

## FINDING FRIENDS AND MOLECULES IN UNEXPECTED PLACES

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**Abstract.** This discussion moves from Princeton, where the author and Pierre Encrenaz first became acquainted at a time (the late 1960's) when molecular clouds were unknown and the Copernicus satellite was being readied to study H<sub>2</sub> in diffuse clouds, to present-day Paris where at Pierre's 60th birthday science party it was discussed how IRAM's Plateau de Bure Interferometer came to discover – almost inadvertently – an unexpectedly complex polyatomic chemistry in these same (well, almost the same) diffuse clouds.

### 1 My earliest memories of Pierre Encrenaz

I first met Pierre in 1968 or so while a beginning graduate student at Princeton University. Pierre arrived there on some sort of fellowship, married, ready to do research, and seemingly much further down life's path, although we are pretty much the same age.

Princeton was a bastion of astrophysical theory, led by Lyman Spitzer and Martin Schwarzschild (with Jeremiah Ostriker as the young faculty member) but in fact there were a variety of connections with observation and experiment. The basement of Peyton Hall housed spectroscopy labs in which I and other students worked to provide basic data (f-values and the like) needed to interpret the much-anticipated results of Princeton's upcoming OAO-3 – eventually *Copernicus* – satellite observatory, which

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would study molecular hydrogen in diffuse clouds. At that time the idea of fully molecular clouds was just on or over the intellectual horizon. However, there were some hints of radio astronomy, courtesy of Bell Labs at Crawford Hill which was something more than an hour away by car. Arno Penzias gave an informal radio astronomy course but there was no connection with the cosmic microwave background studies conducted just up the street by Bob Dicke and Dave Wilkinson in Princeton's physics department.

Anyway, Pierre and Arno connected very productively and several years later, while I was doing my thesis at Bell Labs for Arno, Pierre was along on some of the observing runs at Texas's 5m telescope at McDonald Observatory. I keenly remember the excitement we all felt when searching for CO emission from NGC604 on Pierre's initiative (at that point, Bell Labs had a complete monopoly on  $\lambda 2.6\text{mm}$  CO). We might even have been detecting it, but the small bandwidths of even the broadest available filter banks worked against ever knowing that.

One day during an observing run, a bunch of us were in Ft. Davis (the nearest village) standing in front of the beer cooler in the general store, wondering which brew to bring back to McDonald. While we were deliberating, the proprietor wandered over to see what we needed and Pierre replied in the thickest imaginable French accent that we were wondering what kind of bierrre to buy. The store owner then asked where we were from, some astronomer piped up with "we're from back East", which caused the proprietor, genuinely curious, to ask "Oh, are you guys from Austin?"

This story was the source of amusement for years afterward at Bell Labs as we tried to imagine the provincial store owner's world-view extending no further East than the 400 miles to Austin, where there might be a source of people who spoke English like Pierre. However, the truth was quite other. The owner well knew the famous French astronomer Gerard de Vaucouleurs, who was, of course, 'from Austin' at that time, and he simply assumed that Pierre and de Vaucouleurs were professionally connected in some way.

Eventually I left the wilds of West Texas long enough to write a thesis and get married myself, and in fact it was at my wedding in 1973 that I last saw Pierre for what was to be quite some years, certainly not in Paris until 1999 during the meeting "H<sub>2</sub> in Space" at the IAP. Which brings us much closer to the present, and even past some relevant science.

## 2 The problem of $\text{HCO}^+$ in diffuse clouds

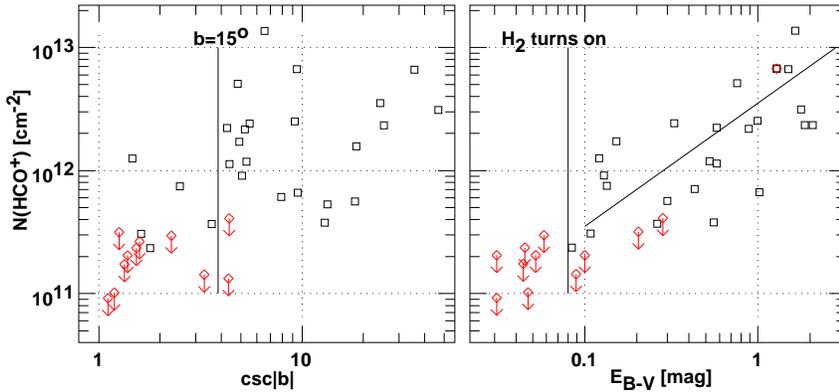


Fig. 1. Total  $\text{HCO}^+$  column density vs  $\text{csc}(|b|)$  and  $E_{B-V}$ .

