Solving the CH_4^- Riddle: The Fundamental Role of Spin to Explain Metastable Anionic Methane

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Several types of experiments showed the existence of negative methane ions CH_4^- over a period of 50 years but the nature of this elusive species remains unknown. A benchmark study has shown that the experimentally observed species cannot be described by the attachment of an electron in the doublet ground state of CH_4^-. Here we find CH_4^- as being a metastable species in its lowest quartet spin state, a $CH_2^-:H_2$ exciplex with three open shells lying ca. 10 eV above the methane singlet ground state but slightly below the dissociation fragments. The formation of charged high-spin exciplexes is a novel mechanism to explain small molecular anions with implications in a plethora of basic and applied research fields.

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The CH_4^- *puzzle*.—Methane has ten electrons in a noble gaslike configuration so that electron capture by this very stable molecule is considered impossible. Nonetheless, electron attachment in methane has consistently been evidenced by several groups over five decades [1–10] though the true nature of this anionic species still remains unknown. Therefore, the elucidation of the origin and nature of anionic methane would be an important finding with implications on several fields, like our current understanding of atmospheric chemistry, hydrocarbon plasma, flame science, cluster science, space physics, planetary science, and quantum chemistry models. Molecular hydrocarbon anions are called upon to explain charge distributions in plasma and to interpret spectroscopic observations. Based on available theoretical models and emission spectroscopic experiments, molecular anions have been detected in plasma atmospheric environments such as in a comet's coma, Titan's ionosphere, or in the interstellar medium. Molecular anions are believed to have important roles in the formation of aerosol dust in the chemical composition of Titan's atmosphere and in plasma plumes. These cold plasma are extremely complex and the explanation of their behavior frequently resorts to negative molecular species [11]. For instance, in a simulation of Titan's atmosphere, Horvart *et al.* [12] propose negative molecular anions resulting from rather complex dissociative electron attachment channels to interpret the charge distribution in a N_2-CH_4 plasma. Despite the fact that methane is the most abundant species, they did not consider negative methane to be present in their plasma; perhaps this is because CH_4 is believed to be incapable of capturing an extra electron. However, CH_4^- would provide a much simpler explanation for the presence of metastable molecular anions.

Another field where the confirmation of this anion would be an important discovery is quantum chemistry. Dipole-bound anion formation is the most accepted mechanism to explain the capture of an extra electron by neutral molecules. This mechanism explains the formation of several molecular anions that are important in astrophysics [13]. Since methane has zero dipole moment, the confirmation of CH_4^- challenges the dipole-bound model as the only mechanism for the formation of simple molecular anions. We report here a new quantum mechanical mechanism capable of explaining the observed methane anionic species.

The first observations of electron attachment in methane were reported by Trepka and Neurt [1] and by Sharp and Dowell [2], who used a beam technique and found that dissociative electron attachment in CH_4 took place over the 8–13 eV range of electron energies, with H^- and CH_2^- as dissociative product ions. Later, using a pulsed Townsend technique, Hunter *et al.* [4] measured the density-normalized electron-attachment coefficient for methane over the density-normalized electric field strength, E/N, in the 52.5–250 Td range. Electron-impact ionization processes have been thoroughly studied for gaseous methane over a very wide range of the density-normalized electric field strength up to 5×10^4 Td, also suggesting the presence of the methane anion [6]. In refined Townsend measurements [8] large amounts of heavy negative ions were clearly observed so that the electron-attachment process in CH_4 is certain, thus providing irrefutable evidence of the presence of the methane anion [10].

