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Radiative electron attachment to small linear carbon clusters and its significance for the chemistry of diffuse interstellar clouds

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Abstract

Recent spectroscopic studies of carbon chain anions in the gas phase, and more specifically of C_7^-, have brought insight into the long-standing mystery of the unexplained diffuse interstellar bands. Previously, negative ions had not been considered highly abundant in interstellar clouds, and the question of efficient mechanisms leading to their formation had not been investigated in great detail. This work presents a statistical calculation of the rate coefficients for radiative attachment of an electron to small linear carbon clusters containing 4–9 atoms. We conclude that for molecules with 6 or more C atoms, the attachment occurs on every collision at the low temperatures of diffuse interstellar clouds. (Int J Mass Spectrom 201 (2000) 135–142) © 2000 Elsevier Science B.V.

Keywords: Radiative electron attachment; Carbon cluster anion; Interstellar clouds

1. Introduction

The diffuse interstellar bands (DIBs), which are broad features of unknown origin in the absorption spectrum of the interstellar medium in the direction of background stars, have been a mystery for more than 70 yr. Many species of different kinds and nature have been proposed as candidates for the source of this phenomenon [1]. It is believed that most, if not all, of the carriers are molecules in the gas phase, but the answer to the question as to the possible gas-phase carriers that can form and survive under diffuse interstellar conditions is unclear. Diffuse interstellar clouds have typical gas densities $n = 10–10^3$ cm^{-3}, temperatures in the range 50–100 K, and total continuous extinction A_V of less than 2 mag by dust particles at visual wavelengths [2]. Such clouds appear to contain gas mainly in the form of atoms and atomic ions, with a sparse population of interstellar molecules and some dust grains. Ultraviolet radiation penetrates through the diffuse interstellar clouds, and atoms with ionization potentials less than 13.6 eV are photoionized and contribute electrons. It has been suggested that the candidate species for the DIBs need to be large molecules (50 atoms or more, [3]) to be photostable in the interstellar radiation field. The absence of DIBs in the near-UV part of the spectrum excludes many large neutral molecules as carriers, but perhaps not those that have large conjugated systems. Recent laboratory investigations on the electronic absorption spectra of linear carbon anions in Ne matrices [4] followed by gas phase studies [5,6] have brought new hope for at least partially solving the

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DIB mystery. The origin bands in the electronic spectra of C_6^-, C_7^-, C_8^-, and C_9^- appear to match DIBs and, most importantly, the bands of linear C_7^- appear to show very good agreement not only with position but also with the equivalent bandwidths of five DIBs. The assignment has been partially confirmed for four out of these five DIBs with high resolution visible spectroscopy of stars [7], although some discrepancies remain [8].

This discovery was a bit of a surprise for two reasons. First, only atomic and diatomic neutral species and positively charged ions have been observed up to now in diffuse interstellar clouds and negative ions were not thought to be highly abundant. Second, C_7^-, as well as other small chain clusters, was considered rather fragile to be photostable under the harsh interstellar conditions, despite its large electron affinity [5]. Under UV irradiation in the laboratory, both photodetachment and photodissociation of carbon cluster anions have been detected, with complete domination of the electron photodetachment channel for the ions between C_4^- and C_7^- [9]. The detection of C_7^- is plausible only if its formation mechanism counteracts its rapid destruction. Carbon is the fourth most abundant element in the universe and there are a number of theoretical scenarios to explain how neutral linear carbon chains can be formed on grains or in the gas phase of interstellar space. One such scheme for carbon chains and molecules as complex as fullerenes in diffuse interstellar clouds has been proposed by Bettens and Herbst [10]. Carbon insertion and radiative association reactions between C^+ and bare carbon clusters C_n or unsaturated hydrocarbons are critical to the growth of the linear carbon chains. Dissociative recombination of C_nH^+, C_n^+ and other cations with electrons leads to the formation of neutral carbon chains, which upon radiative electron attachment can produce the carbon cluster anions of interest.