The Plateau de Bure Interferometer has proved to be an extraordinarily powerful tool for uncovering an otherwise entirely hidden chemistry in diffuse clouds, but this was never the intention in 1992 when Robert Lucas and I began to collaborate after encountering each other at the 1991 astrochemistry meeting (IAU 150) in Brazil<sup>1</sup>. Rather, we started by asking for time to observe  $^{13}\text{CO}$  absorption toward BL Lac and a few other compact extragalactic sources in whose direction  $^{12}\text{CO}$  emission was known.

Shortly before, Al Marscher and Tom Bania (Marscher et al., 1991) had used the OVRO interferometer to detect  $^{12}\text{CO}$  absorption against BL Lac, a radio source having several Jy flux at mm-wavelengths. At  $b = -10.4^\circ$ , this source was far from the galactic plane where surveys of CO emission would typically study CO, and the reddening adjacent to it was known to be only  $E_{B-V} = 0.3$  mag. However, the absorption was quite optically thick (see Fig. 2 here) which reinforced the preconceived idea that CO emission as strong as that seen toward BL Lac (3–4 K) would have originated in something more like dense than diffuse gas.

<sup>1</sup>Robert and I have been partners in the original work described here and we are now working with Jerome Pety on these problems.

Both Robert and I had modelled the excitation of CO back in the 1970's and we understood the usefulness of comparing emission and absorption data (indeed, imagine our understanding of H I with only emission data in hand). However, it is a very good thing that we were serendipitously diverted from this  $^{13}\text{CO}$  project, both because we could not have understood the  $^{12}\text{CO}/^{13}\text{CO}$  ratios which we later found, and because we lucked into something better.

During the observing Robert came to know that  $\text{HCO}^+$  absorption had accidentally been detected against BL Lac when that source had served as the phase calibrator for an unrelated project. The next time BL Lac flared up, we asked for a grant of discretionary time to try to explore the mm-wave spectrum in a few common molecules ( $\text{C}_2\text{H}$ ,  $\text{HCN}$ ,  $\text{HCO}^+$ ). And of course they were all found and we very quickly realized that the possibilities of mm-wave absorption studies were much much richer than we had imagined. What is more, we had an ideal sort of screen-saver project, observing against strong phase calibrators well below 115 GHz, which could accrue time in poor observing conditions which were unsuitable for more demanding mapping observations.

The first large-scale project we undertook was a nearly flux-limited sample of  $\text{HCO}^+$  absorption spectra (such samples are harder to define when the sources are variable, perhaps even violently variable). From searches toward calibrators in CO (Liszt & Wilson, 1993; Liszt, 1994), it was understood that molecular emission was far more common at galactic latitudes  $|b| < 15^\circ$ , and rarely present further from the plane. The manifestation of this geometry in  $\text{HCO}^+$  is shown in Fig. 1 at left which plots the  $j=1-0$  line absorption profile integrals of all the lines of sight in the most recent version of our  $\text{HCO}^+$  sample (Lucas & Liszt, 1996);  $N(\text{HCO}^+) = 1.03 \times 10^{12} \text{ cm}^{-2} \int \tau_{1-0} dv$  in the limit of no excitation above the cosmic background for an assumed dipole moment of 4.07 Debye, taking the integral in units of  $\text{km s}^{-1}$ .

