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Modelling the role of electron attachment rates on column density ratios for C_nH^-/C_nH ($n = 4, 6, 8$) in dense molecular clouds

F A Gianturco¹, T Grassi² and R Wester¹

¹Institut für Ionen Physik und Angewandte Physik Universität Innsbruck, Technikerstrasse 25, A-6020, Innsbruck, Austria

²Center for Stars and Planet Formation, Niels Bohr Institute, University of Copenhagen, Østervoldgade 5-7, DK-1350 Copenhagen Ø, Denmark

E-mail: francesco.gianturco@uibk.ac.at

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Abstract

The fairly recent detection of a variety of anions in the interstellar molecular clouds have underlined the importance of realistically modelling the processes governing their abundance. To pursue this task, our earlier calculations for the radiative electron attachment (REA) rates for C_4H^- , C_6H^- , and C_8H^- are employed in the present work, within a broad network of other concurrent reactions, to generate the corresponding column density ratios of anion/neutral (A/N) relative abundances. The latter are then compared with those obtained in recent years from observational measurements. The calculations involved the time-dependent solutions of a large network of chemical processes over an extended time interval and included a series of runs in which the values of REA rates were repeatedly scaled over several orders of magnitude. Macroscopic parameters for the Clouds' modelling were also varied to cover a broad range of physical environments. It was found that, within the range and quality of the processes included in the present network, and selected from state-of-the-art astrophysical databases, the REA values required to match the *observed* A/N ratios needed to be reduced by orders of magnitude for C_4H^- case, while the same rates for C_6H^- and C_8H^- only needed to be scaled by much smaller factors. The results suggest that the generally proposed formation of interstellar anions by REA mechanism is overestimated by current models for the C_4H^- case, for which is likely to be an inefficient path to formation. This path is thus providing a rather marginal contribution to the observed abundances of C_4H^- , the latter being more likely to originate from other chemical processes in the network, as we discuss in some detail in the present work. Possible physical reasons for the much smaller differences against observations found instead for the values of the (A/N) ratios in two other, longer members of the series are put forward and analysed within the evolutionary modelling discussed in the present work.

Keywords: efficiency of anion formation processes, modellings of chemical processes in the interstellar medium, molecular anions in molecular clouds

1. Introduction

Molecular negative ions in the interstellar medium (ISM) were first discovered as an unidentified series of lines within a radio astronomical survey of the evolved carbon star IRC +10216 by [1] and were later assigned by [2], who confirmed



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the presence of C_6H^- in TMC-1 on the basis of laboratory rotational spectroscopy. The observation was followed by the detection of both C_6H^- and C_4H^- in the protostellar core L1527 by [3] and by [4]. The following year [5] carried out an extensive dedicated survey of C_6H^- in twenty four different molecular sources: they observed that anion only in two star-forming clouds and confirmed the anion-to-neutral (A/N) ratio of the order of a few percent, in keeping with the earlier measurements.

Those detections had been limited to the Taurus molecular cloud complex until the more recent discoveries of the presence of the C_6H^- anion in the Lupus, Cepheus and Auriga star-forming regions [6, 7] which therefore established the widespread presence of molecular anions in different corners of the ISM. The presence of similar molecular species, the cyanopolyynes, has also been observed in the same star-forming cloud IRC-10216 via the detection of C_3N^- by [8].

The possible chemical importance of molecular anions in the ISM had been put forward over the years even well before their recent detections. The work in [9], in fact, first discussed this possibility suggesting the chief mechanism of formation to be the radiative electron attachment (REA) path: $M + e^- \rightarrow M^- + h\nu$. Attempts at detection using radioastronomy were discussed by [10], while [11] further argued that large interstellar molecules, including the polyynic chains, could efficiently undergo the anionic stabilization process via the REA process. Evolutionary models were later put forward, after the anions' observations of above, by [12] and by [13], although marked discrepancies were found between the estimated A/N ratios for C_4H^- and C_6H^- and those suggested by the above models [4]. It has also been demonstrated later on by [14] that anion measurements have the potential to offer additional information on the molecular properties of interstellar clouds because of the marked reactivity of these ionic species, the latter being very sensitive to the relative abundances of electrons and of C, H, N atoms in the environment.

It therefore becomes important to be able to model the evolutions of the anionic abundances in different molecular clouds in order to find out which are the most important molecular mechanisms that are likely to preside over their chemical formation.

In the present work we shall therefore revisit the A/N ratios recently observed experimentally in the dense ISM [15] by using the existing estimated rates of REA processes which have been obtained by calculations. We shall employ such rates for generating the A/N ratios and the latter quantities will be compared with those from astronomical observations, a comparison that will help us to evaluate what is the expected importance of REA anions' formation vis á vis other chemical routes currently present in the existing databases and routinely used within chemical evolutionary models. In our study we shall refer to a database that we here label as KIDA³, [16].

The following two sections briefly review the existing computational models for the REA anions' formation and

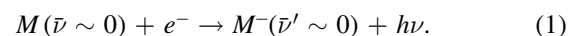
further discuss our use of them in the evolutionary calculations we have employed to produce the A/N ratios over large time intervals. Such calculations involve an extended network of chemical processes that have to be included to realistically describe the environment of a dark cloud core. Our final results and our present conclusions are given in section 5.

