Formation of CN^{-}, C_{3}N^{-}, and C_{5}N^{-} Molecules by Radiative Electron Attachment and their Destruction by Photodetachment

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The existence of negative ions in interstellar clouds has been associated for several decades with the process of radiative electron attachment. In this letter, we report compelling evidences supporting the fact that the radiative attachment of a low-energy electron is inefficient to form the carbon chains anions CN^-, C_3N^-, and C_5N^- detected in interstellar clouds. The validity of the approach is confirmed by a good agreement with experimental data obtained for the inverse photodetachment process, which represents the major cause of anion destruction in interstellar space. As a consequence, we suggest alternative models that could explain the formation of anions.

PACS numbers:

We learn about processes occurring in remote space from astrophysical observations. Laboratory experiments with neutral gases and plasma help to interpret these observations and allow us to understand all steps in long and multi-scale evolution of the interstellar medium (ISM), from elementary processes, such as electron-molecule collisions, to planet and star formation. Understanding the evolution of the ISM involves modeling on different time and space scales. At the microscopic level, the modeling relies on cross sections and rate coefficients describing elementary reactions between species present in the ISM. In an ideal situation, modeling relies on the data obtained in laboratory, but when laboratory data is not available, astronomers are bound to rely on theoretical data. Therefore, interpretation of the observed data and our understanding of processes occurring far in space depends significantly on the adopted theoretical models. Often, accurate data, such as cross sections, are not available, which can lead to a wrong interpretation of observations. Consequently, many modern models of the ISM and parameters used in the models should be systematically revisited. One recent example of a revisited ISM model, where theoretical cross sections [1] played an important role, is the discovery [2, 3] that the ionization constant ζ in diffuse clouds is ten times higher than in dense clouds, although in all previous models the same value of ζ was used for dense and diffuse clouds. The present study is devoted to a critical reevaluation of a generally-accepted mechanism for formation of negative molecular ions in the ISM.

The discovery of several carbon chain anions, C_nN^- ($n = 1, 3, 5$) and C_nH^- ($n = 4, 6, 8$) in the ISM has prompted a discussion about mechanism of their formation in the ISM [4–7]. Well before their discovery, the formation of molecular anions in the ISM was theorized by Herbst [8], who suggested that the anions could be formed in the ISM by radiative electronic attachment (REA). A simple statistical approach, the phase-space theory (PST), has been developed [4, 8] to evaluate REA rate coefficients for a number of carbon-chain anions. The resulting abundances agree with the observed ones in the ISM within a factor 2 to 4 for large anions, but disagree significantly, by factor of 100 or more, for the CN^- and C_4H^- anions. Therefore, the problem of anion formation in the ISM is still unsolved.

The present study is devoted to a fully-quantum treatment of anion formation by REA. There are no experimental measurements of REA cross sections or rate coefficients for the anions observed in the ISM. However, cross sections of the process inverse to REA, photodetachment (PD), have been measured for a number of anions [9, 10]. Theoretically, cross sections for REA and PD are obtained from the same transition dipole moment (TDM) matrix elements between continuum states of the $M + e^-$ system and bound electronic states of the molecular anion M^-. The comparison of the theoretical PD cross sections with experimental data allows evaluating the accuracy of the calculated TDM elements and, therefore, the validity of the related REA cross sections.

Theoretical approach. The cross section for PD of a molecular ion M^- in the initial vibrational level v_i with energy E_i by a photon of energy $\hbar\omega = E_n + E_{el} - E_i$, leaving a neutral molecule M in a vibrational level v_n of energy E_n and an outgoing electron of energy E_{el} is given in [11, 12]

$$\sigma_{PD} = \frac{4m_e\pi^2\omega}{3\hbar^2 c} \sum_{l\pi} \left| d_{\pi,\Gamma l\lambda}^{(v_i \to v_n)} \right|^2, \qquad (1)$$

where m_e is the electron mass. The quantities $d_{\pi,\Gamma l\lambda}^{(v_i \to v_n)}$ are matrix elements of the components $\pi = -1, 0, +1$ of the dipole moment operator between the continuum