From the theoretical side, the electron affinity (EA) was calculated as it is usually done [14], i.e., as the difference between the energy of the doublet ground state $^2A_1$ of the negative ion minus the energy of the singlet ground state $^1A_1$ of neutral methane plus a free electron. The extra electron in the ground doublet state of CH_4^- goes into a quasispherically symmetric Rydberg molecular orbital described as mainly carbon $3s$ [15]. It was found that the EA of methane was large, ranging from 6.1 to 1.2 eV using second and fourth order Möller-Plesset perturbation theory (MP2 and MP4) and even applying variational configuration interaction methods with a variety of Gaussian basis sets ranging from $6\text{–}31\mathrm{G}(d,p)$ up to $6\text{–}3111++\mathrm{G}(3df,2p)$. When the complete basis set (CBS) extrapolation [16] was applied, the EA was estimated to be 0.5 eV. However, while the decrease of the EA with basis set quality is clear, none of the electronic structure methods used the more accurate correlation-consistent polarized valence ($cc\text{-}pVnZ$) basis sets [17]. From the electronic structure point of view, the fact that the negatively charged $CH_4^-(^2A_1)$ species will eventually produce $CH_4(^1A_1)$ plus a free electron means that, for a given level of theory, the energy of the ground doublet state of the anion should approach that of methane as the quality of the atomic basis sets improves. This stems from the fact that larger and more diffuse basis sets allow the extra quasispherical electron to move away from the neutral tetrahedral molecule, which has no dipole moment capable of inducing an attractive charge-dipole interaction, thus lowering the total energy of the (CH_4, e^-) pair at infinite distance. Therefore, a recent study addressed the evolution of the electron affinity of methane with highly correlated benchmark *ab initio* calculations with Dunning's aug-$cc\text{-}pVnZ$ basis sets up to aug-$cc\text{-}pV6Z+\text{diffuse}$ [17]. The electron affinity was calculated at the MP2 and coupled cluster [CCSD(T)] levels including extrapolations to the CBS limit [18]. This study showed that the energy of the $^2A_1$ state of the anion asymptotically approaches that of the $^1A_1$ ground state of CH_4 plus a free electron with increasing basis set quality. The inescapable conclusion of that work is that an excited electronic state of anionic methane must be at the root of the experimental observations of CH_4^-.

The comparison of the experimental evidence and these quantum-chemical results suggests that the detected negative ion is not correlated to a ground state ion but to a metastable negative ion. This type of negative ion is well known for atoms, He^- being the most striking case, but many other examples are known, as reviewed in the paper by Bunge *et al.* [19]. The case of He^- has been much studied since its discovery [20]: He^- is in the $1s2s2p$ (^4P_J) levels, with an electron binding energy equal to 77 meV with respect to the $1s2s$ ($^3S_1$) first excited state. The lifetimes of the ^4P_J levels have been calculated and measured, with the $J=5/2$ level having the longest lifetime, with an experimental value of 343 ± 10 μs, in agreement with the theoretical prediction [21]. Methane is isoelectronic with neon and, following Bunge *et al.* [19], neon has no metastable negative ion. However, CH_4^- is isoelectronic with sodium and Feldman and Novick [22] showed that the alkalis have long-lived quartet states that are in the ionization continuum and metastable with respect to ionization. These quartet states have large internal energies, varying from 57.3 ± 0.3 eV for the lithium $1s2s2p$ (^4P) level to 12.6 ± 0.3 eV for the potassium $3p^5 4s3d$ (^4F) [23] level (zero energy corresponds to the atomic ground state). The lifetime of these states is surprisingly long for autoionizing states: if autoionization was fully allowed, their lifetimes should be of the order of 10^{-15} to 10^{-13} s, while the observed lifetimes vary from 5.1 ± 1 μs for lithium to 90 ± 20 μs for potassium [23]. There is no measurement of the lifetime of the sodium quartet state $2p^5 3s3p$ (^4D), but a theoretical evaluation of the decay rates of the quartet states of sodium has been made by Holmgren *et al.* [24]. It is interesting to note that three levels, namely, the $2p^5 3s3p$ ($^4D_{7/2}$), the $2p^5 3s4s$ ($^4P_{5/2}$), and the $2p^5 3s3d$ ($^4F_{9/2}$) levels, have negligibly small autoionization rates and the decay of these levels is dominated by radiation emission toward states of the quartet symmetry, the lowest quartet states having very long lifetimes.

