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H^- PHOTODETACHMENT IN ATOMIC PHYSICS AND ASTROPHYSICS

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The negative hydrogen ion H^- plays an important role in the continuum opacity of late-type stars and in the kinetics of low-metallicity gas. We review the H^- photodetachment cross section along with other processes involving H^-. We address H^- in early Universe chemistry, the role of oscillator-strength sum-rules in constraining its continuum cross section, and the influence of auto-detaching resonances on the efficiency of H^- photodestruction in the reionization era.

Keywords: atomic processes - early universe - galaxies: formation - galaxieis: high redshift

1. Introduction

While H_3^+ is a key species in the complex chemistry of metal-rich interstellar clouds, another two-electron hydrogen ion, H^-, plays a similar role in low-metallicity gas. H^- has long been known to be an important opacity source in the sun and other late-type stars, but it has yet to be detected through resonant spectroscopic features in any astronomical source. In this article, we review the processes important in the non-equilibrium chemistry of H^- with a particular focus on photodetachment and radiative attachment. We discuss the various astronomical environments where H^- plays a fundamental role, the history of H^- investigations from an atomic physics perspective, and the many contributions that Alex Dalgarno has made to the study of this anion.

2. H^- in Astrophysics

It has often been the case that problems in astronomy have driven advances in atomic physics and the hydrogen negative ion is a prime example. In the 1930s, the continuum absorption in the solar spectrum, as well as that of similar late-type stars, was not understood. It was first proposed by Wildt[1] that H^-, which has a small electron affinity of 0.754 eV, might be responsible for this continuum opacity due to its bound-free absorption. This lead Chandrasekhar[2] and Chandrasekhar and Breen[3] to make the first quantum mechanical calculations of bound-free and free-free absorption coefficients for this two-electron anion, respectively. This early history of H^- has been discussed by Rau[4] and recently summarized in Ross *et al.*[5] who mention that the role of H^- as the dominant opacity source in the solar visible and infrared (IR) spectrum was cemented in 1945 by good agreement between Chandrasekhar's calculations and empirically-derived absorption coefficients derived for the Sun by Münch.[6]

The role of H^- as a continuum opacity does not, however, constitute a direct detection. There is a peak in the photodetachment cross section near 0.8 μm, but it is broad. H^- is interesting in that it has only one bound singlet state, the electronic ground level $1s^2\ {}^1S$, and therefore lacks a bound-bound electric dipole spectrum of electronic transitions. These facts make the direct detection of H^- problematic outside the laboratory. However, it is well known, as will be discussed below, that a series of auto-detaching resonances exist in the ultraviolet (UV). These features result from the simultaneous ejection of one electron to the continuum and the excitation of the remaining electron into excited ${}^2P$ states of the residual neutral atomic hydrogen. The physics of these resonances will be discussed below, but their existence prompted searches for them in the interstellar medium (ISM) in the 1970s with the UV satellite *Copernicus*[7] and more recently with the *Far Ultraviolet Space Explorer (FUSE)*.[5] Unfortunately, these searches have only been able to place an upper limit on the H^- abundance in the ISM.

Nevertheless, H^- is believed to play an important role in a variety of astronomical contexts. We consider a number of cases focusing primarily on photo-processes and non-equilibrium chemistry as opposed to opacities.

2.1. *Primordial Gas*

Prior to the formation of the first star or luminous object, the early Universe consisted of a nearly homogeneous expanding and cooling gas of primordial species dominated by protons and electrons. Hydrogen atoms formed by radiative recombination at the start of the recombination era. It was first proposed by McDowell[8] that the first neutral molecule, H_2, would form via the associative detachment process

$$H^- + H \longrightarrow H_2 + e^- \qquad (1)$$

following the creation of H^- via radiative attachment

$$H + e^- \longrightarrow H^- + \nu. \qquad (2)$$

Interestingly, McDowell quotes an unpublished estimate of process (1) by Dalgarno. In the same year, Dalgarno and Kingston[9] presented calculated rate coefficients for process (2), to be discussed further below.