$\Psi_{\Gamma l \lambda}$ (M+outgoing electron) and the bound Ψ_i electronic state wave functions, integrated over the initial $\chi_i(\vec{q})$ and final $\chi_{v_n}(\vec{q})$ vibrational wave functions of M^- and M, respectively, where $\vec{q}$ denotes collectively all internuclear distances. The $d_{\pi,\Gamma l \lambda}^{(v_i \to v_n)}$ matrix elements are

$$d_{\pi,\Gamma l \lambda}^{(v_i \to v_n)} = \int \chi_{v_n}^*(\vec{q}) \langle \Psi_i | d_\pi | \Psi_{\Gamma l \lambda} \rangle \chi_{v_i}(\vec{q}) d\vec{q}, \qquad (2)$$

where l is the electronic partial-wave angular momentum and λ its projection on the molecular axis, and Γ designates collectively all quantum numbers of M. The electronic transition is characterized by the matrix element $\langle \Psi_i | d_\pi | \Psi_{\Gamma l \lambda} \rangle$ of the dipole moment operator d_π, where Ψ_i and $\Psi_{\Gamma l \lambda}$ are the initial energy-normalized and final electronic wave functions, respectively. The matrix element in Eq. (2) varies weakly with vibrational coordinates over the Franck-Condon region for the three molecules, CN, C_3N, and C_5N, considered in this study. Thus, the TDMs can be calculated using a simpler expression

$$d_{\pi,\Gamma l \lambda}^{(v_i \to v_n)} \approx \langle \Psi_i | d_\pi | \Psi_{\Gamma l \lambda} \rangle_{\mathcal{Q}_0} \int \chi_{v_n}^*(\vec{q}) \chi_{v_i}(\vec{q}) d\vec{q}, \qquad (3)$$

where the subscript $\mathcal{Q}_0$ refers to the equilibrium geometry of the negative ion.

The cross section for REA to a neutral linear molecule M, which is initially in a vibrational level v_n, depends on the same matrix element as in Eq. (1) [11, 12]

$$\sigma_i = \frac{g_f}{g_i} \frac{8}{3} \frac{\pi^2 \omega^3 m_e}{k^2 \hbar^2 c^3} \sum_{l\pi} \left| d_{\pi,\Gamma l-\pi}^{(v_i \to v_n)} \right|^2, \qquad (4)$$

where g_f/g_i is the ratio of multiplicities of the final and initial states. For the considered molecules $g_f/g_i = 1/4$. Below, we discuss the results of REA and PD calculations performed for the three molecules.

CN/CN^- *molecules.* The structure of the CN and CN^- molecules was determined previously in a number of theoretical and experimental studies [13–15]. The ground electronic state of CN is $X^2\Sigma^+$ and the only stable electronic state of CN^- is $X^1\Sigma^+$. The internuclear distances in CN and CN^- (1.173 Å and 1.182 Å respectively) calculated [12] in this study agree well with the previous accurate experimental and theoretical data. The CN electron affinity (EA) of 3.8 eV and its dipole moment, d=1.45 D, obtained in the present study [12], also agree with the published data, EA=3.862 eV [13] and d=1.45 D [16].

In this study, the continuum electronic functions of the $e^- + M$ system were calculated using the UK R-matrix code [17–19] with Quantemol interface [20]. In our previous study [11, 12, 21], we used the complex Kohn variational method [22–25]. The use of the R-matrix code for the CN and CN^- molecules allows us to compare results of the two methods. Here, we will only give computational details specific to the e^-–CN system. The CN target was represented using complete active space

configuration interaction (CASCI) build on Hartree-Fock (HF) orbitals. We used the `cc-PVQZ` atomic orbital basis set including partial waves up to $l = 4$ and the R-matrix sphere radius of 13 bohrs.

The obtained PD cross section is shown in Fig. 1. The shoulder-like feature near 5 eV is due to the opening of the excited $A^2\Pi$ state of CN. Evaluating the uncertainty (shown in the figure) the following parameters were independently varied: the basis set, the number of active and virtual states, and the R-matrix sphere radius.

Calculating the PD and REA cross sections, it was assumed that the molecules before and after the process are in the ground vibrational levels, $v_n = v_i = 0$. For CN/CN^-, cross sections for the PD or REA processes with a final vibrational level different than the initial vibrational level $v_n \neq v_i$ is much smaller than for the process with $v_n = v_i$. It is because the electronic potential curves of the ground electronic states of CN and CN^- are almost parallel to each others (see Fig. 1 in [11]). For the $v_n = v_i$ processes, the vibrational integral in the cross section formulas was performed in two different ways: (a) The integral of Eq. (2) was computed explicitly from the geometry-dependent matrix as discussed in Refs. [11, 12] and (b) an approximate formula of Eq. (3) was used. Due to a weak dependence of transition dipole moments on molecular geometry near the CN and CN^- equilibrium positions [12], the difference between the results of the two ways is negligible.