The exceptional properties of these high-lying metastable states of the alkali atoms have given us the idea that a methane negative ion could also be described by the spin quartet symmetry. As in the study by Holmgren *et al.* [24], one may expect that some quartet states have sufficiently small autoionization and radiative decay rates to explain the observed CH_4^- species. Thus, two key questions arise. First, what is the energy of the lowest quartet state of the CH_4^- ion with respect to the ground state of CH_4? And secondly, is the resulting anionic species stable enough for it to be detected in experiments at room temperature? We address these issues in two ways. First, through benchmark *ab initio* quantum-chemical calculations, including both nondynamic and dynamic electronic correlation effects with the complete active space self-consistent field (CASSCF), the second order Möller-Plesset perturbational scheme (MP2) and the coupled cluster CCSD(T) method (the golden standard in electronic structure calculations). We have also applied the CBS extrapolation using both methods. Secondly, but crucially aimed at explaining experimental evidence, we focus on the dynamical behavior of the excited quartet methane anion at room temperature through Born-Oppenheimer molecular dynamics (BOMD) based on density functional theory using a calibrated hybrid exchange-correlation functional. Computational details can be found in Supplemental Material [25].

The structure of CH_4^- *at 0 K.*—The electron capture process by which this anionic methane is formed is completely unknown; however, the formation of the quartet negative ion of CH_4 in a discharge is probably due to a two-step process, the first step being the formation of CH_4 in its lowest triplet state and the second step being the capture of an electron. This second step requires a third body to take away the excess energy. In very dilute media encountered in astrophysics, the third body is the emission of a photon but the associated formation rate is very low. In the relatively dense gases used for electrical discharges, the third body is any electron, atom, or molecule present in the discharge. The experiments showing the existence of anionic methane are done in plasma conditions so that many neutral, anionic, and cationic molecular species can be found at the same time in the mixture, even at low pressures. Experimentally, the relative abundance of anionic methane is higher than those of CH_2^-, CH^-, and C^- species (see Fig. 3 in Ref. [10]). Thus, the formation of the quartet state could involve a first excitation of thermally distorted neutral methane leading to a triplet neutral state of CH_4, which then captures the extra electron leading to the anionic species with total $S = 3/2$; this high-spin electron capture process might be more efficient than those leading to the dissociation channels.

On the other hand, the energy required to produce the first quartet state of methane close to its T_d equilibrium geometry is *ca.* 10 eV and this energy is readily available within most plasma environments. Here we address the energy and the structure of the CH_4^- species in its lowest quartet ($S = 3/2$) spin state by fully unrestricted MP2/aug-*cc*-*pVnZ* optimizations to obtain the CBS energy limit with the $n = 3, 4, 5$ series; the lowest quartet state energies are relative to those of the neutral methane molecule at a given level of theory. We explored the possibility that the lowest quartet state might have some multireference character through CASSCF(7, 7)/aug-*cc*-*pVnZ* calculations; we found that this is not the case so that the single-reference-based methods such as MP2 and CCSD(T) yield reliable results. Geometry optimizations at the CASSCF, MP2, and CCSD levels lead to the same molecular picture where a weakly bound $CH_2^-{:}H_2$ exciplex is produced upon relaxation of the excited anionic methane. The energies of the separate optimized fragments were also determined at the MP2/aug-*cc*-*pVnZ* and CCSD(T)/aug-*cc*-*pVnZ* levels, leading to our best-calculated CBS values (1.2 and 0.85 kcal/mol, respectively) for the dissociation of the exciplex into $CH_2^-(S = 3/2) + H_2(S = 0)$. Since the thermal energy at 300 K is 0.59 kcal/mol, at the highest level of theory, the CCSD(T)/CBS limit, this well holds the exciplex together at room temperature, and this remains true even neglecting equipartition of the thermal energy among all the vibrational modes of the exciplex. Total and relative energies, the optimized geometry of the quartet exciplex, charge and spin distributions are given in the Supplemental Material [25].

Stability of the $CH_2^-{:}H_2$ *exciplex at 300 K.*—Since the experimental detection of negative methane has been done at room temperature, we analyze the behavior of the lowest excited quartet state at 300 K through Born-Oppenheimer molecular dynamics. We utilized the same BOMD approach [26] as that reported in [27].

