Dissociative recombination and electron attachment in regions of star formation

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Abstract.  Dissociative recombination and electron attachment are important in interstellar chemistry, which is heavily dominated by ions and ionic processes. Here we consider how the competition between dissociative recombination and other reactions, such as H-atom transfer, can explain the unusually high observed abundances of the reactive cations OH\textsuperscript{+} and H\textsubscript{2}O\textsuperscript{+} in the dense outflow source in front of the Orion Nebula. We also show how dissociative recombination and other processes might block the achievement of an equilibrium ortho-to-para abundance ratio for H\textsubscript{2}O\textsuperscript{+} in diffuse interstellar clouds. Finally, we consider the formation and destruction rates of molecular anions observed in the interstellar and circumstellar media, especially the formation mechanism of radiative attachment, the rate of which has only been estimated by a simple phase space theory, which is surprisingly successful in most instances.

1. Introduction
Peering at the sky in the THz region of the electromagnetic spectrum at frequencies up to 1.91 THz, the \textit{Herschel Space Observatory} has changed our perception of some aspects of our Galaxy and many others \cite{1}. In the Milky Way, Herschel observations with the \textit{HIFI} heterodyne receiver have looked in a preliminary manner at emission from giant molecular clouds containing star-forming regions, and absorption from the outer and cooler environments surrounding these regions as well as from diffuse clouds in spiral arms along the line of sight from the more distant continuum sources, such as the Galactic Center. Among the regions studied in emission is the well-known bright extended object known as Orion KL, which is located in the larger Orion Molecular Cloud. This complex source contains several star-forming regions, known as “hot cores,” which are of higher density ($n \approx 10^{6}$ cm\textsuperscript{-3}) and temperature (100 – 300 K) than the standard conditions of dense interstellar clouds. Previous studies at lower frequencies of these hot cores and similar sources in other giant molecular clouds have shown a high density of rotational emission lines, many of which have been assigned to common terrestrial organic molecules such as methanol, ethanol, methyl formate, dimethyl ether, and ethyl cyanide. A preliminary study of this source with Herschel \cite{2} shows a somewhat lower density of rotational emission lines, most of which can be assigned to the same species, often known as “weeds” because their high spectral densities obscure the search for more exotic species with sparser spectra, known as “flowers.” Further studies of these and other hot cores in the galaxy with \textit{Herschel} will be undertaken shortly in a search for additional organic species.

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Somewhat more unusual are the results of rotational absorption studies towards objects such as Orion KL, which emit a continuum in the THz region partially contaminated by emission spectra. The sources seen in absorption, whether they surround the star-forming regions or lie in galactic spiral arms between them and the earth, contain strong spectral features assigned to the light molecular cations OH$^+$ and H$_2$O$^+$ [3, 4]. This result is highly unusual, especially in the outer regions of the giant molecular clouds, because it is well known from laboratory studies that these cations are rapidly destroyed by reactions with H$_2$, the dominant neutral species in the dense interstellar medium, which lead to the saturated molecular ion H$_3$O$^+$; i. e.,

$$\text{OH}^+ + \text{H}_2 \rightarrow \text{H}_2\text{O}^+ + \text{H},$$  

$$\text{H}_2\text{O}^+ + \text{H}_2 \rightarrow \text{H}_3\text{O}^+ + \text{H}.$$  

The hydronium ion subsequently undergoes a dissociative recombination reaction to produce the well-known neutral species H$_2$O and OH [5]:

$$\text{H}_3\text{O}^+ + e^- \rightarrow \text{H}_2\text{O} + \text{H}; \text{OH} + 2\text{H}, \text{etc.}$$  

One thus expects to see a strong signal from H$_3$O$^+$ and weaker signals from the simpler ions in dense regions. Although the hydronium ion is indeed detected, albeit weakly, in the diffuse spiral arm clouds along with OH$^+$ and H$_2$O$^+$, where much of the hydrogen is in the atomic form, it is not at all seen in the outer region surrounding Orion KL.