The obtained PD cross section agrees with the only experimental data point [10] within experimental and theoretical uncertainties, however, there is an appreciable disagreement between the present result and the previous calculations [11, 12]. The disagreement is due to the
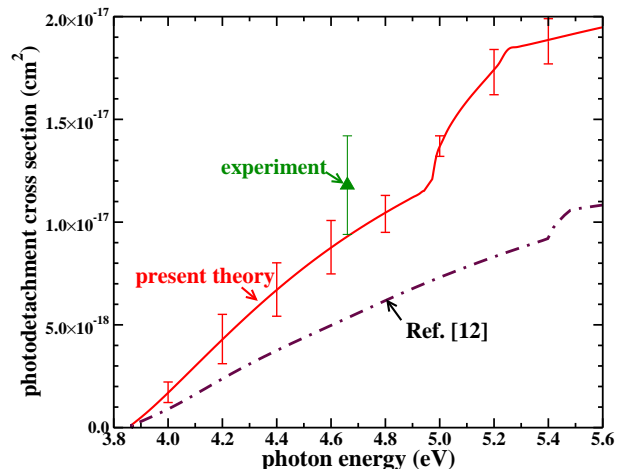

FIG. 1: Theoretical and experimental photodetachment cross sections for the ground vibrational level of CN^-. The cross section obtained in this study (solid red line) is compared with available experimental data (green triangle) [10] and with the previous theoretical calculation (dot-dashed line) [12] performed using the complex Kohn method.

fact that, on one hand, in the UK R-matrix code the transition dipole moments are calculated with the anions orbitals for the initial bound and final continuum state. On the other hand, in Ref. [11, 12], in order to optimize the affinity, averaged natural orbitals of CN and CN$^-$ has been used.

C_3N/C_3N^- *molecules.* The electronic structure of C_3N and C_3N^- was studied in several theoretical studies (see, for example, Ref. [26] and references therein). Collision of C_3N with electrons and C_3N^- resonances were also studied in Ref. [27]. The ground electronic states of C_3N and C_3N^- are of $\tilde{X}^2\Sigma^+$ and $\tilde{X}^1\Sigma^+$ symmetry, respectively. Internuclear distances in C_3N and C_3N^- obtained in the present study agree reasonably well with the previous accurate experimental and theoretical data [28, 29]. For REA and PD cross sections calculations we use the same geometry, namely, the equilibrium geometry of C_3N^- determined in [29]. The uncertainty introduced by a difference in equilibrium geometries of C_3N and C_3N^- is included in the final uncertainty of the cross sections shown in Figs. 2 and 3. The C_3N electron affinity of 4.6 eV and its dipole moment, d=3.0 D, obtained in the present study agree reasonably well with the published data EA=4.305 eV [26] and d=2.864 D [16]. Similarly to CN, in continuum-state calculations, the target molecule was represented using CASCI build on HF orbitals. A number of different sets of parameters of the computational model was used for assessment of uncertainty of obtained cross sections. In the PD calculations for photoelectron energies above 0.229 eV [26], when the first excited state $\tilde{A}^2\Pi$ of the neutral molecule is open for detachment, a sum over the two possible final electronic states in the PD cross section calculations was evaluated.

Equilibrium geometries and vibrational frequencies of C_3N and C_3N^- molecules in their ground electronic states are very similar: Internuclear distances in C_3N and C_3N^- differ by 0.01-0.05 bohrs [26, 28, 29]. The small difference in equilibrium geometries reduces the Franck-Condon factor in Eq. (3), which should be accounted for in the PD and REA calculations for C_3N/C_3N^-. The Franck-Condon factor of 0.79 between the two ground vibrational wave functions was calculated using the normal modes of C_3N and C_3N^- and an expression derived in [21].

Figure 2 shows the C_3N^- photodetachment cross sections and the corresponding uncertainties obtained using the procedure described above. The dashed red line takes into account the Franck-Condon factor and gives the cross section for photodetachment without change in the vibrational level $v_i = v_n = 0$. To obtain the PD cross section with any possible final level v_n, a sum of cross sections for different v_n should be evaluated. If the energy of the photon is large compared to energy difference between vibrational levels of the neutral molecule, the sum over v_n could roughly be approximated by the

cross section obtained for the fixed geometry of the anion equilibrium, i.e. the total cross section would be closer to the values given by the solid red line in Fig. 2. In the experiment [10], the vibrational structure of final states of C_3N was not resolved. Thus, the experimental data shown in the figure should be compared with the solid red line. As one can see, the agreement between theory and experiment is within theoretical and experimental uncertainty intervals.

