct the full cycle of outflow chemical activity represented by other very young outflows. An important limitation for any statistical approach is the lack of good samples. This is partly the result of the small number of outflows that so far have been explored in molecular lines other than CO, but also because of the need for full maps to identify chemical hot spots in the flows. Despite the limitations, some work has been done in this direction. Fig. 4 shows an example of how an statistical approach can further illuminate the origin of the observed abundances. This plot represents the CH_3OH/H_2CO ratio for the sample of low-mass outflows studied by Santiago-García *et al.* (in preparation), and shows that this gas-phase ratio remains approximately constant over a relatively large range of individual abundances.

The (gas-phase) ratio, in addition, matches closely the solid-phase ratio derived from ice mantles in a different sample of objects, and this good match supports strongly the interpretation that the CH_3OH and H_2CO abundance enhancements in outflows result from the release of these species from the mantles of grains due to sputtering in a shock.

While observations tend to concentrate on one object at a time, chemical models tend to solve one species at a time, and this makes it difficult to asses whether a single set of physical conditions can explain the variety of observations, even for a single object like L1157. A more important limitation of the chemical models is their reliance on plane-parallel shock models. In a plane parallel shock, there is a single velocity for the shock, and all the material suffers the same type of acceleration. As a result, the predicted emerging spectrum is characterized by a single spike at the velocity of the shock and a rapidly declining tail of pre-shocked material towards low velocities (e.g., Figs. 8 in both Gusdorf *et al.* 2008 and Flower & Pineau Des Forêts 2010). This shape of the spectrum is the opposite to what it is observed in a typical outflow wing, which has most of the material moving at low velocities and a minority of the gas moving at top speeds (see next section for a discussion of the different nature of the spiky extremely high velocity regime). As the optical depth of the emission is proportional to the amount of material per unit velocity, the compression of shocked gas into a small range of velocities predicted by the plane parallel model leads to a substantial overestimate of the optical depth. By comparing in the figures mentioned above the width of the spikes with the full velocity extent of the spectrum, we estimate that the optical depth overestimate resulting from the artificial limited range of velocities in the emission must range from factors of a few to more than order of magnitude. Thus, comparing observations with the predictions from chemical models must be done with care when the model predicts a non-negligible of optical depth in the emission.

The systematic reliance on plane-parallel models in the analysis of outflows is more a reflection of our poor understanding of the internal kinematics in the outflow gas than a conviction in the model providing the correct geometry. In fact, the observation of a wing feature in the emission spectrum of almost every outflow indicates that a multiple-velocity description is needed, and that most of the gas in the outflow moves at intrinsically low velocities. How to incorporate this description to chemical models is not yet clear, although a first step may be to parametrize the mix of velocities with a power-law description like that used in the multi-temperature analysis of the H_2 data by Neufeld *et al.* (2006) and described above. Using such a more realistic description of the outflow velocity field will clearly bring a better agreement between the predicted and observed spectra. More interestingly, a multiple-velocity description of the shocked gas will allow exploring the changes in the gas composition as a function of the velocity that a number of observations are starting to uncover (Codella *et al.* 2010, Tafalla *et al.* 2010).