However, the abundance of H^- is controlled by two processes that can efficiently destroy it: photodetachment

$$H^- + \nu \longrightarrow H + e^- \qquad (3)$$

and mutual neutralization

$$H^- + H^+ \longrightarrow H + H. \qquad (4)$$

In the post-recombination era of the early Universe, the photons in process (3) are those due to the cosmic background radiation (CBR) field. The CBR is a black-body corresponding to a radiation temperature of $T_r = 2.7(1+z)$ K, where z is the redshift. Once the radiation temperature falls below ~ 500 K, photodetachment becomes inefficient and process (1) becomes the dominant formation mechanism of H_2. Studies of the hydrogen molecular chemistry in the early Universe have been carried out by

numerous authors.[10–12] Due to the expansion of the Universe, the fractional abundance of H_2 with respect to atomic hydrogen reaches a value of only a few times 10^{-5} in the post-recombination gas for $z < 100$.

2.2. *Radiative Feedback from Primordial Objects*

At some intermediate redshift ($z \sim 20-50$), the small perturbations in the primordial gas density will grow and ultimately collapse to form a star or other luminous object. H_2 will form by the same processes as discussed in Section 2.1 and it is radiative cooling of H_2 which provides the dominant means of removing the heat generated by the adiabatic collapse as the gas density grows. The efficiency of H_2 cooling depends on the abundance of H_2 which is dependent on the availability of free electrons, H atoms, and H^-. Since the CBR is the only radiation field present and the temperature of the CBR is small by this redshift, H^- photodetachment is not important. While the efficiency of H_2 ultimately declines as the gas becomes optically thick to the cooling lines ($\sim 10^8$ cm^{-3}), the cloud continues to collapse until a star is formed.

The first stars, known as Population III stars, are believed to have been more massive than contemporary Population I stars. Therefore they were likely to have large effective temperatures and would have produced copious UV, FUV, and x-ray radiation. This radiation would then have propagated into the surrounding primordial gas resulting in two possible feedback effects on the abundance of H_2: i) enhancement[13,14] or ii) suppression.[15,16] In the former case, a so-called positive feedback effect, the UV photons ionize atomic H producing electrons which drive the chemistry enhancing the formation of H_2. Since H_2 is the dominant coolant in primordial gas, it was proposed by Haiman, Rees, and Loeb[13] that this effect would accelerate the gravitational collapse and eventual fragmentation of high redshift halos. In turn, this would lead to increased efficiency in Pop III star formation and acceleration of the UV background radiation field responsible for reionization.

In the alternate scenario, UV photons within the Lyman and Werner bands of H_2, energies between $\sim$11 eV and the H ionization threshold, can penetrate large primordial clouds due to the small optical depths of these lines. These photons can then destroy H_2 by absorption to electronically excited states followed by fluorescent decay into the continuum of the electronic ground-state – the so-called Solomon process:

$$H_2 + \nu \rightarrow H_2^* \rightarrow H + H + \nu'. \qquad (5)$$

This results in a negative feedback on the abundance of H_2, n_{H_2}, for which an equilibrium estimate

$$n_{H_2} = \frac{k_1 n_H n_{H^-}}{\beta_5} \quad (6)$$

where k_1 is the rate coefficient for associative detachment, β_5 the rate for process (5), and n_H and n_{H^-}, the number densities of H and H^-. A reduction in the abundance of H_2 will directly suppress its cooling efficiency which indirectly influences the efficiency of subsequent Pop III star formation.

Numerous authors have considered such feedback effects, but it is unclear which scenario will dominate.[13–17] Further, only UV photons in the Lyman and Werner bands have been addressed. It was recently pointed out by Glover[18] and Chuzhoy, Kuhlen, and Shapiro[19] that the negative feedback effect could be further enhanced by considering photodetachment of H^-, process (3). Photons with energies between the H^- photodetachment threshold (0.754 eV) and the Lyman limit could efficiently destroy H^- suppressing the formation of H_2 which occurs through the associative detachment process (1).

Chuzhoy *et al.*[19] considered a number of situations and estimated the effect of H^- photodetachment with the suppression factor

$$F_b = 1 + \frac{\beta_3}{k_1 n_H} \quad (7)$$

where β_3 is the H^- photodetachment rate. The abundance n_{H^-} is divided by F_b which directly reduces the abundance of H_2 as given in Eq. (6) assuming that only the three considered processes are important for H_2 formation. They considered the following radiation fields for photodetaching H^-: i) H recombination lines below 10.25 eV, which result from photoionization from the first luminous sources on the surrounding gas, ii) black-body radiation from massive Pop III stars with a upper energy cut-off at the Lyman limit, iii) a power-law spectrum typical of miniquasars, and iv) a FUV background generated from x-ray sources.

