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Invited review

# $HCO^+$ IN DARK MOLECULAR CLOUDS

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**SUMMARY: Formyl ion is one of the most important molecules, and primary molecular ion to be found in molecular clouds. This paper reviews chemical pathways of formation and destruction of the molecule, as well as its use as a tool in the study of dark molecular clouds.**

**Key words. ISM: molecules**

## 1. INTRODUCTION

As of August 2007, in the interstellar medium (ISM), including circumstellar shells and comets, there is a total of 141 molecules detected[1], not counting the rare isotopomer species which would bring the count up to 230[2]. Beyond our galaxy, 35 different extragalactic molecules are observed. This number is certain to grow with increased sensitivity and opening of new windows for observations. The size of the detected interstellar Galactic molecules range from diatomic, molecular Hydrogen $H_2$ being by far the most abundant, to 13–atom, Cyanodecapentayne $HC_{11}N$, and include electrically neutral species as well as ions. Interstellar clouds are predominantly neutral, ionised fractions being in the range of $10^{-4}$ for clouds translucent to UV starlight to $10^{-9}-10^{-10}$ for dark clouds where the main source of ionisation is penetrating cosmic rays (Black 1998).

Molecules are found in a variety of environments, with very different, and in some cases extreme physical conditions e.g., in the presence of energetic radiation, high temperatures and superthermal components of molecular velocity distribution, in the diffuse ISM, in dark and giant molecular clouds, PDRs, in circumstellar shells of the evolved stars and in comets and planetary atmospheres, with some molecules having strong preferences for certain environments. The abundance of a molecular spacies always depends on the balance between the formation and destruction reactions.

In astrophysical environments lacking dust, molecules can only be formed through gas – phase chemistry, primarily involving radiative processes:

[1.] the radiative association of two neutral species, or a neutral and an ion: $X + Y \rightarrow XY + h\nu$ and
[2.] the negative-ion sequence of radiative attachment $X + e^- \rightarrow X^- + h\nu$ followed by associative detachment $X^- + Y \rightarrow XY + e^-$ (e.g. Stancil and Dalgarno 1998).

In dark clouds where the gas–to–dust ratio is of the order of $\sim$ 100, an additional process contributes to increasing molecular abundance, namely, grain surface formation reactions. For the formation of molecules at low densities and temperatures typical of molecular clouds, the radiative association is the most important reaction (Gerlich and Horning 1992).

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[1] see `http://www.ph1.uni-koeln.de/vorhersagen/`

[2] see `http://www.astrochemistry.net/`

Molecules can be destroyed in photodissociation process, dissociative recombination, collisional dissociation, charge transfer reactions, ion–molecule and neutral—neutral reactions.

The early chemical models of molecular clouds and accretion disks, using mainly ion chemistry were already quite successful (e.g. Herbst and Klemperer 1973, Black and Dalgarno 1973). This success can be attributed mostly to an absence of energy barriers for ion – molecule reactions (Gerlich 1993, Smith 1993). However, recent experiments (Brownsword et al. 1997), Chastaing et al. 1998, 2001) have again raised the question how slow, and thus how important, are the neutral – neutral reactions at low temperatures typical for dark clouds.

Detection of Formyl ion, $HCO^+$ ($\mu = 3.3\,\mathrm{D}$, formation heat $825.6\,\mathrm{kJ\,mol^{-1}}$, Buhl and Snyder 1970, Klemperer 1970), in the interstellar medium has validated theoretical chemical models which incorporated ion – molecule reactions as the dominant synthetic scheme for the ISM molecules. $HCO^+$ is thenceforth thought to be one of the key molecules in the ISM chemical network. It is observed everywhere: in stellar envelopes of very old stars, with typical abundance relative to $H_2$ of $6 \times 10^{-7}$ according to Tafoya et al. (2007), and very young stars where typical abundance relative to $H_2$ is from $5.5 \times 10^{-12}$ to $1 \times 10^{-10}$ (Thi et al. 2004), in giant molecular clouds and massive star – forming regions (e.g. Apponi and Ziurys 1997 give values of $X(\mathrm{HCO^+}) \sim 1 \times 10^{-9}$), photodissociation– and photon– dominated regions (Fuente et al. 2003 derived fractional abundances in the range of $2 - 5 \times 10^{-9}$), molecular outflows (Russell et al. 1987, Gibb and Little 2000), the dense cores of dark molecular clouds (e.g. Nikolić et al. 2003: $X(\mathrm{HCO^+}) \sim 3 - 5 \times 10^{-9}$), diffuse interstellar medium (e.g. Liszt and Lucas 2000, $X(\mathrm{HCO^+}) \sim 1 - 2 \times 10^{-9}$), comets (Womack et al. 1997), as well as external galaxies (even for $z = 3.911$, García-Burillo et al. 2006).

