

# Validation of the Formation of Negative Methane Ions.

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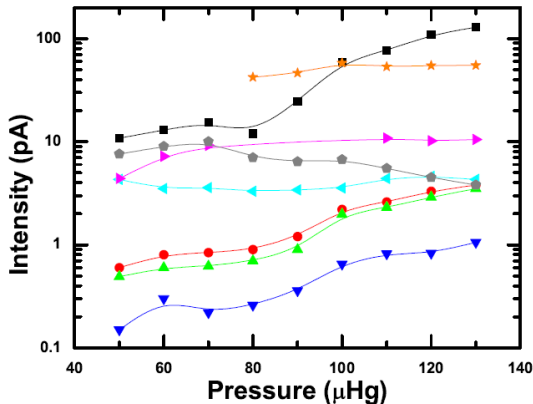
Second part (Physical Review Letters, **124**, 056001 (2021))

- Alejandro Ramírez-Solíz.
- Humberto Saint Martín-Posadas.
- Jacques Vigué

First part (Plasma Sources Science and Technology, **23**, 015018 (2014)).

- Edgar Hernández (doctorante), Lorenzo Hernández (Postdoc).
- Natalia Trujillo, César Martínez Flores (Advanced Lab.).
- Martín Salazar (Ph. D. Candidate), Arturo Chavez (U. de G.).

Voilà!



Ion source output of negative ion species measured with the Faraday cup as a function of pressure. The data correspond to 100% of methane gas in the source: Black squares,  $\text{H}^-$ ; stars,  $\text{C}_2\text{H}_2^-$ ; right triangles,  $\text{C}_2^-$ ; pentagons,  $\text{C}_2\text{H}_3^-$ ; **left triangles,  $m/q = -16$  !!!**; circles,  $\text{C}^-$ ; up triangles,  $\text{CH}^-$  and, down triangles,  $\text{CH}_2^-$ .

Negative methane would be important.

It would:

- help improve models of plasma, specially carbohydrate plasma.
- help identify other species in the ISM.
- methane is a powerful green house gas, we would learn something else about it.
- may help understand more on how they form...

## Why negative methane should not exist:

... like Ne:

- It is the iso-electronic molecular analogous to neon. Hence, it must have similar characteristics.
- It has a close-shell electron configuration, like Ne. Therefore it should not admit any extra  $e^-$ , not even in an excited state: like Ne.

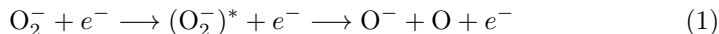
... like  $O^-$

- It has a  $m/q = -16$ : like  $O^-$
- Oxygen forms a very stable and well known anion.
- Oxygen is present (forcibly) in ALL vacuum systems because is an (inevitable) contaminant.
- Therefore, any appearance of  $m/q = -16$  should or must be  $O^-$ .

## The Negative Methane Hypothesis

- 1 The gas injected into the chamber was high purity. Therefore, the pollutant should be observed, at most, on a trace-scale.
- 2 The observed signal was large: inconsistent with a contaminant in the chamber.
- 3 The signal did not wane as a function of time: as expected for a contaminant.
- 4 The chamber had been carefully (to a fault) de-gasified.
- 5 The plasma-chamber was made of quartz, therefore, must be easy to clean.
- 6 The  $m/q = -16$  signal was directly correlated to the injection of methane in the ion source.
- 7 The  $m/q = -16$  (relative) intensity showed dependence on the plasma chamber pressure, indicating a native species of the plasma, rather than an impurity.

Absence of the auto-detachment signal below 1 keV. This signal is characteristic when  $O_2$  is injected into the ion source.



Has anyone seen  $\text{CH}_4^-$ ??

Has anyone seen  $\text{CH}_4^-$ ??  
NO!

Has anyone seen  $CH_4^-$ ??

NO!