Prompted by the probable detection of C_7^-, Ruffle et al. [11] have expanded an earlier model of diffuse interstellar clouds [12] to account for the production of linear carbon chain anions. These authors assumed a rate coefficient $k = 1 \times 10^{-7}$ cm^3 s^{-1} for radiative electron attachment to C_n $(n = 7\text{–}23)$. For C_7^- in particular, this value is an order of magnitude smaller than the s-wave collisional rate coefficient [13], and an increase in this rate coefficient has been suggested as the most likely remedy to obtain better agreement between the model results and the observed fractional abundance of C_7^- [11]. The purpose of this article is to report the evaluation of radiative attachment rate coefficients leading to the formation of small linear carbon cluster anions using a statistical phase space approach.

Section 2 of this article contains a description of the theoretical strategy we have used for the calculations and a discussion of our results. A brief conclusion is given in Sec. 3.

2. Theoretical treatment and results

Radiative electron attachment can be defined as a process in which a gas phase neutral species collides with an electron to form a temporary negative ion (also called a "collision complex"), which stabilizes itself by emitting a photon. Once the collision complex is formed (with rate coefficient k_f), there are four possibilities for its termination: electron detachment (with rate coefficient k_d), radiative stabilization (k_r), collisional stabilization (k_c), and decomposition to products different from the reactants (k_{dec}) [14]. The possibilities for complex termination are schematically given below:

$$C_n + e^- \underset{k_d}{\overset{k_f}{\rightleftarrows}} [C_n^-]^* \xrightarrow{k_r} C_n^- + h\nu \tag{1}$$

$$[C_n^-]^* + M \xrightarrow{k_c} C_n^- + M \tag{2}$$

$$[C_n^-]^* \xrightarrow{k_{\mathrm{dec}}} C_k^- + C_m, \qquad k + m = n \tag{3}$$

and all involve unimolecular rate coefficients (s^{-1}) except for the collisional stabilization. Because of the low densities of gas-phase species in the interstellar medium, which is a vacuum by laboratory standards, collisional stabilization can be disregarded. The possibility for decomposition to smaller carbon chains can be ignored as well because these reactions are endothermic and thus energetically unfavorable [15]. The remaining process, of interest to this study, is described by Eq. (1). An approach based on the statistical state-specific phase space theory [16,17] and similar to that of Petrie and Herbst [13] will be used for the calculation of the radiative attachment rate coefficient k_{ra}. Although to the best of our knowledge no other phase-space treatment of radiative attachment has appeared in the literature, the formation of a temporary negative ion has been treated extensively [18,19] by a variety of approaches. Phase space approaches to electron-impact dissociation [20], dissociative recombination [21], and electron detachment [22] have been reported.

Linear ground states are well known for the carbon cluster neutrals with an odd number of C atoms and for the anions C_n^-, with $n = 4$–9 [23]. On the other hand, the neutral C_4, C_6, and C_8 species have linear and cyclic isomeric structures of comparable stability [23,24], and we have limited our calculations to electron attachment to the linear isomers of C_n, where $n = 4$, 6, and 8. The C_n linear chains with an even number of C atoms have ${}^3\Sigma_g^-$ ground state symmetry, and those with an odd number have ${}^1\Sigma_g^+$ (closed-shell) symmetry, while the carbon anion chains C_n^- ($n = 4$–9) have $X\ {}^2\Pi_u$ or $X\ {}^2\Pi_g$ symmetry [25].