Through semi-empirical arguments, Chuzhoy *et al.* deduced that the abundance of H_2 would be significantly reduced, by a factor of $F_b \sim 1000$, if photodetachment of H^- due to recombination photons (case i) was considered. This reduction was further increased by from 10% to a factor of 10 ($F_b \sim 1100 - 10,000$) if continuum black-body flux from massive Pop III stars was added (case i and case ii). The largest suppression factor occurs for the smaller mass stars which have lower effective temperatures $T_{\rm eff}$.

Instead of a black-body spectrum, a power-law spectrum can be adopted which has the typical form

$$J = J_{21}\left(\frac{E_{\rm ph}}{E_H}\right)^{-\alpha} \quad (8)$$

where J_{21} is the intensity in 10^{-21} ergs cm^{-2} Hz^{-1} sr^{-1}, $E_{\rm ph}$ the photon energy, E_H the ionization energy of H, and α the power-law index. For $\alpha = 1.7$, typical of a miniquasar, Chuzhoy *et al.* find a further suppression enhancement, or $F_b \sim 5000$ (case i and case iii).

Chuzhoy *et al.* considered only the background H^- photodetachment cross section based on a fit to the calculations of Wishart[20] as shown in Fig. 1. Recently, Miyake *et al.*[22] have shown that the contribution from the auto-detaching resonances, not considered by Chuzhoy *et al.*, could be significant. If we consider the ratio of photodetachment rates due to the background (b) and the sum of the background and resonances (r+b), this is approximately equal to the H_2 suppression factor due to H^- photodetachment through the resonances only

$$\beta_3{}^{\rm r+b}/\beta_3{}^{\rm b} \sim F_{\rm r+b}/F_{\rm b} = F_{\rm r}. \quad (9)$$

Therefore, the total H_2 suppression factor is $F = F_b \times F_r$. Here and in Miyake *et al.*, the H^- photodetachment cross section of McLaughlin *et al.*[21] is adopted in the computation of F_r.

For the scenario of black-body radiation from a Pop III star (case ii), Miyake *et al.* found an additional enhancement with the suppression factor typically increasing by ~5% for 25,000 K and asymptotically exceeding $F_r \sim 1.2$ as $T_{\rm eff}$ exceeds 150,000 K. This behavior is different from the results of Chuzhoy *et al.* who found the black-body contribution to increase with decreasing $T_{\rm eff}$. Overall the effect of the black-body field becomes less important with $T_{\rm eff}$ since the majority of the intensity falls beyond the 13.6 eV cut-off. Nevertheless, the suppression factor is doubled (case i and ii) for $T_{\rm eff} = 40,000$ K with the resonant contribution increasing this by 20%.

Miyake *et al.*[22] also considered the possible enhancement due to the H^- auto-detaching resonances for power-law spectra. Quasars typically have power-law radiation fields for $\alpha \sim 0.5$ - 0.7, massive black holes $\alpha \sim 1$, and the high redshift intergalactic medium (IGM) $\alpha \sim 0.7$ - 1. Constraining the radiation field to photon energies between 10 and 13.6 eV, a resonant enhancement factor of $F_r \sim 1.8$ was found, insensitive to the power-law index over the range $\alpha = 0.1 - 5$. This photon energy bin includes the H Lyman lines, the H^- resonances, and the H_2 Lyman-Werner bands, up to the Lyman limit. If the background radiation field after the formation of

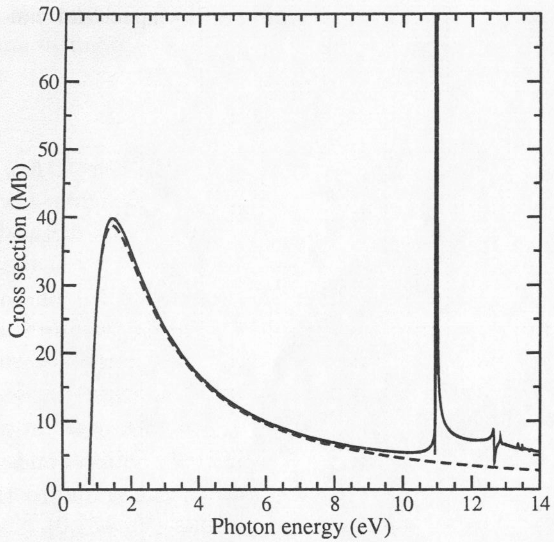

Fig. 1. H^- single photodetachment cross sections. Background from fit to Wishart[20] (dashed line); full cross section from McLaughlin *et al.*[21] (solid line).