2. The molecular steps of REA

In order to gain a better physical insight into the process of anion stabilization by photon emission, frequently considered the most likely mechanism in the ISM and originally put forward to explain their formation by various authors [9–11], an extensive modelling for polyatomic species was discussed, and applied to both polyynes and cyanopolyynes by [17]. Here we shall call this treatment the Herbst–Onamura (HO) model for the REA mechanism. More recently, a different model based on more realistic scattering calculations was put forward by [18] who found in general similar results for the electron attachment rates to polyynes as those suggested by [17], although uniformly smaller than the latter over the whole range of temperature examined in both studies. Here we shall call this model the Carelli–Satta–Grossi–Gianturco (CSGG) modelling of REA processes of anion formation.

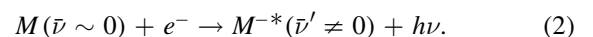
Both models essentially consider the presence of two different, albeit cooperating, steps in the stabilization of the final molecular anions:

- (i) The direct photon emission during the electron attachment process, whereby the incoming electron is taken to have rather little excess collision energy, finds the neutral radical in the ISM to be largely in its ground vibrational normal mode ($\bar{\nu} \sim 0$) and the emitted photon releases the necessary excess energy to form the corresponding anion in its ground vibrational mode ($\bar{\nu}' \sim 0$) without fragmentation of the target



Both models take this process to occur in competition with the autodetachment event, without explicit inclusion of the latter decay process within their computational treatments.

- (ii) The indirect electron stabilization path, whereby the incoming projectile is temporarily trapped by the neutral target into a metastable state of the corresponding anion:



Here the above two models treat differently the non-adiabatic (electron–molecule) couplings within the metastable anionic complex:

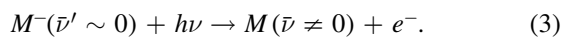
- (i) The HO model uses a phase-space theory (PST) approach whereby strong coupling exists among the

³ <http://kida.obs.u-bordeaux1.fr/>

initial state of the anion and any of the excited states of the latter with the same spin. The REA efficiency increases with the size of the radical and the number of its normal modes which are energetically available.

- (ii) The treatment of the CSGG model explicitly includes the occurrence of either low-energy shape resonances or of intermediate dipole driven states near the scattering threshold (above and below it) for the systems with supercritical dipoles ($\mu > 2.0$ Debye). Such metastable states increase the efficiency of radiative stabilization versus autodetachment and the model found that the REA paths become more competitive with autodetachment as the size of the molecular system increases [18].

One should note that in both models, once the bound anionic molecules are formed, the competing reaction of photodetachment, which can be induced by the environmental photons, is also present:



On the other hand, in modelling the anions' formation processes in the core of the dense molecular clouds one expects marginal penetration by photons. It has been noted, in fact, that essentially no molecular anions were observed in the PDR regions [4], thereby confirming the important role of process (3) in those external regions but its reduced importance in the dark clouds which constitutes the object of the present study.

Recent calculations for the photodetachment rates in C_2H^- , C_4H^- , and C_6H^- [19] have further shown that, for the cases of C_2H^- , C_4H^- , and C_6H^- the agreement with existing experiments [20] varies from system to system and the cross section behaviour at threshold strongly depends on dipole strength effects. They have later analysed explicitly the REA process in the same series of linear anions by further including a model treatment of the indirect processes [21]. They found that the REA rates for C_2H^- species were practically negligible and that those for the C_4H^- member were also rather small. As done before, by using the initials of all the authors in that paper, here we shall call this model the Douguet–Fonseca–Raoult–Dulieu–Orel–Kokoouline (DFRDOK) modelling of the REA processes of the present study.

In conclusion, the existing models for generating REA cross sections and rates indicate the processes to come from combined contributions of direct and indirect electron attachment paths that can generate effective competition with the autodetachment and photodetachment channels, thereby yielding significant rates for the anion-forming process. As briefly outlined above, the HO model includes no scattering calculations, while the CSGG approach carries out realistic scattering calculations but includes only indirectly non-adiabatic couplings with the internal vibrational modes. Such effects are modelled explicitly in the DFRDOK treatment for small molecules. They however found these effects to be inefficient for the two smallest members of the polyynes chains, thus making that channel essentially non-existent for

the C_2H^- and rather marginal for the C_4H^- , the only two systems analysed by that model [21].

In order to gain further insight on the global effects that the REA rates, as given by the existing calculations, might have on producing agreement with the A/N ratios experimentally observed, we shall carry out in the following section a more comprehensive computational analysis of the anions' evolutions within an extended kinetic treatment of the network of chemical reactions generally considered to be relevant for their formation in the core of molecular clouds.

3. Role of REA rates in chemical evolution calculations

The recent observations of [15] have given us specific indications for the C_4H/C_4H^- and C_6H/C_6H^- ratios over seven nearby galactic star-forming cores and molecular clouds. The new measurements include four sources in which no molecular anions had been previously detected and indicate that for the C_6H the observed A/N ratio the value is $\geq 1\%$ in every source, providing a mean value of 3%. On the other hand, for C_4H the detected A/N ratio value turned out to be much smaller, i.e. $1.2 \pm 0.4 \times 10^{-5}$. Furthermore, the earlier measurements for the C_8H^-/C_8H ratio in the galactic molecular source TMC-1 [22] and in the circumstellar envelope IRC+10216 [23] indicated the ratio of the total column densities to be between $\sim 5\%$ and $\sim 3.8\%$.