Another mystery concerns the H$_2$O$^+$ cation, which is detected in both its ortho and para forms [6]. The ratio of ortho-H$_2$O$^+$ to para H$_2$O$^+$ (OPR) is $\approx 4.8:1$ in the diffuse spiral arm clouds, a ratio that can be converted to a spin temperature of $\approx 20$ K but that must eventually be explained by a complex competition involving formation, equilibration, and destruction of the two spin modifications. In the body of this paper, tentative explanations for the surprising strength of the OH$^+$ and H$_2$O$^+$ spectral features, and the unusual OPR of H$_2$O$^+$ will be suggested.

As unusual as these detections are, the detection of molecular anions was equally unexpected by most astrochemists, although some very old papers had discussed their possible detection in cold interstellar clouds [7, 8]. Starting a few years ago, laboratory studies of the rotational spectra of a number of strongly-bound molecular anions were performed by Thaddeus, McCarthy and co-workers [9, 10]. Almost immediately, some of these anions were found in cold regions of interstellar clouds and one circumstellar source (IRC+10216) either from previously observed but unidentified lines or from new detections in the millimeter region of the electromagnetic spectrum [9, 11]. The anions detected, discussed below, come from precursor radical neutrals also known to be relatively abundant in cold dense clouds, especially the so-called cold core TMC-1 and the circumstellar source IRC+10216. The chemistry of formation and depletion of these anions is characterized by processes that, for the most part, have not been studied in the laboratory or by detailed theoretical methods, so that the reasonable agreement between simulations and observations obtained must be regarded as at least partially serendipitous.

2. The Orion Outflow Source

The absorption spectrum from material in front of Orion KL is dominated by a broad spectral feature which, when translated from frequencies to radial velocities, ranges from 0 to $-50$ km s$^{-1}$ [3]. The negative velocities mean that the source is moving towards us, and so is known as an outflow. At 1 THz, the 50 km s$^{-1}$ range corresponds to a line width of 170 MHz! Such line widths are often associated with turbulence and/or shocks, although it is also possible that there are a number of different outflows along the line of sight and that we are not resolving them. As a preliminary model, we first adopted what is known as a PDR, an acronym for “photon-dominated
region.” [12]. Such a region lies close to a strong source of vacuum ultraviolet radiation, which can strongly affect layers of the source closest to it. In our case, we assumed the radiation field to be $4 \times 10^4$ as strong as the standard radiation field in interstellar space. To try to explain the observations of $\text{OH}^+$ and $\text{H}_2\text{O}^+$, it is necessary to not only assume a strong VUV field, but also a high flux of either cosmic rays or X-rays to ionize a significant portion of the gas. The standard ionization rate coefficient used for cosmic rays (mainly high-energy protons), labelled by the letter $\zeta$, is in the vicinity of $10^{-17}$ s$^{-1}$. This rate of ionization results in a fractional ionization in a dense region of approximately $10^{-7}$, a very weak plasma, in which ions prefer to react with $\text{H}_2$ than with electrons. To break the cycle of reactions with $\text{H}_2$, one must raise the ionization rate by a factor of 1000 to 10000, a very dramatic increase but one in agreement with what another analysis indicates [13]. With a resulting greatly increased fractional ionization of perhaps $10^{-3}$, dissociative recombination can compete with reaction with hydrogen. If we assume that the rate coefficient for dissociative recombination of an ion is $10^{-6}$ cm$^3$ s$^{-1}$ and the rate coefficient for its reaction with $\text{H}_2$ is $10^{-9}$ cm$^3$ s$^{-1}$, the rate of reaction of the ion with electrons and with $\text{H}_2$ is the same. Thus, although reaction with $\text{H}_2$ still occurs, it must compete with dissociative recombination. Nevertheless we still need additional formation mechanisms to produce the $\text{OH}^+$ and $\text{H}_2\text{O}^+$ ions.