Before starting the BOMD simulations we tested several generalized gradient approximation, meta-generalized gradient approximation, and hybrid exchange-correlation (XC) density functionals to find which one is capable of reproducing the MP2 and CCSD(T) results; i.e., we verified that it does indeed lead to the $CH_2^-{:}H_2$ exciplex at 0 K. This calibration revealed that the hybrid B3LYP functional qualitatively reproduces the CASSCF, MP2, and CCSD(T) picture for the lowest quartet state. Then, 1.2 ns BOMD B3LYP-based simulations (including 2.4×10^6 configurations) were done for the CH_4^- system imposing a total spin of 3/2 (details in Supplemental Material [25]). The optimized T_d geometry of neutral methane was used as starting point with no preferred nuclear velocities other than those obtained by a Boltzmann distribution at 300 K. Figure 1 shows the energetic and structural evolution of anionic methane in its lowest spin quartet state. Note that a quasilinear stable $CH_2^-{:}H_2$ excited complex is formed in the first 10 *ps*. The infrared spectrum (Fig. 2) was obtained from the Fourier transform of the velocity autocorrelation function after thermalization was achieved (10 *ps*) at 300 K.

The CH_4^- spectrum should be compared to the vibrational spectra of the separate $CH_2^- + H_2$ species at the same level of theory. The isolated $CH_2^-(S = 3/2)$ anion has three modes, two stretching at 923 and 1600 cm^{-1}, and one bending mode at 399 cm^{-1}; the vibrational mode of H_2 is at 4410 cm^{-1}. The CH_4^- spectrum clearly reveals the weakly bonded nature of this anionic species since the intermoiety stretching mode is found at 180 cm^{-1}. The lowest frequency peak is associated with the weak bond of the

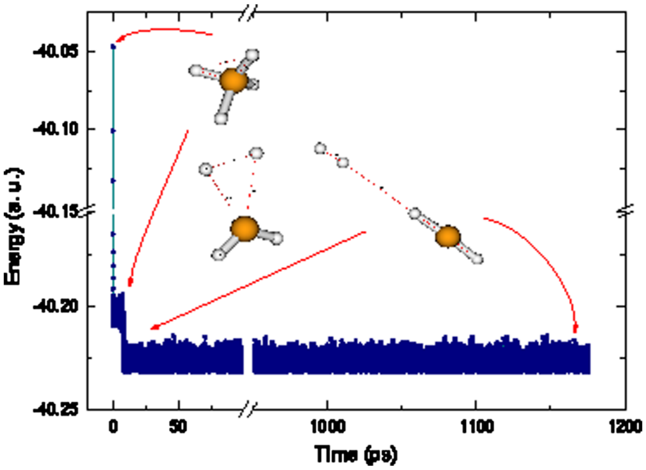

FIG. 1. Energy evolution of the excited quartet state of CH_4^- at 300 K. The deep about 8 *ps* indicates the appearance of the $CH_2^-{:}H_2$ exciplex. Metastability with respect to the separate $CH_2^-(S = 3/2) + H_2$ ($S = 0$) fragments was found, at least, over the next 1 *ns*.

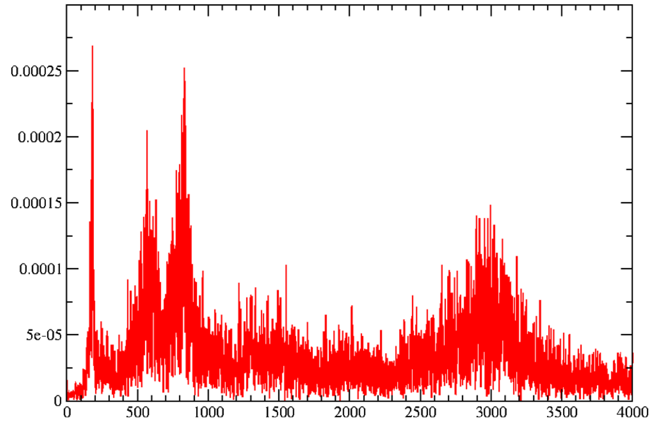

FIG. 2. Vibrational spectrum of the lowest quartet state of CH_4^- at 300 K; the lowest frequency peak at 180 cm^{-1} corresponds to the intermoeity stretching mode of the $CH_2^-:H_2$ exciplex. Intensity (arb. units) vs energy (cm^{-1}).