It therefore becomes relevant to revisit the current chemical models for these quantities and to see how important the REA path could be in providing realistic A/N ratios in molecular clouds from evolutionary calculations. As a preliminary test, we have employed a one-zone time-dependent scenario representing a dark cloud core (described e.g. in [24]). The selected model of the cloud evolves from a chosen set of initial abundances at constant temperature, number density, cosmic-ray flux, and gas visual extinction. We employ the rates for the chemical database KIDA⁴, using their most updated available set of reactions, i.e. `kida.uva.2014` [16].

This set includes anions for C_nH^- ($n = 4, 6, 8$) which take part in initial mutual neutralization reactions, photodetachment, associative detachment, anion-neutral reactions, and REA processes, as described in KIDA. When we include all the reactions within a temperature range that is realistic for our model ($T_{\text{gas}} = 10$ K), the total number of species selected was 486, with a total number of reactions up to 6962. The only difference we adopt here is to take REA reactions rate coefficients for ($n = 4, 6, 8$) anions formation from the recent scattering model termed CSGG in our present study [18], rather than their simpler Langevin-type estimates currently included in the recent databases. The present calculations employ the open-source code KROME⁵ [25] to solve the time-dependent system of differential equations. In order to ensure numerical accuracy we set relative and

⁴ <http://kida.obs.u-bordeaux1.fr/>.

⁵ <http://kromepackage.org/>.

Table 1. A sample of the key reactions for the formation/destruction of C_nH^- from KIDA database included in the present study, except reaction 1 that is also from [18]. The species X represents a generic metal ($X = Mg, Na, Fe, C$). Note that the reactions are not necessary equally effective for $n = 4, 6, 8$, e.g. reaction 6 is only important for $n = 8$. Also, the reactions are not sorted by their relative effectiveness, however 7–12 are less important than 1–6 for our discussion. See the main text for more details.

1.	$C_nH + e^-$	\rightarrow	$C_nH^- + h\nu$
2.	$O + C_nH^-$	\rightarrow	$CO + C_{(n-1)}H + e^-$
3.	$O + C_nH^-$	\rightarrow	$CO + C_{(n-1)}H^-$
4.	$O + C_{(n+1)}H^-$	\rightarrow	$CO + C_nH^-$
5.	$X^+ + C_nH^-$	\rightarrow	$X + C_nH$
6.	$H + C_{(n+2)}H^-$	\rightarrow	$C_2H + C_nH^-$
7.	$HCO^+ + C_nH^-$	\rightarrow	$HCO + C_nH$
8.	$HCO^+ + C_nH^-$	\rightarrow	$H + CO + C_nH$
9.	$C + C_nH^-$	\rightarrow	$C_{(n+1)}H + e^-$
10.	$H_3O^+ + C_nH^-$	\rightarrow	$H + H_2O + C_nH$
11.	$N + C_nH^-$	\rightarrow	$C_{(n-3)}H + C_3N^-$
12.	$N + C_nH^-$	\rightarrow	$C_{(n-1)}H + CN^-$

absolute tolerances for the numerical solver to 10^{-12} and 10^{-40} respectively.

We also selected the initial abundances for the different species, as reported in earlier work following table 1 of [15], but we will also show the results by employing model EA2 from [24], that takes into account more metals, i.e. He, F, Na, Mg, Si, P, Cl, and Fe. Furthermore, to guarantee global cloud neutrality in the initial conditions, we choose the number density of the free electrons to be $n_e = \sum_i n_i$ by running the index i over all the positive ions present in the network, while during the system evolution the electron abundance is solved by using the same set of differential equations employed for the other chemical species, that guarantees global charge neutrality by construction. With these initial conditions the reactions including C_nH^- are 236, and a sample of them is listed by table 1. The mutual neutralization reactions of line 5 in the table also include the C^+ partner.

The other parameters of our calculations are the gas temperature $T_{\text{gas}} = 10$ K, the visual extinction $A_V = 10$ mag, the cosmic-ray ionization rate $\zeta = 1.3 \times 10^{-17} \text{ s}^{-1}$ and the dust/gas mass ratio $D = 0$, i.e. a dust-free model. We are aware that the latter assumption could affect the chemical evolution, since dust (and PAHs) may have a large impact on the gas charge [26] and enable surface chemistry [27]; however, since we are interested in the role of the new REA calculations, we consider this approximation satisfactory. To reduce the uncertainties of our analysis this model employs a chemical network taken from KIDA, which includes for the above reactions the most recently available reaction rate coefficients. On the other hand, the calculations reported in [15] are based on the earlier data from UMIST06⁶. It should be also mentioned here that to vary the gas temperature in each run of our model is likely to affect the final abundances, although the chosen value is considered the most emblematic

⁶ <http://udfa.ajmarkwick.net/>.