In this paper we present a short analysis of the most important production and destruction routes for $HCO^+$ and review current observational success and problems in dark molecular clouds of our Galaxy.

## 2. GAS – PHASE CHEMICAL NETWORK

The UMIST[3] database (Le Teuff et al. 1999) states that the Formyl ion in the interstellar medium can be formed through ion – neutral charge exchange reactions, photoprocesses, cosmic ray – induced photoreactions, collider reactions and sundries (not classified reactions) - in total 117 different reactions. Both in number and speed, the ion – neutral reactions are dominant. Total of 131 reactions that remove the Formyl ion from the ISM involve ion – neutral and charge exchange reactions, reactions of dissociative recombination and radiative associations, collider reactions and sundries. Again, ion – neutral reactions are dominant.

In dark clouds, the reactive species $H_3^+$ provides important entries into the ion – neutral chemistry. In fact, the mayor production of the Formyl ion is due to

$$\mathrm{H_3^+ + CO \rightarrow HCO^+ + H_2}\,, \qquad (1)$$

which has the reaction rate of $k = 1.7 \times 10^{-9}\,\mathrm{s^{-1}}$ (see, e.g. Jorgensen et al. 2004, Savage and Ziurys 2004). The CO can increase the abundance of Formyl ion also through reaction with the protonated dihydrogen, $H_2D^+$ (e.g. Plume et al. 1998).

For $H_3^+$ the main formation route is through cosmic ray ionisation of molecular hydrogen:

$$\mathrm{H_2} + \nu_{\mathrm{cr}} \rightarrow \mathrm{H_2^+} + e^-$$

$$\mathrm{H_2^+ + H_2 \rightarrow H_3^+ + H.}$$

According to the analysis of Jorgensen et al. (2004), the main removal mechanism for $H_3^+$ is the very same reaction which contributes mostly to the Formyl ion formation, but only when the CO abundance is close to the "standard" value of $10^{-4}$. When CO is depleted, which is often the case in cold and dense cores in preprotostellar stage (e.g. Caselli et al. 1998), $H_3^+$ is removed through reaction with $N_2$.

The $HCO^+$ is lost through dissociative recombination

$$\mathrm{HCO^+} + e^- \rightarrow \mathrm{CO + H}\,, \qquad (2)$$

which has reaction rate of $k = 1.1 \times 10^{-7}\,\mathrm{s^{-1}}$; reaction with water

$$\mathrm{HCO^+ + H_2O \rightarrow H_3O^+ + CO}\,, \qquad (3)$$

and charge transfer with low ionisation potential elements

$$\mathrm{HCO^+ + Na, Mg \rightarrow Na^+, Mg^+ + CO + H}\,. \qquad (4)$$

It should be noted that in all reactions listed in the UMIST database, some rate coefficients are results of theoretical calculations which often include significant approximations, and some are experimental results. Further importance bear physical conditions of the experiments, densities involved and temperature ranges observed. Only few reactions have been studied experimentally with the lower temperature limit that corresponds to ISM gas kinetic temperatures of ∼ 10 K. Most measured reaction rates vary from ∼ 100 K, sometimes even from a room temperature i.e., ∼ 300 K and up to 1000–3000 K. However, in chemical models of molecular clouds (e.g. Langer and Graedel 1989, Millar et al. 1999), the fact that dynamical effects of evolution such as, for example, cloud collapse, internal sources and shocks are not taken into account has potentially much greater influence on the results, than uncertainty of the colisional coefficients.