... wait a minute

## Dissociative capture in Townsend experiments

### Über die Entstehung von negativen Ionen aus einigen Kohlenwasserstoffen und Alkoholen durch Elektronenstoß

Von L. v. TREPKA und H. NEURT

Aus dem I. Institut für Experimentalphysik, Hamburg  
(Z. Naturforsch. **18a**, 1295–1303 [1963]; eingegangen am 3. Oktober 1963)

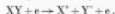
Es wird mit Hilfe eines Massenspektrometers und Sekundärelektronenvervielfachers als Anzeiger die Bildung stabiler negativer Ionen durch Elektronenstoß, insbesondere durch Elektronenresonanzeinfang, in einigen gesättigten Kohlenwasserstoffen, sowie in niedrigen Alkoholen untersucht. Dabei werden zahlreiche stabile Ionensorten neu gefunden. Infolge der Vielzahl der Dissoziationsmöglichkeiten können nun in einigen Fällen Aussagen über die Elektronenaffinitäten gemacht werden. Vermutlich ist  $EA(CH_3) \geq 3.1$  eV,  $EA(C_2) \geq 2.9$  eV;  $EA(C_2H_5) \geq 2.8$  eV;  $EA(C_4H_{10}) \geq 1.5$ , wahrscheinlich  $\approx 1.5$  eV; einige Reaktionen lassen sich deuten mit  $EA(H) \approx 0.7-0.9$  eV.

Negative Ionen können durch Elektronenstoß auf zwei Arten gebildet werden:

1. Durch einen Elektronenresonanzeinfangprozeß mit Dissoziation



2. durch die Bildung eines Ionenpaares



Beide Prozesse sind schon vielfach untersucht und diskutiert worden, so daß hier auf vorhandene zusammenfassende Literatur verwiesen werden kann, z. B. <sup>1-3</sup>. Solche Untersuchungen sind auch von praktischer Bedeutung, da sie Aufschluß geben über die Existenz stabiler negativer Ionen und in günstigen Fällen über die Elektronenaffinität ( $EA$ ). Die Messungen solcher Vorgänge erfolgen in vielen Fällen unter Verwendung eines geeigneten Massenspektro-

meters. Die hier verwendete Meßanordnung ist schon von KRAUS <sup>4</sup> beschrieben worden. Die meisten Untersuchungen sind bisher an anorganischen Molekülen durchgeführt worden. Über die Bildung negativer Ionen an Kohlenwasserstoffen wurde nur selten berichtet. Den Prozeß der Paarbildung an einigen einfachen Kohlenwasserstoffen und Alkoholen studierten MELTON und RUDOLPH <sup>5</sup>, Resonanzeinfangprozesse sind von SMITH <sup>6</sup> sowie von REISS und Mitarbeitern untersucht worden <sup>7</sup>. Hier soll über Ergebnisse von Untersuchungen an niedrigen Paraffinen und Olefinen, einfachen Alkoholen sowie Acetylen und Benzol berichtet werden. In erster Linie wurden die Resonanzeinfangprozesse untersucht; dabei wurden Intensitäten und Appearance-Potentiale ( $AP$ ), z. Tl. unter Verwendung der RPD-Methode nach FOX <sup>8</sup> bestimmt. Zur Orientierung wurden auch die

<sup>1</sup> H. S. W. MASSEY u. E. H. S. BURROF, *Electronic and Ionic Impact Phenomena*, Oxford University Press, Oxford 1952.

<sup>2</sup> H. S. W. MASSEY, *Negative Ions*, University Press, Cambridge 1950.

<sup>3</sup> F. H. FIELD u. J. C. FRANKLIN, *Electron Impact Phenomena*, Academic Press, New York 1957.

<sup>4</sup> K. KRAUS, Diplomarbeit, Hamburg 1961.

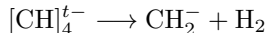
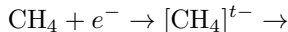
<sup>5</sup> C. E. MELTON u. P. S. RUDOLPH, *J. Chem. Phys.* **31**, 1485 [1959].

<sup>6</sup> L. G. SMITH, *Phys. Rev.* **51**, 263 [1937].

<sup>7</sup> R. M. REISS, H. DUBOIS u. F. L. MOHLER, *J. Res. Natl. Bur. Stand.* **57**, 367 [1956].

<sup>8</sup> R. E. FOX, W. M. HICKAM, D. J. GROVE u. T. KJELDGAARD, *Phys. Rev.* **84**, 859 [1951].

In cold plasma: Ever since Trepka and Neurt, other authors often report the presence of negative ions in methane plasma. They attribute then to the process of dissociative attachment:



Zeitschrift für Naturforschung A,  
18a(12): 1295–1303, 1963

## METHANE TEMPORARY NEGATIVE ION RESONANCES

F.K. BOTZ and R.E. GLICK

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Received 17 January 1975

Revised manuscript received 24 February 1975

Methane temporary negative ion resonances, of the Feshbach or closed channel type, have been observed at 6.53, 7.37 and 8.15 eV and assigned to Jahn-Teller distorted states designated as  $^2B_1$ ,  $^2B_2$  and  $^2B_{1g}$ .