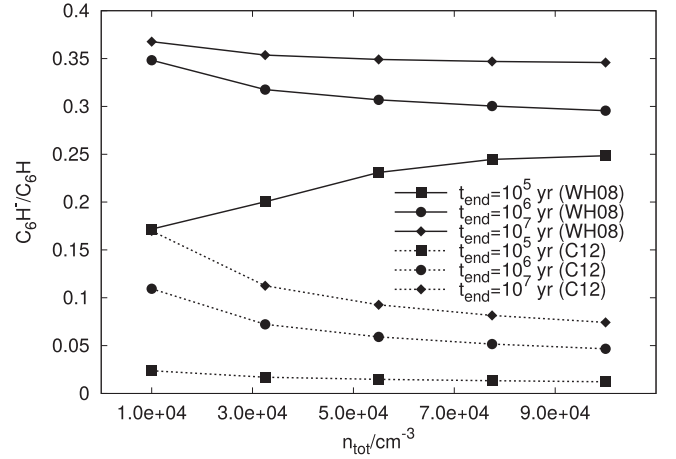


Figure 1. Computed A/N ratios for the C_6H^- anion following the evolutionary model described in the main text. The curves are referring to different times in the evolutionary modelling, i.e. $t_{\text{end}} = 10^5$ s (squares), $t_{\text{end}} = 10^6$ s (circles), and $t_{\text{end}} = 10^7$ s (diamonds), and initial conditions, i.e. from [14] (C12, dashed) and [24] (WH08, solid). The figure reports the changes in the A/N ratio as a function of the total density over the same range discussed by [15].

temperature value when modelling a cold core in a dark molecular cloud. Hence, we shall restrict our analysis to the chosen value of T .

We have run our calculations using the REA rates we had reported in our earlier CSGG modelling [18] and which turned out to be rather close to those produced by the earlier estimates in the HO modelling [17], albeit uniformly smaller than the latter. A detailed, albeit simpler comparison of the REA rates produced by the existing calculations has already been done by us [18] and will not be repeated here. What we shall analyse instead are the effects from scaling the computed REA rates on the A/N ratios of the polyyne anions available from experiments, as well as the effects on their absolute abundances.

4. Results and discussions

In the survey on A/N ratios reported by [15] it was also found by their simulations that, in the case of the C_6H^- anion, there was a positive correlation between the value of that ratio and the total number density. Their figure 5 indicated, in fact, that the ratio varied between $\sim 2.5\%$ and $\sim 4.4\%$ when the hydrogen molecule's density was varied by about one order of magnitude. Similar calculations were carried out by us using the present model with the chemical set-up previously described (see figure 1): the general behaviour is seen to depend on the time evolution (t_{end}) and on the initial conditions employed. In the case of [14], given by the initial conditions (C12), we find a negative dependence of the A/N ratio with the total density that, as expected, converges to a constant value for long evolutions ($t_{\text{end}} = 10^8$ yr). In the case of [24], given by the initial conditions (WH08), we note that the positive trend is found for $t_{\text{end}} = 10^5$ yr, but this