The $^1\Pi$ shape resonance in the PD spectrum around 6.2 eV is formed by three electronic partial waves, $p\pi$, $d\pi$, and $f\pi$ contributing almost equally, respectively, 20%, 20%, and 30% of the total cross section.
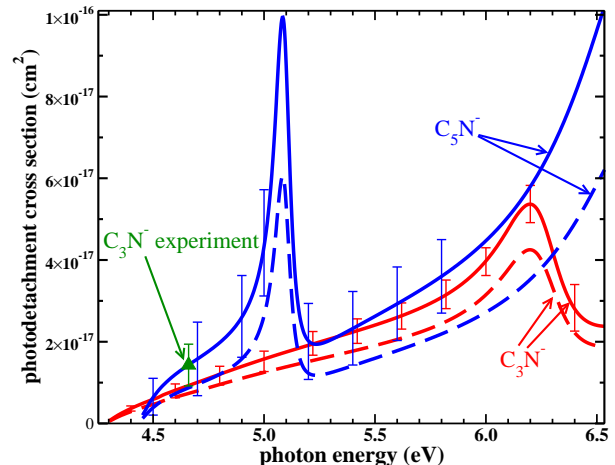

FIG. 2: C_3N^- and C_5N^- photodetachment cross sections obtained for a fixed geometry (the solid lines) and for the process where the final vibrational level of the molecule is the same as the initial one, $v_i = v_n = 0$ (the dashed lines), accounting for the Franck-Condon factor of Eq. (3). Available experimental data for C_3N^- [10], also shown in the figure, should be compared with the cross section obtained for a fixed geometry (red solid line).

C_5N/C_5N^- *molecules.* For about two decades, the electronic structure of C_5N and C_5N^- has been a matter of controversy (see the discussion in Ref. [26]). Only recently, it has finally been established that, similarly to C_3N and C_3N^-, the ground electronic states of C_5N and C_5N^- are $\tilde{X}^2\Sigma^+$ and $\tilde{X}^1\Sigma^+$ respectively. The energy difference between the ground $\tilde{X}^2\Sigma^+$ and the first excited state $\tilde{A}^2\Pi$ of C_5N is only 69.4 meV [26]. The C_5N electron affinity of 4.5 eV and its dipole moment, d=3.5 D, obtained in the present study agree quite well with the published data EA= 4.45 ± 0.03 eV [26] and d=3.333 D [16]. The present PD and REA calculations were performed for the geometry of C_5N^- equilibrium [30]. Similarly to CN/CN$^-$, in the REA calculations, the initial electronic state is the ground state $\tilde{X}^2\Sigma^+$ of the neutral molecule, the final state of the anion is $\tilde{X}^1\Sigma^+$. In the PD calculations the initial electronic state of C_3N^- is $\tilde{X}^1\Sigma^+$ and for photoelectron energies above 69.4 meV,

the PD contribution to the $\tilde{A}^2\Pi$ state is accounted for in the total PD cross section. The Franck-Condon vibrational factor calculated for the $v_i = 0 \rightarrow v_n = 0$ process in C_5N/C_5N^- is 0.61. The resulting PD cross section is shown in Fig. 2. The resonance in the C_5N^- PD spectrum around 5.1 eV is of the $^1\Pi$ overall symmetry with the major contribution from the $p\pi$ and $d\pi$ partial waves.
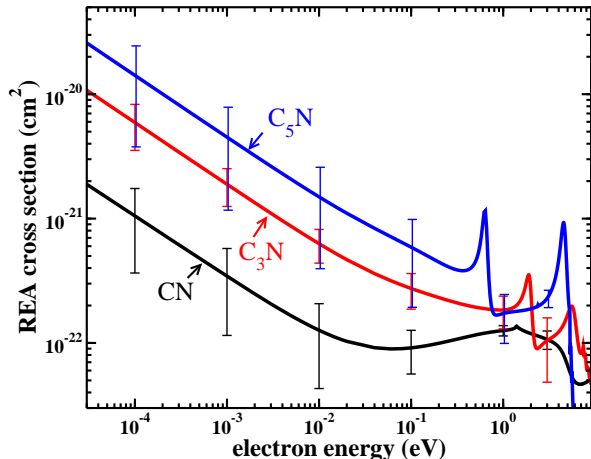

FIG. 3: REA cross sections for CN, C_3N, and C_5N molecules. The C_3N and C_5N cross sections are calculated with the Franck-Condon factor for the $v_n = 0 \rightarrow v_i = 0$ process.