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[3] `http://www.udfa.net/`

## 3. DUST CONSIDERED

Chemical models that include dust have two different approaches: the "accretion–limited" regime and the "reaction–limited" regimes (Van Dishoeck and Blake 1998). In the first approach, the time for a mobile species to travel over the surface is much shorter than the accretion time of the other reactant. Therefore, reactions are limited by the accretion rate of new species. In the second case, a species is trapped *in situ* and can react only with a migrating molecule that visits. How molecules return into the gas phase is the next critical step. If no desorption was included, then for typical dark cloud with $n_{\mathrm{H}_2} \approx 10^4\,\mathrm{cm}^{-3}$, most molecules would disappear from the gas phase in less then $10^6$ years. This is inconsistent with observations. Therefore there must be some efficient desorption mechanisms, e.g., thermal evaporation by cosmic–ray spot heating, or explosive heating due to exothermic reactions between radicals which can be triggered by cosmic rays or by grain-grain collisions at velocities greater than $0.1\,\mathrm{km\,s}^{-1}$ (Van Dishoeck and Blake 1998).

Although experiments on the grain–surface chemical reactions have improved with time, the results are not straightforward to interpret and use for calculation of the reaction rates in interstellar clouds (Herbst et al., 2005). One of the important items that remains to be included in detailed gas–grain chemical models is the effect of the grain size distribution and surface inhomogeneities. This may be specially important in dark clouds, where there is now an ample evidence of a grain growth of the dust particles in the dense and cold cores (e.g. Vrba et al. 1993, Strafella et al. 2001, Kandori et al. 2003).

The role of the dust in molecular clouds is mainly to shield and protect molecules from short–wavelength stellar radiation i.e., photodissociation and photoionisation. Only for CO the self–shielding is more important. In addition, some chemical reactions that can occur on the dust surface might have different outcomes than the corresponding gas–phase reactions. It may not be the case for HCO$^+$ though, based on the studies of Aikawa et al. (1999) by the classical trajectory approach. They have studied grain surface recombination of HCO$^+$ in high density environment of $n_{\mathrm{H}_2} \leq 10^8\,\mathrm{cm}^{-3}$ and concluded that the process is mostly dissociative, as in the gas–phase dissociative recombination with free electrons.

## 4. THE DEGREE OF IONISATION IN DARK CLOUDS

The fractional electron abundance, i.e., the degree of ionisation, $x(e) = n(e)/n(\mathrm{H}_2)$, is an important physical parameter in chemistry of molecular gas, controlling formation of the molecular ions such as HCO$^+$, N$_2$H$^+$, their abundance in the gas, and is thought to be the fundamental parameter regulating the rate of star formation through the process of ambipolar diffusion (Shu et al. 1987). McKee (1989) shows that for a uniform homogeneous layer beyond visual extinctions, $A_V \geq 4$, the ionisation balance is dictated by cosmic rays alone. Photo–ionisation by the ambient interstellar radiation field dominates the ionisation in molecular clouds for low extinction. Within the cores significant role in the value of fractional electron abundance plays metal depletion (e.g. Caselli et al. 1998, Bergin et al. 1998).

The best hope for determining the electron abundance is on the basis of measured column densities of molecules sensitive to the electron density. In case of Formyl ion two methods are frequently used: The first of them follow the idea of Watson (1976), who introduced use of the HCO$^+$/DCO$^+$ abundance ratio as a measure of the $\mathrm{H}_3^+/\mathrm{H}_2\mathrm{D}^+$ ratio where the production and destruction rates of H$_2$D$^+$ are balanced by the dissociative recombination and reactions with neutrals such as CO, O, C, N and N$_2$ (Dalgarno and Lepp 1984). The second method (Wooten et al. 1979) involves the fractional abundance of HCO$^+$ and CO together with the ionisation rate of $\mathrm{H}_2(\zeta)$. In a simple steady state model, the DCO$^+$/HCO$^+$($\equiv R_D$) and CO/HCO$^+$/($\equiv R_H$) abundance ratios are given by (see, e.g. Wooten et al. 1979):