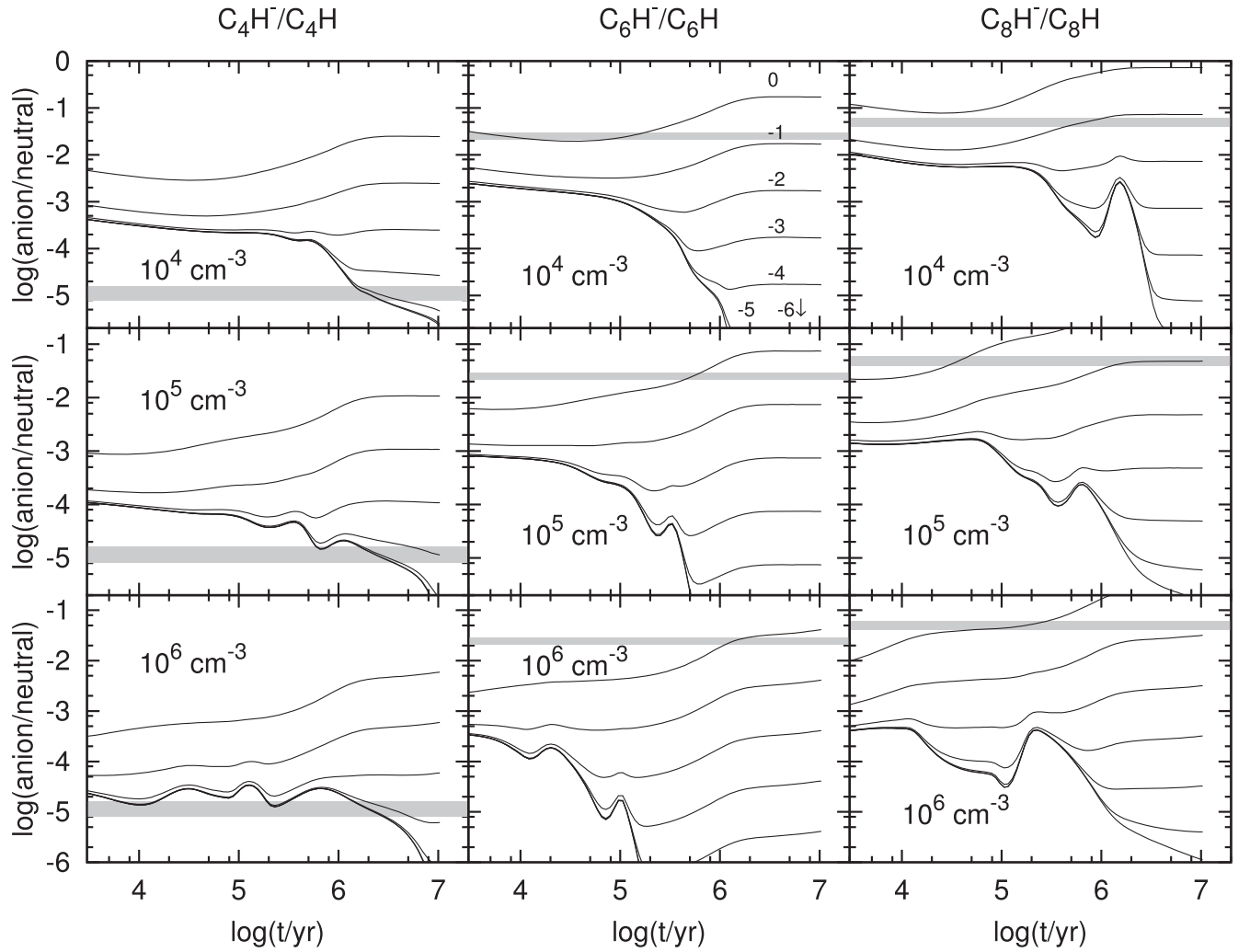


Figure 2. Computed A/N ratios for C_nH^- ($n = 4, 6, 8$), obtained by following the evolutionary model described in the main text. In each of the panels the ratios have been artificially scaled over six orders of magnitude from top to bottom, see as a reference the labels with $\log(n_{\text{tot}}/\text{cm}^{-3})$ in the second panel, top row, where the powers of ten used in the scaling for all panels are explicitly reported. The scalings have been obtained by varying of the same factors the REA rates employed in the calculations. The A/N experimental values (with errors) are given by the grey-shadowed areas in each panel. Note that observed values are valid for TMC-1 CP, that has density of 10^4 cm^{-3} and an age of 10^5 yr . The choice of the varying total densities indicated in each panel are explained in the main text when discussing this figure. The experimental values with their errors are from [15, 22]. Initial conditions are from [14]. The second panel, top row, is also discussed in figure 4.

dependence is cancelled at later evolutionary stages ($t_{\text{end}} \geq 10^6 \text{ yr}$).

The difference with the results found by [14] is due to the different set-up employed by us and the more recent rates and chemical network values used within our modelling. We note here, in fact, that the initial conditions play a key role in determining the comparison with the observed quantities, especially when more metals are present (WH08 case). The effects due to the presence of the dust are not taken into account but, as mentioned in the previous section, they could modify the behaviour found in all models.

We have carried out a further, and more extensive, test on the dependence of the A/N ratios on the total density (i.e. H_2 density) and evolution time for C_nH^- ($n = 4, 6, 8$). In particular, we have run simulations based on three different choices of such densities (see figure 2): the low-density values

typical of a quiescent cloud (10^4 cm^{-3} , upper panels), the middle-range densities relevant for the star-forming regions (10^5 cm^{-3} , middle panels), and the high-density values associated with protostars (lower panels, 10^6 cm^{-3}). Analogously, in figure 3 we report the absolute evolutions of neutral and corresponding anion species for different densities and initial conditions that show a behaviour similar to the one found by [14].

When we examine figure 2, we see there that the ratio for the C_4H^- matches the experimental ratios only when the REA value, initially taken from the calculations of the CSGG or OH models and included in all the simulations of the cloud shown in the three panels of that figure, is reduced by nearly six orders of magnitude. This indicates that, within the quality of our chemical network, the REA path to the formation of that anion must make only negligible contributions to the