Following symmetry selection rules, an s-wave attachment to C_n ($n =$ odd) with ${}^1\Sigma_g^+$ symmetry ground state is expected to form a ${}^2\Sigma_g^+$ state. Similarly, attachment to C_n ($n =$ even) may initially form an anion in a ${}^2\Sigma_g^-$ or ${}^4\Sigma_g^-$ state. To account for the formation of ${}^2\Pi$ ground and excited states of the temporary negative ion, one may need to either consider p-wave capture or allow for vibronic coupling. According to quantum scattering theory, p-wave attachment is very unlikely to occur at the low temperatures ($T = 50$–100 K) and corresponding energies ($E = 0.005$–0.01 eV) in diffuse interstellar clouds. Such a problem of symmetry has been detected previously in experimental studies of low energy scattering from benzene, in which only f-waves can attach according to electronic symmetry, but s-waves have been observed to make a contribution, presumably via vibronic coupling [26]. In the particular case of C_4^-, the dipole-forbidden transition $A\ {}^2\Sigma_g^+ \leftarrow X\ {}^2\Pi_g$ has been detected [27], which indicates the existence of vibronic interactions in such systems. Generalizing, we consider that the temporary negative ion, initially formed in a ${}^2\Sigma_g$ state (we ignore the quartet manifold), can rapidly (on the time scale of a vibration period) form all energetically allowable doublet electronic states via vibronic coupling. A number of the vibrational modes of C_n^- possess the required Π_g and Π_u symmetry and, in this manner, the attachment of s-wave electrons can lead to the formation of the temporary negative ions in their ground ${}^2\Pi$ and assorted excited ${}^2\Pi$ states. In our statistical treatment, we assume that all vibrational states accessible to the complex have an equal probability of being occupied and thus the probability of formation of a specific electronic state is proportional to its density of vibrational states. We take into account all experimentally confirmed, bound electronic states of C_n^- below the energy of reactants; for C_n^- ($n =$ even) both ${}^2\Sigma \leftarrow X\ {}^2\Pi$ and ${}^2\Pi \leftarrow X\ {}^2\Pi$ electronic transitions have been seen in the laboratory [27,28], while for C_n^- ($n =$ odd) only ${}^2\Pi \leftarrow \mathrm{X}\ {}^2\Pi$ transitions are evident [29,4].

A more descriptive form of Eq. (1), which emphasizes the initial formation of the ${}^2\Sigma_g$ state, is

$$C_n + e^- \underset{k_d}{\overset{k_f}{\rightleftharpoons}} [C_n^-]^*_\Sigma \Leftrightarrow [C_n^-]^*_{\mathrm{all}} \xrightarrow{k_r} C_n^- + h\nu \tag{4}$$

where $[C_n^-]^*_{\mathrm{all}}$ stands for all electronic states that form from the ${}^2\Sigma_g$ state via vibronic coupling. The quantity $[C_n^-]^*_{\mathrm{all}} = \Sigma_\ell\ [C_n^-]^*_\ell$, where ℓ corresponds to different electronic states of C_n^- and the symbols [ ] refer to concentration. Using the steady-state approximation for $[C_n^-]^*_\Sigma$ and for $[C_n^-]^*_{\mathrm{all}}$, and considering that the vibronic coupling occurs much more readily than any of the other steps in Eq. (4), an expression for the radiative attachment rate coefficient (k_{ra}) is obtained

$$k_{\mathrm{ra}} = \frac{k_f k_r}{k_d + k_r} = \frac{k_f \sum_\ell k_r^\ell P_\ell}{k_d^\Sigma P_\Sigma + \sum_\ell k_r^\ell P_\ell} \tag{5}$$

The rate coefficient for detachment k_d is given by the product of the rate coefficient k_d^Σ for detachment of an electron from the initially formed ${}^2\Sigma_g$ state, which is the only state to correlate directly with ground state reactants, and the probability P_Σ that the complex is in this state. The rate coefficient for radiative stabilization k_r is represented by the sum over all allowable electronic states of the rate coefficients k_r^ℓ for radiative stabilization from the ℓth state multiplied by the probability P_ℓ.