$$R_D = \frac{1}{3}\frac{k_f\,x(\mathrm{HD})}{k_e\,x(e)\,+\delta} \tag{5}$$

$$R_H = \frac{[\zeta/n(\mathrm{H}_2)]\,k_{H_3^+}}{[\beta\,x(e)+\delta]\,\beta'\,x(e)}\,, \tag{6}$$

where $k$ is the forward rate coefficient for the exchange reaction $\mathrm{H}_3^+ + HD \leftarrow \mathrm{H}_2\mathrm{D}^+ + \mathrm{H}_2$, $k_e$ is the dissociative recombination rate of H$_2$D$^+$, $\beta$ and $\beta'$ are, respectively, dissociative recombination rate coefficients of $\mathrm{H}_3^+$ and HCO$^+$, $k_{H_3^+}$ is the rate coefficient for reaction (1), $x(\mathrm{HD})$ is the fractional abundance of HD relative to H$_2$, $\delta$ is the total destruction rate of the protonated dihydrogen ions due to reactions with neutral species, and $\zeta$ is the cosmic–ray ionisation rate. From these equations it is possible to estimate directly the ionisation fraction and the cosmic–ray ionisation rate (see, e.g. Caselli et al. 1998):

$$x(e) = \frac{2.7\times10^{-8}}{R_D} - \frac{1.2\times10^{-6}}{f_D}\,, \tag{7}$$

$$\zeta = [7.5\times10^{-4}\,x(e) + \frac{4.6\times10^{-10}}{f_D}]\,x(e)\,n(\mathrm{H}_2)\,R_H\,, \tag{8}$$

where $f_D$ is the depletion factor of carbon and oxygen atoms, i.e., only a fraction $1/f_D$ of the C and O remain in the gas phase.

In the past, no results of any chemical modelling were taken into account in derivation of the $x(e)$. Caselli et al. (1998) were first to fit observations of $R_H$ and $R_D$ for a large sample of nearby dark cloud cores (Butner et al. 1995) with the pseudo time-dependent models of Lee et al. (1996), varying the density, the cosmic ray ionisation rate, the refractory metal abundances and the C and O depletion.

They showed that the range of fractional ionisation extends from $10^{-6} - 10^{-8}$, with inferred cosmic–ray ionisation rates in the range of $10^{-16} - 10^{-18}$ s$^{-1}$. The results were strongly dependent on the depletion of elemental carbon and oxygen from their cosmic abundances, especially for cores with a low degree of ionisation. Williams et al. (1998) used observations of $C^{18}O$, $H^{13}CO^+$, and $DCO^+$ toward 23 low-mass cores, coupled with a steady state chemical model discussed in Bergin et al. (1995), to constrain the fractional ionisation (electron abundance). The derived ionisation fractions lie within the range $10^{-7.5} \leq x(e) \leq 10^{-6.5}$. Chemically, best fit for majority of the clouds in the sample is achieved for densities of $n_{\mathrm{H}_2} = (1-3) \times 10^4\,\mathrm{cm}^{-3}$, moderate C and O abundance variations, and a cosmic–ray ionisation rate of $\zeta = 5x10^{-17}\,\mathrm{s}^{-1}$. Following the same method, the fractional electron abundance in dark clouds is derived for B68 $x(e) = 5 \times 10^{-9}$ (Maret and Bergin 2007), which is about an order of magnitude lower than that observed and modelled in the L1544 core (Caselli et al. 2002).