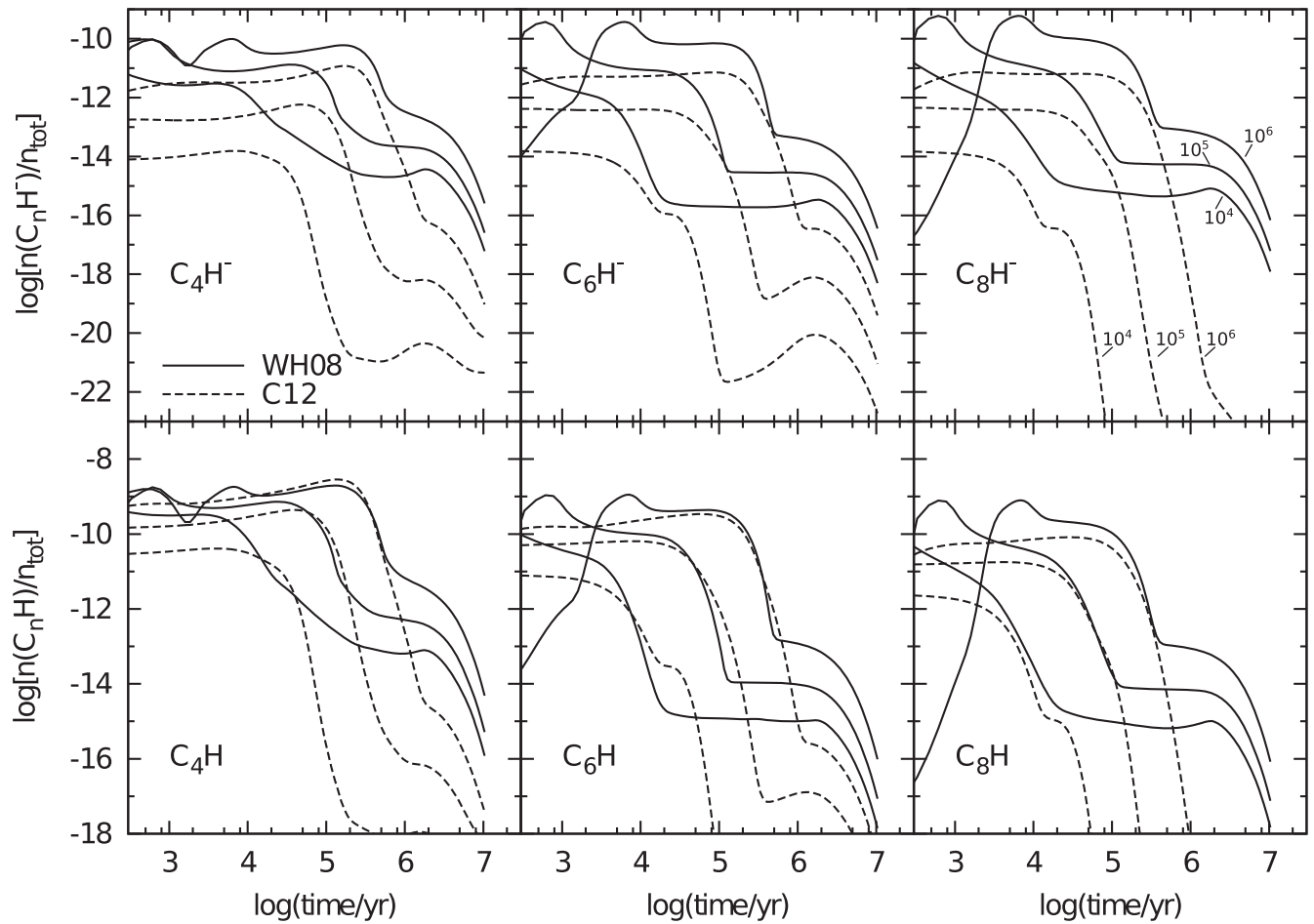


Figure 3. Computed time evolutions for C_nH^- ($n = 4, 6, 8$) and their anions, following the evolutionary modelling described in the main text. In each panel we report the computed evolutions using different choices for the initial conditions: from [24], labelled as WH08, and from [14], labelled as C12. The labels in the third panel, top row, indicate the various values for the total cloud density and are omitted in the other panels because they are the same.

overall rates of its formation. We further see that when the macroscopic system has reached later stages in the time of its evolution, sometime even later than the estimated cloud age, the scaling can be reduced to only about three orders of magnitude to match experimental values. Furthermore, the analysis of the evolutionary models indicates that at low-densities it is chiefly the reaction $O + C_5H^- \rightarrow CO + C_4H^-$ that supports the anions formation while there are no significant contributions to its formation coming from the REA process.

It is important to note, especially at later times in the cloud's evolution, that the results of our simulations reported in the centre- and right-columns of panels of figure 2 for the behaviour for the other two members of the present series of anions indicate a significant role of the REA mechanism (from the CSGG model which we have included in our study) to match the experimental values given by the shadowed areas in all the panels. In fact, the larger anions show that the efficiency of the REA channel to their formations produced by the present CSGG theory is matching the experimental observations: they are in fact reproduced by using less than an order of magnitude reduction of the theoretical values. It is

also interesting to note that the theoretical values we have employed are orders of magnitude smaller than the Langevin-type estimates usually included in the databases: for the C_4H^- case the corresponding value reported is $1.10 \times 10^{-8} (T_{\text{gas}}/300 \text{ K})^{-0.5}$. Likewise, for the cases of C_6H^- and of C_8H^- the Langevin estimates are also much larger than the ones provided by the CSGG theoretical modelling: $6 \times 10^{-8} (T_{\text{gas}}/300 \text{ K})^{-0.5}$. It therefore follows that the values produced by the CSGG model for the REA rates for the longer chain anions are much more realistic than the Langevin rates. They further show a temperature dependence, feature which is absent in the latter approximation [18].

If we now compare the evolutions of the absolute abundances, in figure 3, for both the neutral compounds and their anions, we note that for ages of the cloud larger than 10^6 yr the amount of both the neutral C_nH and of their anions reaches very low concentrations with respect to the total gas density, especially for the initial conditions labelled C12. This suggests that in the employed models the error carried by the A/N ratios after long evolutionary times could become larger than expected, since the uniformly small values of their absolute quantities naturally have a substantial effects on the errors of their ratios. It then follows that the role played by

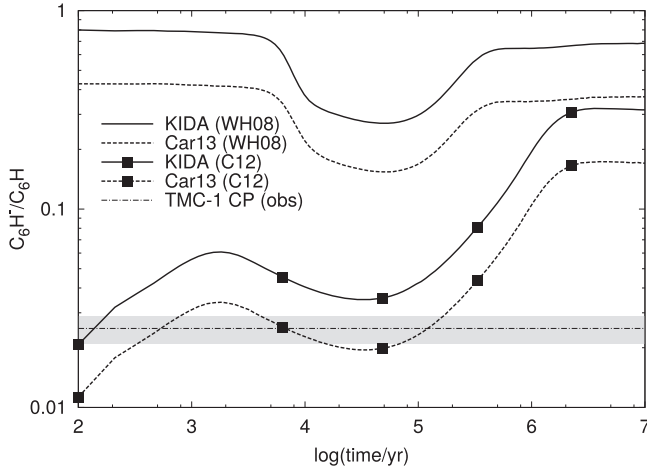


Figure 4. Computed time evolutions of the A/N ratio for C_6H , using different initial conditions, i.e. [14] (C12, lines with squares) and [24] (WH08, lines without squares), and also employing different electron attachment (REA) rate coefficients. The latter are from [18] (Car13, dashed lines) and from the KIDA database (KIDA, solid lines). The observational values from [15] for TMC-1 CP are also reported (dashed-dotted line) in the figure, together with their errors (grey-shadowed area).

