

**THE DISCOVERY OF A NEW ANION.  
AFTER ALL, NEGATIVE METHANE ION EXISTS AND IS VERY STABLE.**

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Negative ions form when an atom or a molecule captures an extra electron. Explanation models for the subtle process of electronic capture to form this kind of ions still rise eyebrows. Even the first encounters with negative ions were perplexing and game changers. An example comes from astrophysics. In the thirties, astrophysicists were looking for the origin of one particular spectroscopic absorption line in the Sun. Most believed it was caused by metals. It was Rupert Wild, in what is now a classic paper, who demonstrated that the carrier of this line and the responsible of the major absorption line of radiation from the Sun was negative hydrogen ( $H^-$ ) lurking in space.

There are good reasons to question the prevalence of negative ions in plasmas. The extra electron is so weakly bound (the highest electron affinities are for Cl and F with no more than 3.7 eV) that one would expect its depletion by collisions, radiation and simply by decay. However, their presence is nowadays well regarded as ubiquitous in cold plasma and mayor contributors to the electron density function.

Methane ( $CH_4$ ) is the isoelectronic molecular analogous to atomic Ne. Nobody has found any excited state of neon that could possibly form metastable negative species and its ground state, a closed shell electronic configuration, forms no stable anions. In addition, methane has a molecular mass of 16.03 as compared to oxygen's of 15.99. Oxygen is expected in most vacuum chambers as an impurity and forms very stable (and metastable) anions. Most mass spectrometers do not conclusively distinguish species that are this close and, if it appeared, then it was likely assigned as the suspected oxygen impurity. Despite of some few experimental reports, negative methane made it unobscurely disguised and undetected probably for these reasons

But what if one considers negative methane as isoelectronic to Na. Sodium is known to have some high spin (quartet) excited states above its ionization limit that are incredible stable having very long lifetimes. The question is if negative methane, with 11 electrons, one carbon and four hydrogen atoms could form something similar to these high-spin sodium excited states into a stable configuration. The answer is yes. It forms a quartet excited state composed of an overall negative complex looking like methylene  $CH_2$  bound to an  $H_2$  molecule that proves to be stable with respect to the dissociation channel. These weakly bound molecular species are known as exciplexes, and in the case of methane, resulted in an unexpected stable configuration even at 300K.

Next time you detect  $m/e = -16$  in hydrocarbon plasma or wherever methane could exist do not discard the presence of negative methane, better discard oxygen, especially if your vacuum system is already clean.

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

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