That the excitation is so weak follows from the weakness of  $\text{HCO}^+$  emission *ibid*, if it fills a  $1'$  telescope beam. Of course the medium could be patchy, but it cannot be too full of *lacunae* if point sources are generally occulted, often fully in  $\text{HCO}^+$  and CO since nearly all the flux is absorbed. Anyway, at left in Fig. 1 it can be seen that the  $\text{HCO}^+$  column density increases abruptly below  $|b| = 15^\circ$  but increases little at yet smaller  $|b|$ . The explanation lies in the local geometry of the ISM: because of the local bubble of hot X-ray emitting gas, the nearby neutral gas layer has been excavated and we are sitting in something which resembles the bed of a

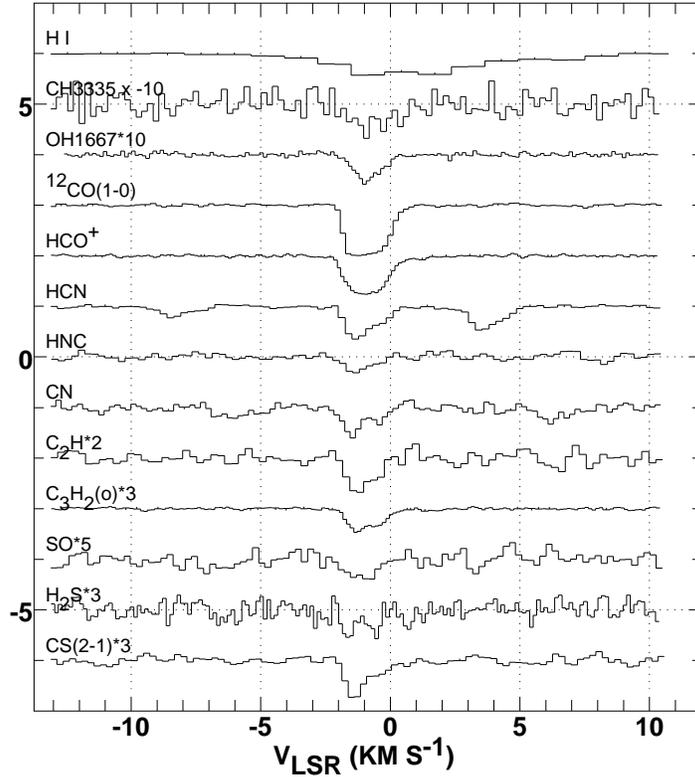
wide crater; to look out cleanly, one must look up. Or conversely, to have one's view occulted by absorbing material it is required to look more nearly horizontally.

At right in Fig. 1, the same integrals are reordered according to the reddening derived from the work of Schlegel et al. (1998), exposing some of the physics and chemistry of the local ISM. We see that  $\text{HCO}^+$  absorption becomes detectable rather abruptly at  $E_{B-V} > 0.08$  mag, which is the famous turn-on of high  $\text{H}_2$ -fractions in the diffuse ISM according to the *Copernicus* results (Savage et al., 1977). At yet higher reddening,  $N(\text{HCO}^+)$  increases about *linearly* with  $E_{B-V}$ , so that  $N(\text{HCO}^+)$  always has about the same proportion relative to  $N(\text{H})$ , or, if  $N(\text{H}_2)/N(\text{H})$  is not too variable, relative to  $N(\text{H}_2)$ . Sources of scatter at right in Fig. 1 include variations in the ratios of  $\text{H}_2/\text{H}$  and  $\text{HCO}^+/\text{H}_2$  in individual clouds, patchiness in the cloudy ISM, and differing proportions of various phases at the same reddening.

In fact, the  $\text{HCO}^+$  abundance ratio  $X(\text{HCO}^+) = N(\text{HCO}^+)/N(\text{H}_2)$  implied by Fig. 1 is very large, nearly as high as in TMC-1. To see this, note the gas-reddening ratio, whereby  $E_{B-V} = 1$  mag corresponds to a column density  $N(\text{H}) = 5.8 \times 10^{21} \text{ cm}^{-2}$  (Savage et al., 1977), so that the slope in Fig. 1 at right,  $N(\text{HCO}^+)/E_{B-V} \approx 3 \times 10^{12} \text{ mag}^{-1}$ , implies  $N(\text{HCO}^+)/N(\text{H}) = 5 \times 10^{-10}$ . Then, if the typical fraction of H-nuclei in  $\text{H}_2$  is 0.2 in the diffuse ISM, as in the *Copernicus* observations, it follows that  $X(\text{HCO}^+) = N(\text{HCO}^+)/N(\text{H}_2) = 5 \times 10^{-9}$ : the usual value quoted for TMC-1 is  $X(\text{HCO}^+) = 10^{-8}$  (Ohishi et al., 1992). In fact in our work Robert and I typically use smaller values,  $X(\text{HCO}^+) = 2 - 3 \times 10^{-9}$ , but these also are far too large to be easily understood.