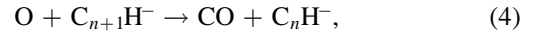
obtaining increasingly more accurate REA rates becomes also crucial in controlling the quality of their A/N ratios.

Another indication of the importance of including the most realistic REA rates is provided, for the case of the C_6H^- anion's A/N ratio, by the evolutionary comparison reported in figure 4, where the low density case associated with the TMC-1 CP conditions of a quiescent cloud [15] are also employed in our calculations. We note here that, when we use the initial conditions employed by [14] (C12), while including the REA rates from the CSGG model [18], the results labelled (Car13) match the observational data for ages that are compatible with that of the TMC-1 CP cloud, i.e. $\sim 10^5$ yr. On the other hand, the A/N ratio given by the present modelling when using the REA rate value given by the KIDA database is larger than the observed one for nearly the whole evolution time. As mentioned in the previous cases, adding more metals to the initial conditions (i.e. using the WH08 prescription) affects the global behaviour of the A/N ratio, as clearly indicated by the upper curves of the present figure 4.

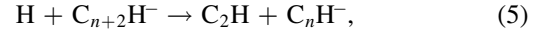
The following general considerations could be made by looking at all the figures' data presented thus far, also keeping in mind the effects from the most efficient chemical reactions already mentioned earlier:

- (i) All the figures consistently show that a reduction in size of the REA rates within the modelling causes an almost linear reduction of the A/N ratios to be compared with observations, in spite of the complexity of the chemical links which are active within each of the networks that we have used in the evolutionary modelling.
- (ii) When the REA rates are reduced by more than five-six orders of magnitude, the 'humps' shown by the time evolution curves, around time evolution values between 10^5 yr and 10^6 yr, were found to be linked to the

following chemical formation channels, an effect occurring independently of the initial conditions:

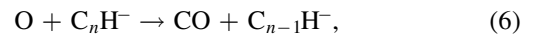


for $n = 4, 6$ at low densities, and $n = 4, 6, 8$ at high densities, while

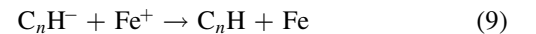
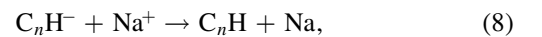
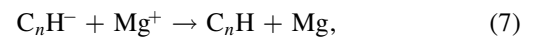


for $n = 8$ at low densities. These reactions turn out to be the main anion formation channels at the times when the REA processes become negligible. Thus, for this reason they represent the lower limits of the anion formation efficiency. Note that both at low and high densities, when REAs are still significant processes in our modelling, the attachment efficiency is always larger than reaction (4), except for $n = 4$, where reaction (4) dominates at low densities.

- (iii) In the database employed here the reactions: $O + C_nH^-$ and $O + C_nH$ have different efficiencies in yielding their products, so that when the REA anion formation rates are very small the chemical kinetics of the anions is faster than the analogous chemistry for neutrals. As expected, when the REA rates are fully operative, or reduced by less than five orders of magnitude, the A/N ratio increases because the REAs reduce the efficiency of the two chemical processes mentioned above. It is important to note here that these reaction rates are still given by the databases as the simple Langevin-type reactions [13], and therefore more accurate calculations, or more modern experiments, on such reactions would help to better clarify this issue.
- (iv) The uniform drops of the absolute densities shown in our model by the data in figure 4 for C_nH^- after time values around 10^5 yr are due to the following contributing reactions:



this being true when using the C12 initial conditions, while for the different choices of WH08 we found that



become an important chemical paths to anion destruction, since more metals are present in the selected cloud's conditions. This result is similar to what we have recently found on CN^- formation [28], where we have shown that when the electron-driven processes become slow and ineffective in forming anions, then other chemical reactions take over and become dominant with respect to the REA mechanism. Furthermore, this inefficiency in the case of the CN^- formation was also shown by the accurate calculations

on the REA path for the same molecule discussed in [21].

- (v) When looking at the C_4H^-/C_4H evolution over time, we see that to match the A/N experimental value [15] requires an electron attachment REA rate which should be $\leq 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. This value, at 10 K, is at least four orders of magnitude smaller than that estimated by the existing calculations with the CSGG modelling [18], which we have employed here, and even smaller than the larger value from the HO modelling [17], which was also around $10^{-8} \text{ cm}^3 \text{ s}^{-1}$. On the other hand, the more recent results from the DFRDOK model [21] include an approximate form of non-adiabatic coupling between the impinging electrons and the molecular vibrations [21]. They found for this system an REA rate of formation around $10^{-16} \text{ cm}^3 \text{ s}^{-1}$ at 30 K. In other words, both the latest modelling for the REA process, and the present modelling that examines several scalings of that rate, suggest that the REA path to C_4H^- formation in the cores of cold molecular clouds should be a more inefficient path than previously indicated.
- (vi) In the case of the C_6H^-/C_6H ratio, the recent experiments by [15] indicate an A/N mean value over all their sources of 3.10%. From the present numerical experiments of figure 2, we see that to match their estimates corresponds to employing in our modelling an REA rate of $5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, which is now only about one order of magnitude lower than the previously calculated values obtained by the CSGG dynamical modelling [17, 18]. Given the uncertainties that we know to exist among several of the chemical rates reported in our employed database (KIDA), one can consider the discrepancy between estimated and computed REA formation rates for this member of the series to be within the expected error bars of the present runs, where the agreement with observations is bested around 10^5 yr.
- (vii) The results of figure 2 for the A/N ratio involving the longest member of the present series, the C_8H^-/C_8H ratio, further indicate that the experimental values between 3.8% and 5% is accurately given when using an REA attachment rate, at 10 K, of about $10^{-8} \text{ cm}^3 \text{ s}^{-1}$. The CSGG computational estimate used in our present study, at 10 K, is $3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$, i.e. only about one order of magnitude larger. This indicates once more that the quantum dynamical models of reference [18] become increasingly more reliable for the larger members of the series, while overestimating REA rates for the smallest members.