## 5. The EHV gas, a different chemical component?

So far we have referred to the "outflow emission" as the one appearing in the spectra forming a wing where the intensity decreases steadily with velocity. Although such type of wing emission is the most characteristic signature of outflow gas, a few very young Class 0 objects show in their spectra an additional outflow component that looks like a close-to-gaussian secondary peak. This component, often referred to as the extremely
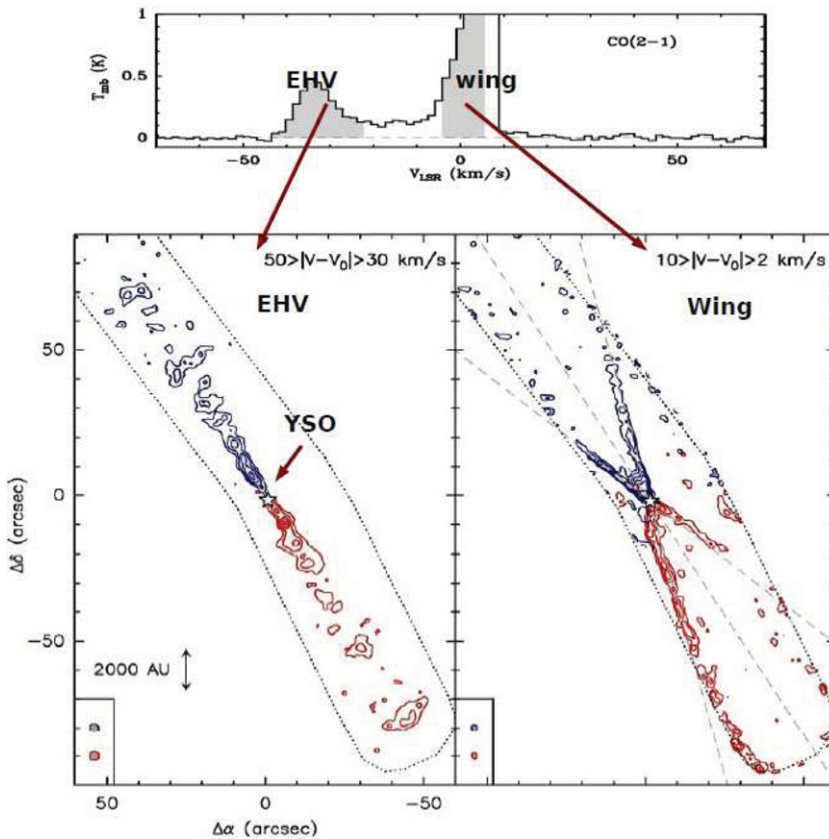
Figure 5. Average blue lobe spectrum and velocity-integrated maps of the CO(2-1) emission from the IRAS 04166+2706 outflow illustrating the different spatial distribution and spectral signature of the wing and the EHV components. Data from Santiago-García *et al.* (2009).

high velocity (EHV) gas given its high speed (tens of km s^{-1}), was first discovered in the outflow powered by L1448-mm (Bachiller *et al.* 1990), and by now it has been observed in a (reduced) number of outflows.

One of the outflows where an EHV component has been recently identified is the one powered by IRAS 04166+2706 (IRAS 04166 hereafter, see Tafalla *et al.* 2004). In Fig. 5 we present the CO(2-1) emission from this outflow as observed by Santiago-García *et al.* (2009) using the Plateau de Bure Interferometer. The figure shows that the EHV emission appears distinct from the wing emission both in spectral signature and spatial distribution. As can be seen, the (lower-velocity) wing component forms in the maps an X-shaped structure centered on the IRAS source and suggestive of tracing the walls of a pair of evacuated cavities (a fact confirmed by the association of the northern blue cavity with an IR cometary nebula). The EHV emission, on the other hand, appears in the maps as a jet-like feature that runs along the middle of the cavities and consists of a collection of discrete peaks. As shown by Santiago-García *et al.* (2009), the peaks of EHV emission are located so symmetrically from the IRAS source that each has a counterpart on the other side less than 2″ away from its expected position. Such a level of symmetry
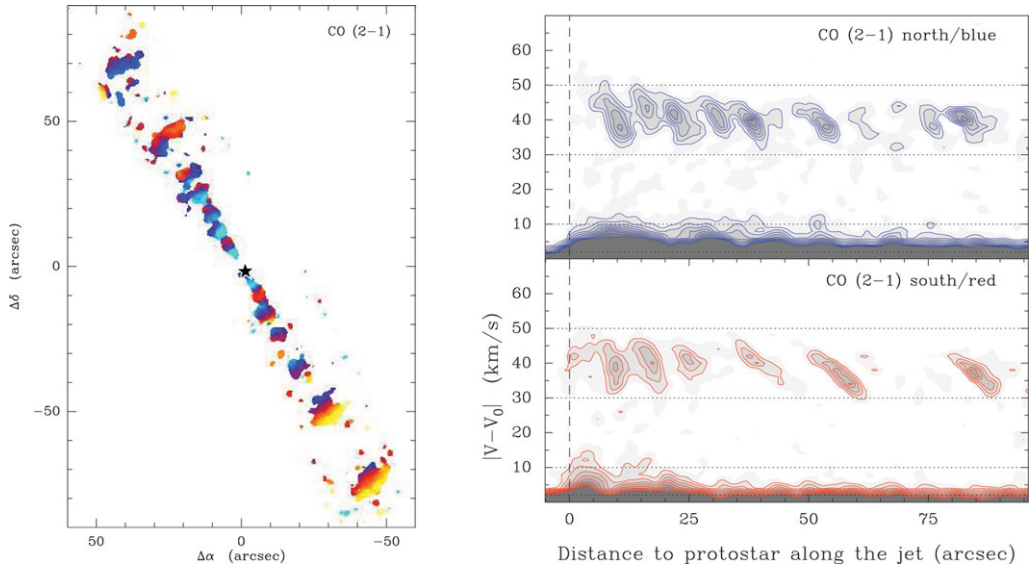
Figure 6. Left: First momentum plot of the CO(2-1) EHV emission towards the outflow from IRAS 04166+2706 illustrating the presence of velocity oscillations. **Right:** Position-velocity diagrams of CO(2-1) along the outflow axis. Note the sawtooth pattern in the EHV regime. From Santiago-García *et al.* (2009).