In diffuse gas, the dominant form of gas-phase carbon is  $\text{C}^+$  and conventional quiescent gas phase chemistry forms CO by first producing  $\text{CO}^+$  via  $\text{C}^+ + \text{OH} \rightarrow \text{CO}^+ + \text{H}$ , after which CO forms either if  $\text{CO}^+ + \text{H} \rightarrow \text{CO} + \text{H}$ , or if  $\text{CO}^+ + \text{H}_2 \rightarrow \text{HCO}^+ + \text{H}$ ,  $\text{HCO}^+ + e \rightarrow \text{CO} + \text{H}$ . All the ion-molecule reactions are relatively fast and dissociative recombination of  $\text{CO}^+$  is unimportant even with the high e/H fractions expected for diffuse gas. So CO is the dominant product of the  $\text{C}^+$ -OH interaction no matter the  $\text{H}_2$ -fraction, but if the region is substantially molecular most  $\text{CO}^+$  will proceed to  $\text{HCO}^+$ . Then, because  $n(e) \approx n(\text{C}^+)$  it follows that the  $\text{OH}/\text{HCO}^+$  ratio will be about constant, largely independent of the density,  $\text{H}_2$ -fraction, *usw* and somewhat dependent on temperature owing to the functional dependence of the  $\text{HCO}^+$  recombination rate coefficient.

In fact, we found such a very tight linear OH- $\text{HCO}^+$  relationship (Liszt



**Fig. 2.** Absorption spectra toward BL Lac at cm- and mm-wavelengths. The H I spectrum was provided by John Dickey and Bob Garwood; the CH spectrum has been inverted, and various of the profiles have been scaled.

& Lucas, 1996, 2000), but with an entirely wrong proportion. With values  $X(\text{OH})/X(\text{HCO}^+) \approx 1000$  expected for typical diffuse cloud conditions, it follows that  $X(\text{HCO}^+) = 10^{-10}$  if  $X(\text{OH}) = 10^{-7}$  as observed along a few sightlines (Felenbok & Roueff, 1996; Liszt & Lucas, 2002), so there is a discrepancy of a factor of 30-50 in the predicted abundance of  $\text{HCO}^+$ . Making OH is generally not a problem for quiescent diffuse cloud models, especially if the cosmic ray ionization rate is as high as needed to understand

HD and  $\text{H}_3^+$  (Liszt, 2003)) but quiescent models of CO formation based on this chemistry fail by similar factors.

Such discrepancies between observation and theory are quite substantial, if not as extreme as for  $\text{CH}^+$ . Because the column densities of  $\text{C}^+$ , OH, and CO are all observable in optical/*uv* absorption toward stars (if not the lines of sight used at the PdBI), there is little wiggle room and the profound failure of this scheme to explain either  $X(\text{HCO}^+)$  or  $X(\text{CO})$  seems pretty damning. So why, then, did we find the constant OH/ $\text{HCO}^+$  ratio it predicted?

### 3 From $\text{HCO}^+$ to CO and other species

If an abundance  $X(\text{HCO}^+) = 2-3 \times 10^{-9}$  can be maintained, direct radiative recombination of  $\text{HCO}^+$  with thermal electrons suffices to account for the observed amounts of CO in diffuse clouds over the entire range  $N(\text{CO}) = 10^{12} - 3 \times 10^{16} \text{ cm}^{-2}$ , when the formation of  $\text{H}_2$  and CO is calculated self-consistently including their self and mutual shielding (see Liszt & Lucas (2000)). A similar case may be made for the origin of CS in the quiescent recombination of the observed, unexpectedly large amount of  $\text{HCS}^+$  (Liszt & Lucas, 2002), at least in one direction, but in general, the chemistry is simply not understandable in the context of a quiescent, optically transparent gas of modest density, such as one expects for diffuse clouds.