Lintott and Rawlings (2006) showed that this approach gives reasonably accurate measure in static quiescent molecular clouds. However, in rapidly evolving (collapsing) clouds significant discrepancies occur. In reality, clouds are clumpy and dynamically evolving sub-structures. Even the ambient UV radiation may play larger role than assumed. Bethell et al. (2007) found that despite the self–shielding of clumps, pristine (i.e., unreddened) radiation penetrates deeply both the clouds volume and its mass, resulting in a brighter and bluer intracloud radiation field compared to that in an equivalent uniform cloud. Typically, the difference in photoionisation rate between the clumpy and uniform clouds significantly increases at even modest extinctions $A_V \sim 2$ and in the clumpy model extends $2-3$ times deeper than in the uniform case, dominating cosmic–ray ionisation throughout almost the entire volume. On the other hand, if supersonic turbulence within a cloud is considered, the effective visual extinction (3D) is found to be always much lower than the extinction derived from a fixed line of sight (Padoan et al. 2004). The consequence is that photoionisation can in some cases be as important as cosmic–ray ionisation.

## 5. RADIATIVE TRANSFER

In many cases profiles of observed lines of the IS molecules are not Gaussian in shape, but contain dips. This is frequently the case with $HCO^+$ (Fig. 1). The observed line profiles are thought to be due to a cloud collapse (e.g. Mardones et al. 1997), or nonuniform rotation of the cloud (e.g. Troitsky et al. 2004). In the case of an optically thick medium, the central dip may be explained as a line self–absorption (e.g. Baudry et al. 1981). In optically thin lines this dip is explained by freezing out of molecules onto dust grains at high densities and low temperatures of the clouds cores (Bergin and Tafalla 2007).

When deriving column densities and fractional abundances of Formyl ion, this must be a problem to consider. Two approaches are pursued: observation of rare isotopomers lines, frequently optically thin, or solving the radiative transfer equations. The first approach has a drawback which comes from, for a particular point, unknown column density/fractional abundance ratios of e.g., $[HCO^+]/[H^{13}CO^+]$, $[HCO^+]/[HC^{18}O^+]$ or $[HCO^+]/[DCO^+]$, or even more uncertain isomer ratio $[HCO^+]/[HOC^+]$. In conversion, "a canonic"

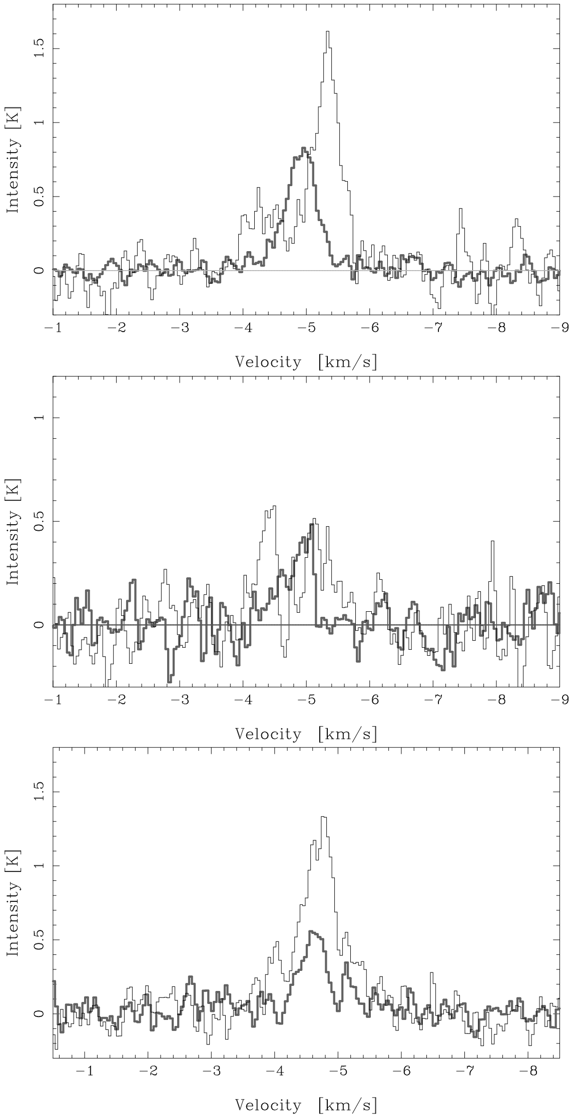

**Fig. 1.** *The* $HCO^+$ *(thin black line) and* $H^{13}CO^+$ *(thick grey line) spectra of the dark cloud L 1219 centre part and outskirt, top and middle panel, respectively (Nikolić et al. in prep.) and in L 1251 T1 (lower panel, Nikolić et al. 2003).*