In the present study, the energy of the excited states of C_3N and C_5N are not highly accurate, since our calculations focus principally on the low energy part. For example, in the C_3N/C_3N^- calculations, the $\tilde{A}^2\Pi$ state is about 1 eV (depending on the model) above the $\tilde{X}^2\Sigma$ state for the fixed geometry of C_3N^- equilibrium, but the experimental energy difference between the $\tilde{X}^2\Sigma$ and $\tilde{A}^2\Pi$ ground vibrational levels is 0.229 eV [26]. This produces an additional source of uncertainty of the obtained results (due to uncertainty in the calculated TDMs), but it is smaller than the uncertainty due to the choice of the computational model.

Discussion and conclusions. The REA cross sections for CN, C_3N, and C_5N molecules were calculated using Eq. (4) and shown in Fig. 3. Evaluating the REA cross sections, we have neglected resonant processes due to rotational and vibrational resonances, which could be formed during electron-molecule collisions. We call this resonant process the indirect REA mechanism in contrast to the direct mechanism discussed above. The role of vibrational resonances in the REA process was studied on the example of CN^- formation [11]. It was found that the contribution of vibrational resonances to the total REA cross section is negligible compared to the direct mechanism for the case of CN/CN^-. The indirect mechanism contribution is small because the formed vibrational resonance is highly-excited vibrationally, such that the vibrational overlap between the formed vibrational level of CN^- and the initial (ground) vibrational level of the target molecule CN is very small. It produces a very small probability for electron capture by the resonance. We evaluated also cross sections for indirect mechanism via vibrational resonances for molecules larger than CN. Our results indicate that the indirect mechanism for these molecules can also be neglected in comparison with the direct mechanism due to the same reason. In previous theoretical models [4], a large cross section for initial electronic capture was assumed. Such a large cross section for electron capture could be justified for a system where the potential energy surfaces of the ground electronic states of the neutral molecule and the formed anion cross in the Franck-Condon region. However, for all carbon chain anions observed in the ISM the potential energy surfaces of the neutral molecule and the anion are almost parallel to each other, which implies that the electron capture cross section is small.

One possibility in the process of REA that was not considered in this approach, is the role of weakly-bound dipole states of molecules with large dipole moments, such as C_5N. Recently, it was suggested [5–7] that the weakly-bound dipole states might enhance the REA cross section, although no quantitative predictions have yet been made. A dipole state with a rotationally or vibrationally excited molecular core appears as a resonance in the electronic continuum spectrum and, therefore, can in principle enhance the REA cross section, at least, in some energy domains. The potential role of the dipole/rotational resonances should be an essential subject of further studies.

The obtained REA cross sections are too small to explain formation of the CN^-, C_3N^-, and C_5N^- anions by the REA process in the ISM: If one assumes that these anions are formed by REA from the corresponding neutral molecules, the REA cross sections and rate coefficients should be much larger than the values obtained in this study. For example, at 300 K the computed REA rate coefficient for C_5N^- is $7.5 \times 10^{-15} \text{cm}^3/\text{s}$, while the value that would explain the observed abundance of C_5N^- by REA is about $2 \times 10^{-7} \text{cm}^3/\text{s}$ [31]. An important result of this study is that the generally-accepted mechanism of anion formation in the ISM, the REA process, cannot explain the observed relative abundances of the molecular anions and their neutral molecules. The agreement of the present PD results with experimental data validates the theoretical approach and obtained REA cross sections.

One realistic alternative for the anion formation mechanism are reactions of the type $HC_nN+H^- \rightarrow C_nN^-+H_2$ with $n = 1, 3, 5$. The HC_nN molecules were detected in the ISM, H^- should also be present, although its abundance is unknown because it has only one bound state and cannot be observed directly. The quantum mechanical calculations have not yet been performed for the mentioned reactions. However, because the reactions are exothermic and barrierless, the classical Langevin ap-

proach [32] for collisions between an atomic ion and a dipolar and polarizable molecule could be used to evaluate approximate cross sections and rate coefficients. For CN/CN^- at 30 K, we obtained the Langevin rate constant of 10^{-7} cm^3/s. For C_3N/C_3N^- the Langevin rate constant is very similar. This suggests a tool for an indirect evaluation of the H^- abundance in the ISM: Assuming that the anion is formed by the above reaction and destroyed by photodetachment, the H^- abundance could be derived from known abundances of HCN and CN^- and the mentioned rate constant.

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