



Dynamical role of metastable anions from Carbon-rich molecules in planetary atmospheres

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Abstract

Quantum computations that follow the electron-attachment process at low energies (< 10 eV) to carbon-rich gaseous molecules are carried out in order to understand the role of transient negative ions (TNIs) which can act as "doorway states" to molecular stabilization and/or fragmentation after resonant attachment of electrons produced in photodissociation region environments. The computed behaviour of the found TNIs suggests that several intermediates could be formed under conditions which justify and explain the existence of stable carbonaceous anions in protoplanetary atmospheres, as suggested by observational and laboratory data.

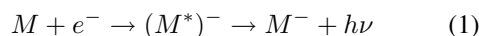
1. Introduction

It is by now a well established fact that microscopic processes give important information about the bulk properties of the interstellar medium (ISM), and further control several macroscopic features of it such as temperature and density [1]. We know already that every process of radiation-induced photoionization of the atoms and molecules which are present in the ISM yields an electron e^- with energy ($h\nu - \text{IP}$), the latter being the Ionization Potential of the species involved. This excess amount of energy can in turn be shared between the surrounding gas and its constituents and therefore provides an important heat source within the ISM.

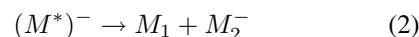
The above features therefore suggest quite convincingly that electrons can provide an interesting, and flexible, energy source for driving nanoscopic reactions within the ISM and thus participate in the possible formation of highly reactive anionic intermediates of both the atoms and molecules present in the stellar atmosphere.

The presence of molecular anions beyond H^- , He^{*-} and HD^- or H_2^- , is of particular interest because, in general, polyatomic species possess well-

known internal energy reservoirs and therefore (especially in the case of permanently polar molecules) can provide efficient pathways for the stabilization of intermediates and for a fairly rapid dissipation of the electron excess energy produced during the primary photoelectric process. The formation of polyatomic anions, therefore, has been predicted in astrophysical environments by earlier model studies [2, 3], where it was suggested that the initial step of the electron-molecule low-energy collisions could produce a metastable species, a transient negative ion (TNI), which then further stabilizes after radiative emission:



We also know that other possible paths could instead involve the loosing of the electron excess energy of the TNI complex by a dissociative electron attachment (DEA) process following Internal Vibrational Rearrangement (IVR) mechanisms:



Recent experimental observations of negatively charged molecular ions like C_4H^- , C_6H^- , C_8H^- and C_3N^- (see [4] and references within) have triggered the search for the possible formation of metastable TNIs in even larger systems and, consequently, for the most likely paths to stable anions which could be proposed to occur in the interstellar environment. The present study is therefore a computational/theoretical analysis that searches for the existence of TNIs species of the linear carbon chains of the type NC_{2n}N and HC_{2n+1}N molecules that has been recently considered both in laboratory experiments and in computational studies [4]. Our quantum modelling aims at uncovering the most likely pathways to DEA events and thus the characteristics of the negative ions that are more likely to be formed and which could either fragment into smaller, albeit permanent, anionic species or directly into full molecular anions.

2. Details of calculations

Once defined the full interaction potential between the target molecular species and the impinging electron [5], we can solve the scattering equations in order to compute the total elastic cross sections and analyse the resonance regions. The elementary process we are considering in the present work is one where the excess energy brought in by the resonant electron gets transferred into the internal energy of the molecular bonds, thereby causing either the breakup of the target with the ensuing formation of stable anionic fragments (DEA), or the creation of a long-lived, full-size metastable anion with little residual energy that can in turn undergo radiative stabilization (RA) into a bound anionic molecule within the highly diluted, practically collisionless ISM environment. Whenever one of the bonds is directly responsible for the breakup of the metastable anion, one should then observe a corresponding shift in the computed resonance positions and widths while that bond is stretched. This is essentially a one-dimensional picture for the DEA mechanism whereby one is searching for a possible dominant fragmentation which finally occurs via the breakup of that particular bond and the stabilization of a residual molecular anion. If a zero-energy TNI is formed for a long enough time interval, the RA dissipative path can also become a possibility due to the relatively small amount of energy that can be distributed within the initial TNI structure, insufficient to cause bond-breaking effects.

We carried out several calculations using different molecular geometries for which the resonant electron density maps showed, at the initial molecular equilibrium geometry, the presence of nodal planes and of a partial localization along specific bonds of the resonant electron density (as shown in Figure (1) for the NC_4N system).

3. Summary and Conclusions

The work reported has dealt with the identification of possible low-energy resonant electron attachment events for the gas-phase Carbon-rich molecules. The search has been motivated by the following reasons: (i) the experimental detection of anionic resonances for these system and the presence of several fragmentation products related to DEA events; (ii) the need to assess the possible molecular mechanisms which preside over the formation of anions in the planetary atmospheres and in the ISM, and (iii) the identification of energy redistribution channels after the primary

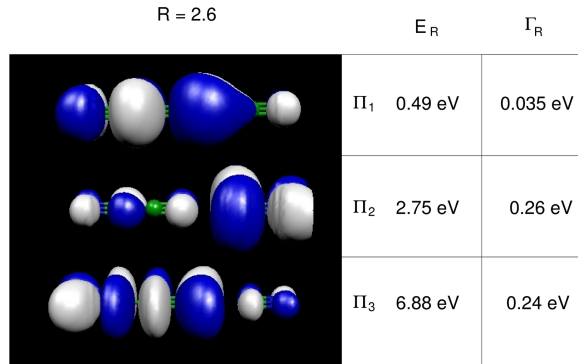


Figure 1: 3D representation of the computed wavefunctions for the metastable electron in each of the Π_i resonances.

electron-attachment resonances. All the above aspects of the problem have been addressed by the present calculations using a quantum modelling of the dynamics. The specific study of the NC_4N molecular target [6] has already shown that the variety of TNIs formed by electron attachment can indeed lead to the stable formation of several Carbon-rich anions like NC_4N^- , C_3N^- and CN^- , as experimentally observed [4].

Acknowledgements

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