Besides the general mechanism for radiative stabilization by vibrational relaxation, an additional mechanism [30] due to electronic relaxation from low-lying excited states will be included for calculating k_r. The existence of low-lying, bound excited states of C_n^- [29,31,32] is expected to lead to an enhancement in the radiative attachment rate coefficient for reaction (4) compared with the case in which only vibrational emission within the ground state is accounted for.

2.1. The rate coefficient for formation of the temporary negative ion

Let us consider the process of attachment of s-wave electrons to C_n, $n = 4$–9, in its ground electronic–vibrational state with rigid-body angular momentum quantum number J to form a temporary negative ion $[C_n^-]^*_\Sigma$ with rigid-body angular momentum quantum number J'. Under the assumption that all collisions lead to complex formation, and that $J' = J$, the thermal rate coefficient k_f for formation of the temporary negative ion $[C_n^-]^*_\Sigma$ is given by the expression [13]

$$k_f(T) = \hbar^2 G\left(\frac{2\pi}{m_e^3 kT}\right)^{1/2} \tag{6}$$

where k is the Boltzmann constant, $\hbar$ is Planck's constant divided by 2π; G is the ratio of the electronic degeneracy of the ${}^2\Sigma_g$ electronic state of the negative ion to that of the reactants, and m_e is the electron mass. Thermalization of the state-specific rate coefficient k_f can be undertaken immediately since all other rates are approximately independent of temperature. Because the C_n linear chains with an even number of C atoms have ${}^3\Sigma_g^-$ ground state symmetry, and those with an odd number have ${}^1\Sigma_g^+$ symmetry, $G = 1/3$ for $n =$ even and $G = 1$ for $n =$ odd. The resulting rate coefficients (in cm^3 s^{-1}) for formation of the temporary carbon cluster anions $[C_n^-]^*_\Sigma$ are $k_f(\mathrm{T}) = 1.66 \times 10^{-7}\ (\mathrm{T}/300)^{-1/2}$ in the case of $n = 4, 6, 8$; and $k_f(T) = 4.98 \times 10^{-7}\ (T/300)^{-1.2}$ in the case of $n = 5, 7, 9$. The values at $T = 50$ K are 4.07×10^{-7} cm^3 s^{-1} and 1.22×10^{-6} cm^3 s^{-1}, respectively. More detailed theories can yield smaller values [18,19].

2.2. The rate coefficient for detachment of an electron from $[C_\mathrm{n}^-]^*_\Sigma$

According to the principle of microscopic reversibility, at equilibrium, any molecular process occurs at the same rate as the reverse of that process. This principle is used to evaluate the rate coefficient for detachment of an electron from the temporary complex $[C_n^-]^*_\Sigma$. This formalism is an alternative to the Rice–Ramsperger–Kassel–Marcus approach and has the advantage that no assumptions associated with the theory of the transition state have to be made [33]. It is a statistical approach since no information about the initial formation of the temporary complex is kept except the total angular momentum J and the total energy.

Under the assumption that detachment leads to the formation of C_n in its ground electronic state (where it presumably was before the electron was attached) and that s-wave electrons are released, the general phase space expression for the rate coefficient k_d^Σ for detachment [17] reduces to the much simpler expression

$$k_d^\Sigma = \frac{c}{\rho_\Sigma(E_\mathrm{vib}^\Sigma)} \tag{7}$$

where c is the speed of light, ρ_Σ ((cm^{-1})$^{-1}$) is the density of vibrational states of the temporary negative ion in its ${}^2\Sigma_g$ state, in which the collision complex was formed initially, and E_vib^Σ is the total vibrational energy available to the complex in the ${}^2\Sigma_g$ state. In order to evaluate the rate coefficient for detachment

$k_d = k_d^{\Sigma} P_{\Sigma}$ (see Eq. (5)), let us first define the probability P_{Σ}. Under the assumption that all vibrational states accessible to the complex have an equal probability of being occupied, the probability P_{ℓ} that the complex is in electronic state ℓ can be calculated using the density of vibrational states $\rho_{\ell}(E_{\mathrm{vib}}^{\ell})$ in the ℓth electronic state as follows:

$$P_{\ell} = \frac{\rho_{\ell}(E_{\mathrm{vib}}^{\ell})}{\sum_{\ell} \rho_{\ell}(E_{\mathrm{vib}}^{\ell})} \tag{8}$$