Let us look at what can happen in more detail. We start with the $\text{OH}^+$ ion, which can be formed in a number of ways, such as the reaction of $\text{O}$ and $\text{H}_3^+$:

$$\text{O} + \text{H}_3^+ \rightarrow \text{OH}^+ + \text{H}_2,$$

and the charge exchange between $\text{O}$ and $\text{H}^+$ followed by reaction of $\text{O}^+$ with $\text{H}_2$:

$$\text{O}^+ + \text{H}_2 \rightarrow \text{OH}^+ + \text{H}.$$

If $\text{OH}^+$ reacts with $\text{H}_2$ to form $\text{H}_2\text{O}^+$, the resulting water ion can undergo dissociative recombination to form $\text{OH}$ and $\text{H}$. The strong VUV radiation field can then photoionize $\text{OH}$ into its cation. Reaction of $\text{H}_2\text{O}^+$ with $\text{H}_2$ instead leads to the $\text{H}_3\text{O}^+$ cation, which is destroyed relatively quickly by dissociative recombination, so that it is hard to detect. Remember that, unlike the smaller ions, $\text{H}_3\text{O}^+$ cannot be produced by any photoionization process. The resulting neutral species $\text{H}_2\text{O}$ and $\text{OH}$, however, are subsequently photoionized by the strong radiation field to produce $\text{OH}^+$ and $\text{H}_2\text{O}^+$. The high ionization rate from cosmic rays also leads to the production of a large abundance of protons, which in turn react with neutral water to produce more $\text{H}_2\text{O}^+$:

$$\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{H}.$$

It turns out that if one assumes that neutral water can flow into the outflow source or can be photodesorbed from icy mantles, the necessary cosmic ray ionization rate can be lowered by an order of magnitude, because of the enhanced photoionization rate of water. With a range of parameters, we can reproduce the observed column densities of $\text{OH}^+$ and $\text{H}_2\text{O}^+$ as well as the upper limit to the $\text{H}_3\text{O}^+$ column density. (Note that a column density is a concentration multiplied by a length; this quantity is what is directly measured along the line of sight.) The cloud is no longer a cold region; however, since the temperature at its edge facing the source of UV radiation is $\approx 400$ K. Moreover, the atomic and molecular hydrogen abundances near the inner edge of the outflow are approximately equal, and the optimum density is perhaps $10^3$ cm$^{-3}$.

3. The Ortho-to-Para Ratio of $\text{H}_2\text{O}^+$

Ortho-para abundance ratios for assorted species in interstellar sources can be the result of many processes, including those that occur both in the gas-phase and on granular surfaces. The case of
H$_2$O$^+$ should be a relatively simple one, since it is likely to occur entirely in the gas phase. Using observations with Herschel, Schilke et al. [6] have just studied the ortho-to-para ratio (OPR) of the water ion in diffuse spiral arm sources, and determined that it is 4.8:1. Since the ground electronic state of H$_2$O$^+$ possesses an asymmetric $^2$B symmetry, the rotational levels associated with the ortho and para forms are reversed from those of neutral water, and it is the ortho form that contains the lowest ($O_{00}$) rotational level while the lowest para rotational level is $1_{01}$, which lies 30.1 K above the ground ortho level. Thus, as the rotational temperature approaches 0 K and dynamic processes interconvert the ortho and para forms, the ortho modification becomes increasingly dominant, while at high rotational temperatures, the OPR approaches its standard value of 3:1. The simplest way of interpreting the observed OPR of 4.8:1 is to assume that it is an equilibrium value, obtained by gas-phase processes in which protons can exchange from one species to another, such as:

$$ p - H_2O^+ + H \rightleftharpoons o - H_2O^+ + H, \quad (7) $$

where we have assumed that atomic hydrogen is the major equilibrant since the spiral arm clouds are diffuse, and because the water ion reacts with H$_2$ rather than be thermalized by it. Since the measured OPR is really a measurement of the abundance ratio between the lowest ortho and para rotational states, it can be expressed in simple terms via a so-called spin temperature $T_s$:

$$ \text{OPR} = \frac{g(0_{00})}{g(1_{01})} \exp(30.1/T_s), \quad (8) $$

where the $g$ are combined nuclear-spin-rotational degeneracy factors and 30.1 K is the energy separation between the two rotational states in K, the astronomer’s favorite unit of energy. Using this equation, an OPR of 4.8 translates into a spin temperature of \( \approx 20 \) K since the degeneracies are both 6. But what can this spin temperature possibly mean? If the system equilibrates to the kinetic temperature of a diffuse cloud, then a temperature of 50-100 K is more likely. Such a temperature would correspond to an OPR for H$_2$O$^+$ closer to 3:1, or 1:1 in the absence of rotational excitation, as expressed in eq. (8), where the high-temperature limit goes to unity rather than to 3:1. Given the low density of a diffuse cloud, the 1:1 value seems more reasonable theoretically although it is far from the observed value of 4.8:1.