In all cases, the large A/N ratio's drops in value as time increases are due to the different chemical efficacy of the reactions $O + C_nH^-$ and $O + C_nH$, where the latter generally exhibits smaller rate coefficients. The slower chemical processes reduce the abundance of the neutrals less efficiently than that of the anions, hence causing the latter to disappear in the dark clouds more rapidly than the neutrals. This behaviour

induces a reduction of their A/N ratios as the evolutionary times of the clouds increase. Analogously, when the A/N ratios increase, the presence of the REA processes offsets the effects of the two reactions with atomic oxygen. They become more significant in controlling anions' formation paths. Our present evolutionary study indicates that the attachment rates existing in the current literature are uniformly larger than those which can match the experimental A/N ratios at 10 K within rather sophisticated chemical networks, as those we have used to describe the molecular cloud's evolutions in time. Finally, we should also note here that we have tested the robustness of our evolutionary model by running it at at least one higher temperature, i.e. at 30 K, and found essentially no changes in all the parameters produced by the model.

Our earlier scattering calculations using the CSGG model [18], which we have employed here within a fairly large chemical network of reactions, had already suggested that the computed REA values using that model were to be considered as upper bounds to the true rates, since no estimates for the autodetachment channels were included explicitly. The present scaling experiments on the A/N evolution in dark molecular clouds confirm that, for the case of the smallest member of the series examined, the actual REA rates have to be smaller than those suggested by calculations: for C_4H^- the rates required to match experimental A/N ratios should be about four orders of magnitude smaller.

On the other hand, as the length of the carbon chain increases, e.g. for C_6H^- and C_8H^- , the CSGG model calculations indicate that, to obtain realistic A/N ratios within the evolutionary model of a dark molecular clouds, our calculated REA rates are only slightly larger: given the general uncertainties for many of the chemical rates contained in the chosen database, the calculated electron attachment rates are closer to reality for the latter molecules than for the case of the C_4H^- anion. As a possible explanation for these differences, it is worth mentioning at this point that C_4H is the only partner molecule in the series which does not possess a critical value for its dipole moment [18] and therefore would not have the dipole-driven metastable states which can contribute to a more efficient REA mechanism, as we have explained earlier in the Introduction. Since the REA rates are expected to increase with molecular complexity (e.g. for larger polyynes), it seems reasonable to surmise that rates obtained using the CSGG model for the longer C-bearing chains of these molecular systems [18] would be likely to match even better future possible observations of A/N ratios in such longer chains.

5. Present conclusions

The present numerical experiments indicate that the efficiency of the electron attachment processes, and therefore their role in forming anions of the linear polyynes discussed in the present work, varies a great deal within the members of the series and is strongly linked to the chemical features of each specific molecular structure.

As a specific example, we have shown that the subcritical dipole moment in C_4H^- , and its fairly small number of vibrational degrees of freedom, can be taken as chemical indicators and physical reasons for its markedly smaller REA rates at low temperatures in comparison with those for C_6H^- and C_8H^- , both longer molecules with larger permanent dipoles.

Our computational modelling of REA processes, the CSGG model based on scattering calculations [18], has been proposed a few years ago and should provide upper bounds to the actual rates of attachment since no direct treatment of autodetachment channels was included in it. The inclusion of such effects for the two smallest members of the polyynic series in the later work of [21] has shown that the corresponding REA rates would be much smaller than expected because of the efficient competition provided by auto-detachment channels.

The direct testing of our CSGG scattering modelling, once we employ it within the evolutionary chemical model discussed in the present study, is therefore showing that REA channels to anion formation are of negligible importance for producing C_4H^- molecules. One should note here that the above is valid within the general quality of the chemical network which we have employed, and which is the most up-to-date selection of chemical rates currently available for such evolutionary models.

The same REA mechanism however contributes to the final densities of C_6H^- and C_8H^- anions with rates that are two-to-three orders of magnitude larger than that of the shorter chain of polyynes. Such rates are now very close to the values proposed by the CSGG and the HO models [17, 18], thereby validating their estimates for these specific rates.

The various features of the chemical network employed in the present modelling also suggest that the evolutionary age (and then the initial conditions) of the object under consideration can play a significant role since the chemical reactions that produce both the neutral members and their anionic counterparts become less efficient over longer time spans and consistently reduce the absolute densities of both members in the A/N ratios we are discussing. As a consequence of it, the expected error bars for such ratios would increase and thus make them likely to be affected by much larger errors.

In conclusion, the present detailed study on the effects of REA rate sizes within a fairly large set of chemical reactions, specific for the members of the C-bearing linear polyynes, indicates that the values of their A/N ratios can vary a great deal within the members of that series and that their specific chemical features directly influence the relative importance of the REA formation of their stable anions. The desire is that such quantitative analysis of the comparison between observational data and computed data from evolutionary models can help our community to better understand the role of the REA mechanism within the larger scene of anion formation in molecular clouds.

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