the first luminous objects was dominated by miniquasars, or similar UV sources, there would have been a significant negative radiative feedback effect on the creation of H_2 and its cooling efficiency and on the ability of the residual primordial gas to coalesce into another generation of primordial stars[a]. The contribution from H^- auto-detaching resonances are seen to be significant and should be accurately treated in future models. A key component therefore, is the accuracy of the H^- photodetachment cross section including the shape, magnitude, and position of the resonances. In the next section, we describe the status of the atomic physics of H^-.

3. H^- in Atomic Physics

3.1. *Non-resonant Photodetachment*

The background photodetachment cross section has been studied by numerous authors using a variety of techniques following the original calculations of Chandrasekhar.[2] A chronological, but not comprehensive, list includes Geltman,[23] Broad and Reinhardt,[24] Stewart,[25] Wishart,[20] Abrashkevich and Shapiro,[26] Venuti and Declava,[27] Pindzola and Robicheaux,[28] Kheifets and Bray,[29] Pazdzersky *et al.*,[30] and Frodov.[31] Experimental studies of the photodetachment cross section within a few eV of the threshold were performed by Branscomb and Smith,[32] Smith and Burch,[33,34] and Popp and Kruse.[35] Reasonable agreement has been obtained between the later calculations and the measurements. Typically the cross sections of Wishart[20] have been adopted in most astrophysical modeling applications. McLaughlin *et al.*[21] have performed new calculations using the eigenchannel R-matrix[36] and R-matrix plus pseudo-state[37] method. A combination of the new calculations, previously published results, and measurements were merged to obtain a photodetachment cross section that satisfies a number of oscillator strength sum rules, similar to the approach adopted by Yan, Sadeghpour, and Dalgarno[38] for photoionization of He and H_2. This recommended cross section of photodetachment of H^- was adopted for the astrophysical environments presented in the previous section.

[a]Note that since the H^- mechanism for forming H_2 is suppressed, other routes such as the charge exchange reaction $H + H_2^+ \rightarrow H_2 + H^+$ would become more important. However, the destruction of H_2^+ due to photodissociation via the FUV radiation field would also contribute to a negative feedback effect.

3.2. *Resonant Photodetachment*

As mentioned in the Introduction, while H^- contains only one electronic singlet state, it possesses a rich set of doubly excited states embedded in the one-electron continuum. These resonant states auto-detach to $H(n) + e^-$, with $n \geq 2$. These resonant structures were first studied theoretically by Macek[39] and observed in the elastic scattering experiments of McGowan, Williams, and Carley.[40] Later experiments summarized in Cohen and Bryant[41] and Balling *et al.*[42] have mapped out the resonances up to and including $n = 8$. Extensive theoretical calculations by Broad and Reinhardt,[24] Sadeghpour *et al.*,[36] Tang and Shimamura,[43] and Kuan *et al.*,[44] among others, have quantitatively reproduced the measurements. In the $H(n = 2) + e^-$ channel, there are three infinite series of Rydberg Feshbach resonances converging to the $H(n = 2)$ threshold, including a sharp Feshbach resonance just below the threshold at 10.924 eV and a broad shape resonance just above the threshold at 10.972 eV. The resonances for $n \geq 5$ occur at photon energies greater than the Lyman limit and are therefore not relevant in most astrophysical applications. Nevertheless, they contribute to the oscillator strength sum rules, and to ensuring the accuracy of the total cross section, as discussed below. New R-matrix calculations of the resonances up to $n = 8$ are presented in McLaughlin *et al.*[21]