The extent of the problem is illustrated in Fig. 2, showing a variety of absorption spectra toward BL Lac; note that the CH spectrum is inverted and that it and others have been scaled to varying degrees (an unscaled profile extending down one unit would be fully opaque; note the  $^{12}\text{CO}$  line). This line of sight does not pass within  $5^\circ$  of other gas having even  $A_V=2$  mag, yet there is a fully-developed sulfur chemistry (Lucas & Liszt, 2002), to say nothing of HCN, HNC, CN (Liszt & Lucas, 2001), the hydrocarbons  $\text{C}_2\text{H}$  and  $\text{C}_3\text{H}_2$  (Cox et al., 1988; Lucas & Liszt, 2000) or  $\text{H}_2\text{CO}$  and  $\text{NH}_3$  (Nash, 1990; Liszt & Lucas, 1995; Moore & Marscher, 1995).

Note that the line profiles in Fig. 2 are fairly narrow, but with considerable structure; of two adjacent H I components with comparable opacity, one is strongly molecular and the other not at all; within the molecular lines, two components are present in most species. Overall we have looked in vain for systematic indications of shocked gas and for differences between the widths of lines from different molecules (see however our discussion of

CN – whose linewidths in optical spectra are smaller than those of CH – and HCN (Liszt & Lucas, 2001)).

Our surveys of such species have shown some marked systematics; OH and  $\text{HCO}^+$  appear in fixed proportion with respect to each other and most likely with respect to  $\text{H}_2$  even at small  $N(\text{H}_2)$ , and these species, along with CO and the hydrocarbons are rather more commonly detected than either the nitrogen or sulfur compounds (or  $\text{H}_2\text{CO}$  or  $\text{NH}_3$ ). In general there are chemical families within which species vary in fixed proportion with respect to each other: examples are OH and  $\text{HCO}^+$ ; HCN, HNC and CN;  $\text{C}_2\text{H}$  and  $\text{C}_3\text{H}_2$ . Between families, the variation is continuous but often very sharp.

Despite the high  $^{12}\text{CO}$  optical depth seen toward BL Lac and in other directions, the  $^{12}\text{CO}$  column densities (Liszt & Lucas, 1998) represent at most only a few percent of the amount of carbon expected in the gas phase at even  $A_V = 1$  mag. Consistent with the idea of a diffuse gas in which carbon is mostly in  $\text{C}^+$ , stronger CO lines show strong  $^{13}\text{CO}$  fractionation ( $N(^{12}\text{CO})/N(^{13}\text{CO}) \approx 15$ ), suggesting a cool diffuse medium. This is one of the reasons alluded to earlier why we were so lucky to be diverted from our original intention to study CO absorption in isolation. The difficulties of interpretation introduced by this fractionation may be seen in the discussion of Kobulnicky et al. (1995).

#### 4 What is going on with diffuse clouds?

Surveys of molecular hydrogen yield mean kinetic temperatures of about 80 K for molecule-bearing gas (Savage et al., 1977), implying rather low densities  $n(\text{H}) = 30 - 40 \text{ cm}^{-3}$  for typical thermal pressures  $p/k = 2 - 3 \times 10^3 \text{ cm}^{-3}\text{-K}$  (Jenkins & Tripp, 2001). Remarkably, quiescent models of such cool diffuse gas will actually reproduce the abundances of some of the most important species, even under such rather modest conditions;  $\text{H}_2$ , HD, and even  $\text{H}_3^+$ , OH and CH may be cited. But why OH and not  $\text{HCO}^+$  (and, therefore, CO) if  $N(\text{OH})$  and  $N(\text{HCO}^+)$  are as tightly coupled as observations show? What comfort may be taken in explaining CH and not NH,  $\text{CH}^+$  or  $\text{C}_2\text{H}$ ? Where do  $\text{H}_2\text{CO}$ ,  $\text{NH}_3$  and sulfur compounds arise in diffuse gas?

In wrapping up the recent astrochemistry meeting at Asilomar, Alex Dalgarno summarized my talk on diffuse cloud chemistry by saying “maybe the chemistry is OK and its just the dynamics that are wrong.” Maybe. But at Pierre’s party Édith Falgarone gave an idea of what is really required

to study the implications of the chemistry at deeper levels. There is much to be learned, and so much work yet to be done.

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