The degeneracy factors are not included since the parity of the original $^2\Sigma_g$ state is preserved. Instead of a direct count of vibrational states, the highly satisfactory semiclassical Whitten–Rabinovitch approximation [34,35] is adopted, according to which $\rho_{\ell}(E_{\mathrm{vib}}^{\ell})$ is given by the formula

$$\rho_{\ell}(E_{\mathrm{vib}}^{\ell}) = \frac{(E_{\mathrm{vib}}^{\ell} + a_{\ell} E_z)^{s-1}}{(s-1)! \prod_i h\nu_i} \tag{9}$$

where E_z is the zero-point vibrational energy, s is the number of vibrational degrees of freedom, the ν_i are the vibrational frequencies of C_n^-, and a is a factor between 0 and 1, which increases with increasing energy. Scaled vibrational frequencies of C_n^- from previous ab initio calculations [36] have been used for the calculations, and the assumption that the frequencies in the electronically excited states are the same as in the ground state of C_n^- has been made. The vibrational energy E_{vib}^{ℓ} is equal to the electron affinity of each of the neutral carbon chains ([15] and references therein) when ℓ corresponds to the ground electronic state $X\,^2\Pi$ of C_n^-. For the excited electronic states, E_{vib}^{ℓ} has been calculated as $E_{\mathrm{vib}}^{\ell} = E_{\mathrm{vib}}^{X\,^2\Pi} - \epsilon_0^{\ell}$, where ϵ_0^{ℓ} is the excitation energy between the ground and the ℓth excited state, for which we have used experimental values [27–29]. Evaluation of P_{Σ}, using Eq. (8), results in a final expression for the rate coefficient for detachment

$$k_d = \frac{c}{\sum_{\ell} \rho_{\ell}(E_{\mathrm{vib}}^{\ell})} \tag{10}$$

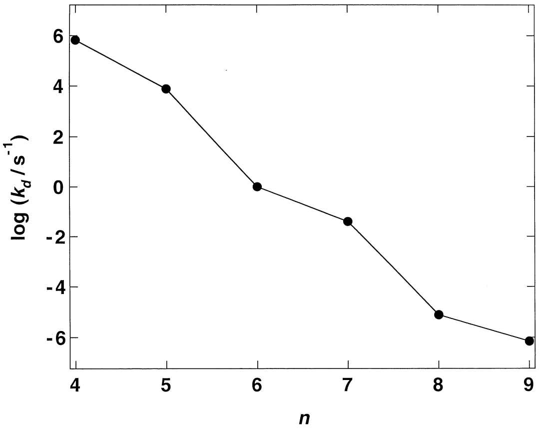

Fig. 1. Dependence of the rate coefficients k_d (s^{-1}) for detachment of an electron from $[C_n^-]_{\Sigma}^*$ on the number of C atoms n.

The dependence of the rate coefficient k_d for electron detachment on the size of the carbon cluster is illustrated in Fig. 1. As expected, the lifetime of the complex increases with the increasing size of the ions due to the increase in the number of degrees of freedom of the complex, which provides an effective distribution of excess energy and delays detachment. The large positive values of the electron affinities result in large $\rho(E_{\mathrm{vib}})$ and small k_d so that *very* stable complexes are produced at small size. Indeed, we predict that the largest complex considered lasts for almost 2 weeks before dissociating! The dependence of the detachment coefficient k_d on the number of C atoms n is not linear but "step-like" because of the relatively larger electron affinities of the even-numbered carbon clusters (C_4, C_6, C_8) compared with the odd-numbered ones.