CH_2^--H2 units, but the present results at 300 K show that the lifetime of this anionic species is longer than 1 *ns* and many experiments have shown that metastability might exist for timescales 3 to 4 orders of magnitude larger at room temperature.

Spin distribution in the $CH_2^-:H_2$ *exciplex.*—One could naturally ask if the spin distribution of the quartet exciplex can be directly linked to the one corresponding to the $CH_2^- + H_2$ separate fragments. For this, two facts should be considered: (a) The $CH_2^-:H_2$ exciplex is a single molecule composed of two dynamically coupled moieties and the notation simply helps as a label to identify them (see Fig. 1); (b) A total spin $= 3/2$ is imposed to perform all the calculations for the anion since the ground anionic state with total spin $= 1/2$ had been explicitly shown to lead to CH_4 plus a free electron in a previous study [18]. The spin distribution in the exciplex at 300 K is quite dynamic and this is reflected by the population analysis we report in Table S4 in Supplemental Material [25] (also note that the CH_2 moiety is nearly linear in the exciplex vs a bent H-C-H angle in isolated methylene). Table S4 shows that the spin distribution varies significantly depending on the particular geometry of the exciplex at a given time in the BOMD trajectory. Note that for some configurations the spin carried by the H_2 moiety can be 1/4–1/3 of the total spin of the exciplex. Therefore, although the anionic species can roughly be described as a $CH_2^-:H_2$ excited complex, the three open shells defining the quartet spin state have significant spatial variations along the Born-Oppenheimer trajectory at room temperature.

Conclusions and perspectives.—Electron attachment in methane has been detected by many groups over several decades. However, the ground doublet state of anionic methane has been shown to be unstable with respect to CH_4 plus a free electron through benchmark *ab initio* calculations [18]. Thus, some excited state must be at the root of the observed CH_4^- species, which has a longer lifetime than the time needed (*ca.* 10^{-6} s) to reach the detection apparatus. Negative methane is isoelectronic with sodium and, based on the exceptional properties of the spin $= 3/2$ high-lying metastable states of the alkali atoms, we have explored the idea that a methane negative ion could also be described by the spin quartet symmetry. We performed benchmark *ab initio* CASSCF, MP2, and CCSD(T) calculations of the anionic system in the lowest quartet state. These methods lead to a stable weakly bound $CH_2^-:H_2$ exciplex. This high-spin exciplex explains, at the same time, the observation of anionic methane but also the detection of the CH_2^- species in cold plasma experiments. The thermal stability of this exciplex was studied at 300 K through Born-Oppenheimer molecular dynamics simulations based on a calibrated hybrid exchange-correlation functional. Although these quantum chemical simulations are not long enough to address the timescale of the order of μs in the experiments, we found thermal stability of the $CH_2^-:H_2$ exciplex at 300 K with a total spin of 3/2 for at least 1 ns. The infrared spectrum predicts a peak *ca.* 180 cm^{-1} that, if detected, can be interpreted as the signature of the $CH_2^- - H_2$ stretching mode of the exciplex.

We propose a bold and new molecular picture that explains the presence of anionic methane in many experiments. The present study shows that when electronic attachment occurs in CH_4 molecules, the spin quantum number of some of the resulting anions is 3/2 instead of 1/2, as one could naively expect, revealing the pivotal role played by the lowest quartet state of this elusive anionic molecular species. These results call for new Stern-Gerlach experiments or the infrared spectrum of the $m/q = -16$ molecular beam in future investigations. Further experimental data on the lifetime or refined electron affinity measurements of anionic methane would also provide crucial information for new interpretations having a tremendous impact on current knowledge of atmospheric chemistry, cluster and planetary science, hydrocarbon plasma, and quantum chemistry models.

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