Let us now consider the complications caused by chemistry. If the destruction of H$_2$O$^+$ is faster or at least competitive with equilibration, then the ortho/para ratio obtained in the formation of H$_2$O$^+$ can be the main cause of the OPR. Consider the formation and destruction of ortho- and para- H$_2$O$^+$ via a small chemical network:

$$ \text{OH}^+ + p - H_2 \longrightarrow p - H_2O^+, o - H_2O^+ + H \quad (9) $$

$$ \text{OH}^+ + o - H_2 \longrightarrow p - H_2O^+, o - H_2O^+ + H \quad (10) $$

$$ H_2O^+ + e^- \longrightarrow \text{Products} \quad (11) $$

$$ H_2O^+ + H \longrightarrow H_3O^+ + H. \quad (12) $$

Let the fraction of p-H$_2$O$^+$ and o-H$_2$O$^+$ produced in the formation steps be labelled $f_{pp}$, $f_{po}$, $f_{op}$ and $f_{oo}$, where the first two parameters refer to the reaction with p-H$_2$, and the second two refer to the reaction with o-H$_2$. Although the steady-state solution to this series of equations and equilibration is rather complex, the result in the limit that equilibration is slow is given by

$$ \text{OPR} = \frac{f_{po} + f_{oo}\text{OPR}(H_2)}{f_{pp} + f_{op}\text{OPR}(H_2)}, \quad (13) $$
where OPR(H₂) represents the ortho-to-para ratio of molecular hydrogen. The \( f \) factors can be calculated using the angular-momentum approach of Oka [14] but an additional complication immediately ensues because it turns out that the \( f \) factors depend upon the mechanism of reactions (9) and (10); in particular, whether they occur via a long-range hopping of a hydrogen atom or via an intimate and long-lived complex. As for OPR(H₂), we can regard it as a variable parameter or we can use a value of near unity, determined by older studies for nearby diffuse clouds. With this value, we estimate that OPR \( \approx 2:1 \) with the complex mechanism. In fact, to reproduce the observed value for OPR of 4.8:1, we appear to need almost pure \( o-H_2 \) for the complex mechanism, which makes little sense. Even worse, the hopping mechanism always leads to an OPR of 3:1. So, our simple chemistry-dominant approach fails.

One additional possibility is to consider ortho/para variations in the destruction reactions, as has been detected for the dissociative recombination reaction of \( H_3^+ \) [15]. Yet another possibility is that the small network used is incomplete. In particular, the charge exchange reaction between \( H^+ \) and \( H_2O \) (see eq. (6)) is a competitive source for both spin modifications of \( H_2O^+ \). Once \( H_2O \) becomes involved in the analysis, it becomes necessary to calculate its ortho-to-para ratio, which may well be governed by processes occurring on the surfaces of dust grains. Moreover, it is unlikely that the equilibration reactions involving atomic \( H \) are much slower than the destruction reaction involving \( H_2 \) in a diffuse cloud environment, since atomic hydrogen probably has a larger abundance than \( H_2 \). In at least some of the diffuse cloud spiral arm sources, an \( H/\text{H}_2 \) abundance ratio greater than unity can be determined based on the observation that \( \text{OH}^+ \) has a greater abundance than does \( \text{H}_2\text{O}^+ \) [4]. Given all of these complications, it is clear that much more work is needed to understand the ortho-to-para ratio of \( H_2O^+ \) and indeed other species exhibiting these spin modifications. It may well be that the OPR will not be reproduced until detailed models are found that reproduce the coupled abundances of all of the species, including their spin modifications, detected in these sources.