3.3. *Oscillator Strength Sum Rules*

It was pointed out by Dalgarno and Ewart,[45] that the accuracy of the H^- photodetachment cross section could be checked by comparing the continuum oscillator strength moments $S(k)$ given by

$$S(k) = \int \frac{df}{dE}(E_0 + E)^k dE \qquad (10)$$

to other values obtained from initial state properties. The latter, which usually involve initial state matrix elements, can be computed to high accuracy (cf. Dalgarno and Lynn[46]). In Eq. 10, E is the photoelectron energy, E_0 the electron affinity of H^-, and $\frac{df}{dE}$ is the differential oscillator strength for absorption into the continuum. This oscillator strength is related to the photodetachment cross section as $\sigma(E) = 4.03 \times 10^{-18} \frac{df}{dE}$ cm^2, and the photon energy is $E_{ph} = E_0 + E$. In Table 1, "exact" values of the sum rules for $k = -3$ to 2 are summarized from the most recent calculations of Pipin and Bishop[47] and Bhatia and Drachman[48] and using the matrix elements tabulated by Drake.[49] These are compared to the sum rules computed using Eq. (10) and the cross section deduced in McLaughlin *et al.*[21] for single, double, and total detachment. The agreement is seen to be very good for $k = -3$ to -1, but begins to deteriorate for larger values of k. For the astrophysical applications discussed here, this is not a significant issue as the larger values of k are dominated by the higher-energy tail of the cross section which falls-off as $E_{ph}^{-7/2}$. Note the sum rules for k larger than 3 are not defined as the integral in Eq. (10) diverges.

Table 1. Computed Sum Rules for H^-.

Sum Rule	"Exact"	Single	Double	Total
$S(2)$	1.37855	1.261	0.051	1.311
$S(1)$	0.747508	0.596	0.027	0.623
$S(0)$	2	1.693	0.025	1.718
$S(-1)$	14.9685	14.351	0.028	14.379
$S(-2)$	206.165	206.27	0.035	206.30
$S(-3)$	3773.40	3807.01	0.046	3807.05

3.4. *Radiative Attachment*

With an accurate form of the photodetachment cross section, the radiative attachment (process 2) rate coefficient is readily obtained via detailed

balance. Using the photodetachment cross sections of Geltman[23] with extrapolations to higher energies by Dalgarno and Ewart,[45] Dalgarno and Kingston[9] computed the radiative attachment rate coefficients from ~1000 to 20,000 K. Thirty-five years later, Stancil and Dalgarno[50] repeated this calculation using more recent theoretical and experimental cross sections and extended the rate coefficients down to 20 K. Both calculations are shown in Fig. 2 and are seen to be in very good agreement for the range of overlapping temperatures. Radiative attachment rate coefficients computed with the recommended cross sections of McLaughlin *et al.*[21] are found to be in excellent agreement with the results of Stancil and Dalgarno.[50] In terms of early Universe postrecombination models, Stancil *et al.*[11] adopted the Stancil and Dalgarno[50] values, while Galli and Palla[10] adopted a fit to the rate coefficients of de Jong.[51] The two fits are in reasonable agreement, with the Galli and Palla values being typically 5% smaller for $T < 2000$ K. The fits do start to significantly diverge above 5000 K. These differences in H^- radiative attachment rate coefficients should not, however, significantly impact the predictions of the abundances of H^- and H_2.

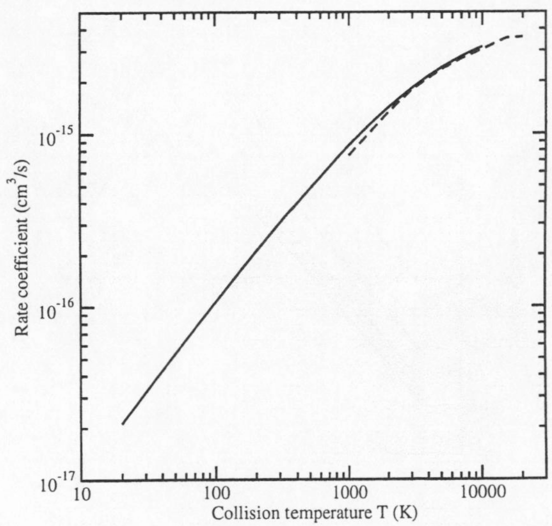

Fig. 2. H^- spontaneous radiative attachment rate coefficients as a function of collision temperature. Stancil and Dalgarno[50] (solid line); Dalgarno and Kingston[9] (dashed line).