Of course, the statistical method and model for detachment used here are approximations to reality, and it will be interesting to see if very long complex lifetimes can be measured in the laboratory. The referee has raised the issue of additional detachment channels. In the statistical model we have presented, detachment via s-waves dominates since it requires no tunneling and other detachment channels contain tunneling probabilities plus the same overall density of vibrational states. In a nonstatistical theory or a different model of vibronic interactions, other factors may come into play.

Table 1
Rate coefficients for each step of the radiative electron attachment to C_n[a]

n	k_f (cm^3 s^{-1})	k_d (s^{-1})	$k_{r(\mathrm{vib})}$ (s^{-1})	k_r (s^{-1})	k_{ra} (cm^3 s^{-1})
4	1.7×10^{-7}	6.6×10^{5}	1.0×10^{2}	6.0×10^{4}	1.4×10^{-8}
5	5.0×10^{-7}	7.7×10^{3}	5.3×10^{2}	5.5×10^{2}	3.3×10^{-8}
6	1.7×10^{-7}	1.0	5.3×10^{2}	2.8×10^{4}	1.7×10^{-7}
7	5.0×10^{-7}	4.0×10^{-2}	1.1×10^{3}	1.7×10^{3}	5.0×10^{-7}
8	1.7×10^{-7}	7.8×10^{-6}	1.2×10^{3}	4.7×10^{4}	1.7×10^{-7}
9	5.0×10^{-7}	7.1×10^{-7}	2.0×10^{3}	4.0×10^{3}	5.0×10^{-7}

[a] The rate coefficients k_f and k_{ra} are given for $T = 300$ K. In order to obtain these rate coefficients at a different temperature T, the values have to be multiplied by $(T/300)^{-1/2}$.

2.3. The rate coefficient for radiative stabilization

There are two general mechanisms for radiative stabilization of the temporary negative ion. If it is formed in its ground electronic state, then radiative stabilization can occur by infrared emission from the quasicontinuum vibrational–rotational levels above the dissociation limit to discrete levels below the dissociation limit. The rate of photon emission is equal to the rate of stabilization since $E_{\mathrm{photon(IR)}} \gg kT$. On the other hand, if the complex is formed in an excited electronic state, vibrational emission is not the only possibility because emission to stable vibrational levels of the ground electronic state can occur.

A statistical approach developed by Herbst [37] can be used to estimate the radiative vibrational relaxation of the temporary negative ion. The rate coefficient for spontaneous vibrational emission $k_{r(\mathrm{vib})}$ is

$$k_{r(\mathrm{vib})} = \sum_{\ell} P_{\ell} A_{\ell}(E_{\mathrm{vib}}^{\ell}) \tag{11}$$

where $A_{\ell}(E_{\mathrm{vib}}^{\ell})$ is the Einstein A coefficient for spontaneous emission between vibrational states within the electronic state ℓ and is a function of the vibrational energy E_{vib}^{ℓ}. An approximate expression for $A_{\ell}(E_{\mathrm{vib}}^{\ell})$ is

$$A_{\ell}(E_{\mathrm{vib}}^{\ell}) = \frac{E_{\mathrm{vib}}^{\ell} + a_{\ell} E_z^{\ell}}{s} \sum_{i=1}^{s} \frac{A_{1\to 0}^{(i)}}{h\nu_i} \tag{12}$$

where $A_{1\to 0}^{(i)}$ is the Einstein coefficient for spontaneous emission of the fundamental transition of mode i. Evaluation of the Einstein coefficients can be undertaken from the integrated intensities of the transitions, which are available from ab initio calculations [36]. The calculated rate coefficients for spontaneous vibrational emission $k_{r(\mathrm{vib})}$ are listed in Table 1. For C_{6-9}^- the time for detachment of an electron from the temporary complex is much longer than the time for relaxation by an infrared photon ($k_d \ll k_{r(\mathrm{vib})}$), and Eq. (5) can be simplified to $k_{\mathrm{ra}} \approx k_f$. In other words, the electron attachment to C_n ($n \geq 6$) is so efficient that the rate of radiative attachment is equivalent to the rate of formation of the temporary anion. For the smaller carbon cluster ions, the contribution of electronic relaxation from excited states needs to be considered explicitly in order to evaluate k_r and, subsequently, k_{ra}.