4. Interstellar Anions and their Chemistry

As of the present, six different negative molecular anions have been discovered in assorted sources, as shown in Table 1. These ions are all radical ions; that is, their neutral forms are all chemical radicals, possessing both an odd number of electrons and a large electron binding energy (“electron affinity”) of \( \approx 3-4 \) eV. All astronomical detections are based on firm laboratory studies with the exception of \( C_5N^- \). The only source containing all of the anions is the outer envelope of the old carbon-rich star IRC+10216, in which the elemental abundance of carbon exceeds that of oxygen. The other sources are all interstellar ones: TMC-1 is the standard cold core studied by radio astronomers for its rich organic chemistry; the heading “other cold cores” includes L1544 and L1521F and a newly discovered source, known as Lupus-1A [16]. These objects, typically at temperatures of 10 K, are denser regions of larger clouds known as dark clouds for their obscuration of background star light. Some of those listed are pre-stellar cores, while one, Lupus-1A, like TMC-1 shows no evidence of collapsing to form stars. The final source, L1527, is a region outside of a protostellar source, and has a somewhat higher temperature. Despite individual differences, the chemistry of all of these objects is dominated by ion-molecule, dissociative recombination, and radical-neutral reactions, which produce large numbers of carbonaceous unsaturated radicals. The family of interstellar radicals with structure \( C_n\text{H} \) is particularly well studied, and consists of molecules with \( n=1 \) to \( n=8 \). None of the anions is abundant in an absolute sense, but their existence has strong implications for the chemistry of complex molecule formation [17].

The production of anions in cold interstellar clouds and in carbon-rich stellar envelopes is very different from their production in the laboratory, typically at much higher densities. In the low-density interstellar and circumstellar media, the most likely process of formation is thought to be radiative attachment, a two-body process in which electrons attach themselves
Table 1. Molecular anions and their sources

| Ion    | IRC+10216 | TMC-1 | Other Cold Cores | L1527 |
|--------|-----------|-------|------------------|-------|
| CN⁻    | X         | –     | –                | –     |
| C₃N⁻   | X         | –     | –                | –     |
| C₅N⁻   | X         | –     | –                | –     |
| C₄H⁻   | X         | X     | X                | X     |
| C₆H⁻   | X         | X     | X                | X     |
| C₈H⁻   | X         | X     | –                | –     |

to neutral species with a large electron affinity to form an unstable complex, which then either auto-detaches or radiates sufficient energy to stabilize the nascent negative ion. The radiation can be produced by relaxation of vibrational levels above the attachment continuum to those below it or by relaxation of a complex in an excited electronic state to stable vibrational levels of the ground electronic state. The former process is thought to be the more common. The first estimate of the rate of radiative attachment was made by Herbst [7], who also suggested the likely anions to be formed. The theory used, updated by Terzieva & Herbst [18] and Herbst & Osamura [19], is a very simple one, and more detailed quantum calculations are urgently needed. Herbst also estimated that the anion-to-neutral ratio achievable via this process could be as high as 1%, and that this ratio could only be achieved for anions with at least 4-5 atoms.

The method used by Herbst [7] is known as phase-space theory, which is a statistical approach with rigorous conservation of angular momentum. The additional assumption was made that only s-wave electrons are involved. The overall mechanism consists of three different processes: complex formation, complex detachment, and radiative stabilization, and can be written as:

\[
A + e^− \rightleftharpoons A^{*−} \rightarrow A^{−} + h\nu, \tag{14}
\]

where the complex is indicated by an asterisk. The rates of complex formation and detachment are governed by microscopic reversibility [20], while the rate of radiative stabilization via purely vibrational emission can be obtained using quantum chemical or experimental information of transition strengths for the various modes [21]. As the size of the complex and its binding energy increase, the rate of detachment lessens, to the point that eventually the complex is stabilized by emission of radiation on 100% of the collisions that form it. Some calculated radiative attachment rate coefficients, \(k_{\text{radatt}}\), are listed in Table 2 [19].

Another formation mechanism is dissociative attachment, in which an electron attaches itself to a neutral molecule with the concomitant breaking of a chemical bond. This process is normally endothermic, but there are odd radicals in the interstellar medium for which the process can indeed be exothermic. The most important example is the reaction between electrons and the high-energy cumulene isomer \(\text{H}_2\text{C}_6\) [19, 22]:

\[
e^− + \text{H}_2\text{C}_6 \rightarrow \text{C}_6\text{H}− + \text{H}, \tag{15}
\]