3.5. *Stimulated Radiative Attachment*

As intense radiation fields are generally a significant feature of most astrophysical environments, stimulated formation processes may play a role in the chemistry. Stancil and Dalgarno[52] investigated stimulated radiative association of LiH due to the high redshift CBR field. They later extended this work to the formation of H^- by[50]

$$H + e^- + \nu \longrightarrow H^- + \nu + \nu. \quad (11)$$

Fig. 3 displays the rate coefficients for spontaneous plus stimulated radiative attachment for various black-body radiation temperatures T_r. The effect of stimulated attachment was found to be small for $T_r < 3000$ K, because the H^- electron affinity is 0.754 eV (~9000 K), but the enhancement grows rapidly with T_r for $T_r > 5000$ K. However, Stancil and Dalgarno[50] found that the process had at negligible effect on H^- formation in the early Universe. Stimulated radiative effects may play a role when the residual primordial gas is exposed to radiation from the first stars, as discussed above, providing a positive feedback effect, though this has yet to be studied.

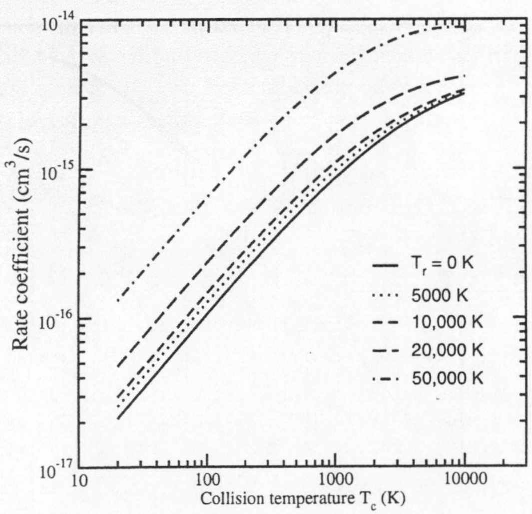

Fig. 3. H^- total (spontaneous plus stimulated) radiative attachment rate coefficients as a function of collision temperature T for various blackbody radiation temperatures T_r. From Stancil and Dalgarno.[50]

3.6. *Other H^- Destroying Processes*

In addition to photodetachment, associative detachment (1) and mutual neutralization (4) are the primary destruction mechanisms for H^-. Calculations for the former process have been made by Dalgarno and Browne,[54,55] Bieniek and Dalgarno,[56] Launay *et al.*,[57] and Cízek *et al.*,[58] while only one experimental investigation has been performed by Schmeltekopf *et al.*[59] Glover, Savin, and Jappsen[53] have pointed out that while there is generally good agreement between the calculations and the measurement, the most recent calculation by Cízek *et al.*, based on a more accurate H_2^- potential energy surface, is a factor of three times larger.

Mutual neutralization of H^- with H^+ has been studied since the early work of Bates and Lewis,[60] but results relevant to astrophysics are primarily limited to the measurement of Moseley *et al.*[61] and the quantum calculation of Fussen and Kubach.[62] Based on the available data, Dalgarno and Lepp[63] deduced rate coefficients which have been adopted in many astrophysical models. However, Glover *et al.*[53] found that the available rate coefficients actually have a scatter of an order of magnitude. Glover *et al.* then investigated the effects of uncertainties in these processes on H_2 formation and cooling in primordial halos. While the uncertainties in processes (1) and (4) led to small variations in protogalaxies forming from cold primordial gas, they found a significant impact if the objects formed from a hot, highly ionized gas. Such a situation is typical of fossil HII regions which are believed to be sites for second generation primordial star formation. More work is therefore needed on both processes to improve models of such environments.

4. Summary

Throughout his career Alex Dalgarno has made, and continues to make, seminal contributions to our understanding of the structure and dynamics of H^-, and other two-electron atomic and molecular species. His remarkable physical insight has shown that even an intractable problem, such as the few-electron Hamiltonian, can be fruitfully attacked with increasing precision, once empirical and numerically accurate facts are employed in a self-consistent manner. Such an approach has allowed us to postulate the importance of H^- photodetachment for the epoch of reionization, where we have been aided by advances in the experimental and theoretical understanding of the absorption continuum and auto-detaching resonant structure of H^-. This knowledge should allow for an accurate treatment of the photodetachment process in astrophysical simulations, once the resonant structure is correctly incorporated. On the other hand, heavy-particle collision processes such as associative detachment and mutual neutralization, important H^- destruction mechanisms, are not known with any sufficient degree of confidence and require further study. All of these processes play key roles in a variety of astrophysical environments. In particular, H^- is a vital, cohesive species that controls the efficiency of Population III star formation, and may influence the time scale of the reionization era of the early Universe.

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