suggests that the EHV peaks arise from events that took place near the central source and that have since propagated outwards with the flow.

A clue to the origin of the EHV peaks comes from a pattern of oscillations in their velocity field. As illustrated in Fig. 6, the oscillations form a sawtooth pattern in the position-velocity diagram indicative of a combination of a close-to-constant mean velocity together with strong velocity gradients inside each EHV peak. The sense of these gradients is the same in all EHV peaks, and indicates that the upstream gas moves faster than the downstream gas. This sawtooth velocity pattern in the PV diagram is in striking agreement with the predictions for a set of internal shocks in a jet modeled by Stone & Norman (1993) to simulate the pattern of knots seen in optical jets (see their Figure 16). Thus, the combination of a symmetric and fragmented structure together with a sawtooth velocity pattern suggests that the EHV emission in IRAS 04166 arises not from ambient accelerated gas (like the rest of the outflow), but from the internal shocks in a pulsating jet.

If the EHV gas represents jet material, it must be coming from the protostar or its nearmost vicinity, and we can therefore expect its chemical composition to differ substantially from that of the wing gas, which consists of ambient gas that has been shock-accelerated, and therefore has had a very different thermal history. To test this possible difference between these two components of the outflow, Tafalla *et al.* (2010) have carried out the first molecular survey of EHV gas by making deep integrations towards two outflow positions known to have bright EHV and wing components, one in the L1448 outflow and the other in the IRAS 04166 outflow. Previous to this survey, only CO and SiO had been detected in the EHV gas of any outflow, despite the large number of species detected in the wing component of outflows like that of L1157 (see above). Thanks to the new deep integrations, carried out with the IRAM 30m telescope, and some of them lasting several hours, the number of species observed in the EHV gas has more than doubled, with clear
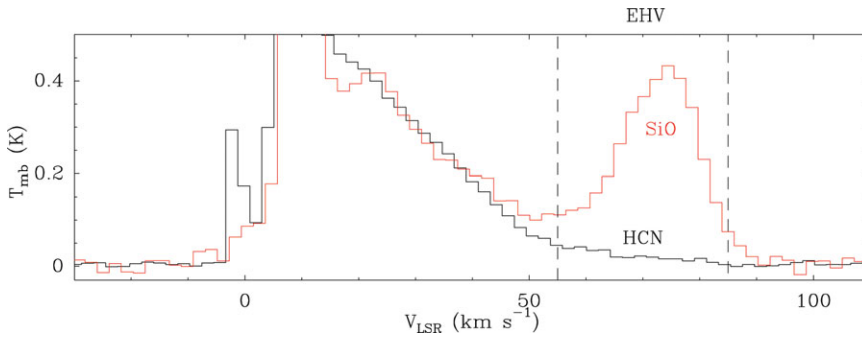
Figure 7. Comparison between SiO(2-1) and HCN(1-0) spectra towards the red lobe of the L1448-mm outflow. The SiO line has been scaled to match the HCN intensity in the wing, in order to better illustrate the sudden drop of HCN/SiO abundance in the EHV component. From Tafalla *et al.* (2010).

detections of SO, CH$_3$OH, and H$_2$CO. Possible detections of HCO$^+$ and CS have also resulted from these deep integrations, although their status remains unclear because of possible contamination with emission from the wing outflow component, which extends at a low level up to velocities comparable to those of the EHV gas. (See also Kristensen *et al.* 2011 for the recent detection of H$_2$O in the EHV gas of L1448.)