which is calculated to be exothermic by 16 kJ mol\(^{-1}\). This reaction appears to be more important than radiative attachment in denser sources where there is little neutral \(\text{C}_6\text{H}\). Finally, negative ions can be formed via normal ion-molecule reactions, especially when the anions are too small to be formed efficiently by radiative attachment. An example is the anion \(\text{CN}^{−}\), recently detected in IRC+10216 [23], which is most likely formed from a large anion of the form \(\text{C}_n^{−}\) by the reaction with nitrogen atoms [24]:

\[
\text{N} + \text{C}^{−}_n \rightarrow \text{CN}^{−} + \text{C}_{n−1}, \tag{16}
\]
Table 2. Estimated Attachment Rate Coefficients for C\textsubscript{n}H\textsuperscript{−}
a
| No. of C Atoms | \( k_{\text{radatt}} \) \( \text{(cm}^3\text{s}^{-1}, 10\text{K}) \) |
|---------------|----------------------------------|
| 2             | \( 1 \times 10^{-14} \)          |
| 4             | \( 6 \times 10^{-8} \)           |
| 6             | \( 3 \times 10^{-7} \)           |
| 8             | \( 3 \times 10^{-7} \)           |

\( a \) Herbst & Osamura [19]

and possibly by other ion-molecule reactions involving H\textsuperscript{−} [25].

Once formed, anions can be destroyed by a number of processes including photodetachment, associative detachment with hydrogen atoms, normal ion-molecule reactions, and positive ion-negative ion recombination. The last process is currently poorly understood, although new experiments are planned in several laboratories [26].

In Table 3, we compare the results of observations and current models for the chemistry of the carbon-rich envelope IRC+2016 in the form of anion-to-neutral ratios [23, 25, 27, 28]. It can be seen that agreement is reasonable (order-of-magnitude) for most of the anions. The largest disagreement concerns the abundance ratio C\textsubscript{4}H\textsuperscript{−}/C\textsubscript{4}H, which is calculated to be roughly two orders of magnitude too large. As can be seen in Table 2, the calculated radiative association rate coefficient for C\textsubscript{4}H lies in between the very small rate coefficient for C\textsubscript{2}H radiative attachment, and the large ones for C\textsubscript{6}H and C\textsubscript{8}H. It is likely that this rate coefficient is calculated incorrectly by the statistical theory, which is typically accurate only for large systems. Detailed calculations of radiative attachment are clearly needed.

5. Radiative recombination??

The very recent detection of C\textsubscript{60} in the interstellar medium [29], currently limited to so-called planetary nebulae and reflection nebulae, raises the question of its synthesis. Bettens & Herbst [30] suggested a synthesis of this species many years ago, based on higher-density laboratory work by Bowers and co-workers [31] In this synthesis, ion-molecule reactions first produce linear carbon chains, which, as they grow, eventually isomerize into single rings. These rings, as they continue to grow, isomerize into triple rings, which finally convert to fullerenes. But only fullerene ions; e.g., C\textsubscript{60}\textsuperscript{+}, are produced, unless the process of radiative recombination; viz., :

\[
\text{C}_{60}^{+} + e^{-} \longrightarrow \text{C}_{60} + h\nu
\] (17)

occurs efficiently. Bettens & Herbst used a very simple statistical theory, known as RRKM theory, to estimate that the reaction is quite efficient for unsaturated hydrocarbon cations of all shapes with more than \( \approx 20-30 \) carbon atoms. To the best of our knowledge, there is currently no information, either experimental or theoretical, on this process. Once again, some detailed work is needed.

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Table 3. Molecular anionic abundances in IRC+10216

| Ratio         | Model | Observation |
|---------------|-------|-------------|
| CN⁻/CN        | 0.001 | 0.0025      |
| C₂H⁻/C₂H      | 1.3 × 10⁻⁵ | < 1 × 10⁻⁵ |
| C₃N⁻/C₃N      | 0.013 | 5.0 × 10⁻³  |
| C₄H⁻/C₄H      | 0.015 | 2.4 × 10⁻⁴  |
| C₅N⁻/C₅N      | 0.059 | 0.12        |
| C₆H⁻/C₆H      | 0.069 | 0.062 - 0.086 |
| C₈H⁻/C₈H      | 0.049 | 0.26        |

a Agúndez et al. [23]; Cordiner & Millar [25]; Agúndez et al. [27]; Cernicharo et al. [28]
b See [25] for a list of observational references.

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