A quantitative theory for radiative association via excited electronic states has been reported by Herbst and Bates [30]. Because the Einstein A coefficient for electronic transition is greater, the stabilization due to electronic emission can be faster than the stabilization due to vibrational emission as long as the excited states are populated. The formula for the rate coefficient $k_{r(\mathrm{el})}$ for radiative stabilization due to electronic emission is similar to Eq. (11) except that the spontaneous emission rates $A_{\ell}^{\mathrm{el}}(E_{\mathrm{vib}}^{\ell})$ for transitions from vibrational levels of the excited states ℓ to stable vibrational levels of the ground electronic state, which are lower in energy, have to be used. This approach does not take into account the possibility for radiation from high vibrational levels of the ground state to lower lying vibrational levels of the bound excited state, which can also lead to stabilization. This latter mechanism requires strongly nondiagonal Franck–

Condon factors [30], which is evidently not the case here since strong origin bands dominate the electronic spectra of C_n^- [6,29]. We ignore nondiagonal Franck–Condon factors so that the spontaneous electronic emission rate coefficients are given by

$$A_\ell^{\mathrm{el}} = \frac{64\pi^4}{3h(\lambda_\ell^{\mathrm{el}})^3}\,|\mu_\ell^{\mathrm{el}}|^2 \tag{13}$$

where μ_ℓ^{el} are the electronic transition moments and $\lambda_\ell^{\mathrm{el}}$ are the electronic transition wavelengths. Experimental values [29,38] have been used for the latter, while the electronic transition dipole moments for the transitions from the ground to the excited bound states of C_n^- have been calculated using GAUSSIAN 98 [39] with the single-excitation configuration interaction method and a standard 6-31+G* basis set. The transition dipole moments of the strongest transitions (with the largest oscillator strength) have been taken from the calculation. Because of large spin contamination, the transition dipole moments of the weaker transitions have been estimated by using scaling factors derived from the relative experimental intensities of the origin bands of different electronic transitions in C_n^- [4,27,28].

The total radiative stabilization rate coefficients k_r have been calculated by summation of $k_{r(\mathrm{vib})}$ and $k_{r(\mathrm{el})}$. Table 1 summarizes the rate coefficients for formation of the complex (k_f), electron detachment (k_d), radiative stabilization ($k_{r(\mathrm{vib})}$ and k_r), and radiative attachment (k_{ra}). Neutral chains with six or more C atoms attach an s-electron at every collision, while smaller clusters have a less efficient rate of radiative attachment.

3. Conclusions

Evaluation of the radiative attachment rate of an s-wave electron to small linear carbon chains, using the statistical phase space approach, shows that carbon cluster anions can be abundant in diffuse interstellar clouds provided that: first, the neutral precursor clusters are abundant and second, the reactions of the anions with major neutral species (such as H_2) are endothermic and do not occur. For molecules with six or more carbon atoms the rate of detachment of the complex is significantly slower than the rate of radiative stabilization and, as a result, the formation of a stable cluster anion occurs on every collision. The radiative attachment rate coefficients k_{ra} for the smaller clusters C_4^- and C_5^- are 12 and 15 times smaller than the equivalent collisional limits, respectively.

If our statistical approach proves to be appropriate for treatment of these relatively small molecules, a similar procedure can be used to estimate radiative rate coefficients for other attachment reactions and to calculate the abundances of other anionic species of astrophysical interest. Such information will improve the reliability of chemical models of interstellar clouds, which may be useful in selecting negative ions for future spectroscopic experiments in search of the carriers of the DIBs.

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