Probably the most interesting result from the EHV molecular survey of Tafalla *et al.* (2010) is the evidence for a change in the carbon-to-oxygen ratio between the wing and the EHV components. This is illustrated in Fig. 7 with a superposition of the SiO(2–0) and HCN(1-0) spectra towards the target position in the L1448 outflow (the IRAS 04166 target position presents a similar behavior but weaker lines). As can be seen, when scaled appropriately, the SiO(2-1) and HCN(1-0) spectra track each other in the (red) wing regime over several tens of km s^{-1}, suggesting that the HCN/SiO abundance ratio remains constant over this range of velocities. In contrast with this smooth behavior in the wing regime, the intensity ratio between HCN and SiO drops by more than one order of magnitude in the EHV regime. This intensity drop is unlikely to result from a difference in excitation between the two velocity regimes, as multi-transition analysis of SiO, SO, and CH$_3$OH show only small changes in the excitation temperature of these molecules between the wing and EHV gas. The most likely cause of the sudden drop in the HCN intensity towards the EHV regime is a similar, order-of-magnitude drop in the abundance of this species towards this outflow component. A similar drop in the abundance of CS is also seen in the data, suggesting that the HCN drop is not a peculiarity of this molecule but a common feature of C-bearing species. Indeed, all molecules with clear detection in the EHV component have so far been O-bearing (CO, SiO, SO, CH$_3$OH, H$_2$CO, and H$_2$O).

The finding of chemical differences between the EHV and wing outflow components in both L1448 and IRAS 04166 opens a new tool to explore the still mysterious mechanism of outflow acceleration. If the EHV gas truly arises from a jet, it must have originated in the innermost vicinity of the central object, and therefore must carry information about the physical conditions in the outflow acceleration region, which is of a few AU or even a few stellar radii, depending on the model, and therefore inaccessible to current instrumentation. To fully exploit the potential of this information, however, a new generation of chemical models is needed. The chemistry of protostellar winds was originally studied by Glassgold *et al.* (1991), but little progress has been done on this issue in the twenty

years past since this pioneering work. It is reassuring to see that there is a renewed interest in the topic, as illustrated by the poster contribution in this meeting of Yvart *et al.* Clearly more modeling and observational progress is needed in this new and exciting line of study of molecules in outflows. Let's hope we can all see its results in the next IAU Astrochemistry Symposium a few years from now.

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Discussion

STERNBERG: Could you comment on whether it might be possible to study angular momentum loss using these molecular diagnostics?

TAFALLA: Rotation in molecular jets has been searched for, and there are a few possible detections in the literature. Our observations on the jet from IRAS 04166, however, suggest that the kinematics of the gas in the jet is dominated by lateral ejection in the internal shocks, and I suspect that this faster motion is going to overwhelm any rotation signature that may be present.

ELLINGER: You have shown similar abundances of HCN in three different objects. Do you observe the same thing for HNC?

TAFALLA: Bachiller & Pérez Gutiérrez (1997) estimated an HNC/HCN ratio of 0.1 towards L1157-B1. In the fast wing of L1448, the non detection of HNC in Tafalla *et al.* (2010) sets an upper limit that is about one order of magnitude lower.

MENTEN: What do we know about deuterium enhancement in the outflow gas, for example for methanol?

TAFALLA: Sugimura *et al.* (2011) have recently presented the first detection of mono deuterated methanol towards L1157-B1, and derive an CH_2DOH/CH_3OH abundance ratio in the range 0.013-0.029, which is significantly lower than that derived for IRAS 16293 but similar to the one measured in Orion KL.

VISSER: You showed that the HCN/SiO abundance ratio is much lower in the EHV component than it is in the wing, and you interpreted this as a lower elemental C/O

ratio in the EHV gas. Could the low HCN/SiO ratio also indicate a low elemental N/O ratio?

TAFALLA: It could be. Still, we find a similar drop in the CS/SiO ratio between the wing and the EHV gas, although we have lower signal-to-noise in the CS data. This seems to point more to a deficit of carbon than of nitrogen, although we are dealing here with a very limited set of observations.