ratio - the Milky Way averaged isotopic ratios, e.g., $^{12}C/^{13}C$, $^{16}O/^{18}O$, is used (Wilson & Rood 1994). These ratios are often derived from the $^{12}CO$, $^{13}CO$ and $C^{18}O$ observations along different sightlines. Thus, the resulting fractional abundances that come out from the conversion and are used to compare with the results of chemical modelling carry an uncertainty of some degree. Note here that the CO–to–$H_2$ conversion factor alone, is not an easy problem.

The transfer equation for the radiation of the cloud molecules, when not possible to solve in an analytic form (Sobolev 1979), is solved numerically by the Monte–Carlo technique (e.g. Bernes 1979, Juvela 1995, Hogerheijde and van der Tak 2000, Troitsky et al. 2004). For example, the latter model is of a spherical cloud of weakly ionised plasma with a spherically symmetric density distribution, with constant gas kinetic temperature threaded by an axially symmetric magnetic field – this being among the first models to consider magnetic fields. Note here that the cloud/core tends to collapse due to a self gravity, but magnetic tension and the kinetic, magnetic and turbulent pressures slow down the process and even induce a temporal expansion instead of collapse. This free–fall time is a key time scale for star formation (Shu et al. 1987). Typical results of Monte–Carlo modelling for dark clouds give the hydrogen number densities of the cloud centre of $10^5 - 10^6\,\mathrm{cm}^{-3}$ and the relative abundance of $HCO^+$ molecules relative to $H_2$ in the cloud centre of $10^{-10} - 10^{-9}$. Large scale motions in clouds are a combination of infall with $\sim 0.1\,\mathrm{kms}^{-1}$, (nonuniform) rotation of the order of $\sim 0.1\,\mathrm{kms}^{-1}$, and turbulent motions which are of the order of magnitude of $\sim 0.1\,\mathrm{kms}^{-1}$.

## 6. SPECTRAL WINDOW EXTENSION BEYOND THE FIRST 30 YEARS

The "Xogen" was fist detected in the interstellar space (Buhl and Snyder 1970) and then identified as the ground rotational transition, $J = 1 \rightarrow 0$, of the Formyl cation in the laboratory (Woods et al. 1975). This defined the lowest frequency of the observable window at 89.1885320 GHz. Most of the observations so far are conducted in the lines in the sub–mm radio frequency domain, including both rotational and rovibrational transitions, in molecular clouds often in emission. In absorption it is observed in the diffuse ISM. Recently, Savage and Ziurys (2005) extended the range of the precise measured frequencies up to the $J = 7 \rightarrow 6$ rotational transition of the ground vibrational state at 624.2083453 GHz. Development of the new instruments, telescopes and receivers, push further the upper observable frequency into the terahertz range, and agreed "borderline" between the radio and the infra–red spectrum. In preparation for the launch of the Herschel Space Telescope Observatory (Pilbratt et al. 2001) and the Atacama Large Millimetre Array (ALMA, Wootten 1999), Latanzi et al. (2007) supply measurements and predictions for transitions at frequencies up to $\sim$ 1.2 THz, for $HCO^+$ and its rare isotopomers, $H^{13}CO^+$, $DCO^+$ and $D^{13}CO^+$. For the Formyl ion this frequency corresponds to the $J = 13 \rightarrow 12, v = (1,1)$ rovibrational transition. More than anything, studies of higher rotational transitions will help separate the effects of chemical versus excitation processes and that on an AU scales.

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## ФОРМИЛ ЈОН У МОЛЕКУЛСКИМ ОБЛАЦИМА

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*Прегледни рад по позиву*

Формил јон је једно од најважнијих једињења и најважнији јон у молекулским облацима. У овом раду дат је преглед најважнијих реакција његове синтезе и разграђивања у тамним молекулским облацима Галаксије. Приказана је његова употреба у израчунавању степена јонизације гаса као и у проблему преноса зрачења.