## 1. Introduction

Electron spectroscopic studies of temporary negative ion resonances which correlate with excited electronic states have been generally limited to atomic or diatomic systems (for recent reviews see ref. [1]). In this report we wish to indicate the existence of excited state negative ion resonances in methane which appear to be of the bound state or closed channel type. These results, extending the range of molecular complexity of systems exhibiting closed channel excited state resonances, are due probably to stabilized Jahn-Teller distorted states expected for negative ions correlating with appropriate methane excited states.

## 2. Apparatus and calibration

The electron spectrometer consisted of a 127° electrostatic velocity selector (design criteria, see ref. [2]), a collision chamber and a Faraday cup detector housed in a vacuum chamber. The electron monochromator, supplied by electrons from a filament powered by a regulated dc source, consisted of entrance and exit slits and inner and outer grids held at

ages were read on a Dymec Integrating Voltmeter, Model 2401. The current from the Faraday cup was amplified and converted to a voltage which was then recorded as a function of electron energy.

The spectrometer was produced from non-magnetic materials, Nuclide Corporation, and was protected from stray magnetic fields by a mu metal shield placed with its long axis perpendicular to the electron motion within the selector and an externally mounted pair of Helmholtz coils. A magnetometer, Hewlett Packard Model 428 BR with probe placed in an axial direction with respect to the mu metal cylinder, monitored the field and was used in the conjunction with the Helmholtz coils for field control.

Sample gases were introduced into the collision chamber, background pressure ca.  $10^{-6}$  torr, from a glass inlet system of sufficient capacity to ensure a constant pressure in the collision chamber for the duration of an experiment. The pressure of the sample gases used in those studies were between  $10^{-3}$  and  $10^{-5}$  torr as calculated using a total elastic cross section method. The argon, nitrogen and methane used in the experiments, obtained from commercial sources, were at least 99% pure and used without further purification.

Temporary negative ion resonances of  $\text{CH}_4^-$ . The existence of (at least) ephemeral negative methane  $\rightarrow$  confirmed.

Botz and Glick, Chem. Phys. Lett., Vol. 33, 279, 1975

# Detected $(\text{CH}_4)_{n=1}^-$

## Anionic clusters in dusty hydrocarbon and silane plasmas

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(Received 4 October 1994; accepted 11 December 1995)

Measurements of anions and cations are reported for hydrocarbon and silane radio frequency capacitive glow discharges. Series of anions were observed by quadrupole mass spectrometry using power-modulated plasmas, and their structures are interpreted from the form of the mass spectra. Various experiments in silane plasmas show that anion confinement results in particles and conversely, anion detrapping can inhibit particle formation. In contrast, the polymerized neutral flux magnitudes, mass spectra and dynamics are independent of the powder formation. Powder is known to form readily in deposition plasmas containing electronegative free radicals, and the general role of anions in particle formation is discussed in the light of these experiments. © 1996 American Vacuum Society.

### 1. INTRODUCTION

Dust appears most readily in plasmas of gas mixtures containing electronegative radicals<sup>1</sup> and negative ions are also retained by the plasma sheath, which suggests that slow plasma-induced polymerization might proceed via an anionic pathway.<sup>2-6</sup> The objective of this work was to investigate polymerized negative ions in various radio frequency (rf) discharges, using quadrupole mass spectrometry of neutrals, cations and anions in power-modulated rf plasmas<sup>6</sup> to assess their role in particle formation.

Anion sequences are identified in silane ( $\text{SiH}_4$ ), methane ( $\text{CH}_4$ ), and acetylene ( $\text{C}_2\text{H}_2$ ) plasmas. The anion composition and spectral pattern is different in each case and is related to the bond structure of the initial molecule. This deter-

mines ON/OFF modulated at kHz frequencies with an excitation frequency of 10 to 30 MHz capacitively coupled to the rf electrode via a  $\pi$  matching network. The specific plasma parameters are given in each figure caption.

8.3 GHz single-pass microwave interferometry (overall response time  $< 3 \mu\text{s}$ ) and a 1 GHz digital storage oscilloscope provided time-resolved measurements of the free electron absolute density, spatially averaged over the electrode gap, with  $10^6 \text{ electrons cm}^{-3}$  sensitivity.

Two different quadrupole mass spectrometers were separately employed,<sup>7</sup> both equipped for neutral analysis, ion extraction, mass and energy measurements. The hidden analytical limited plasma monitor type HAL-EQP 500 measured negative ions up to the limit of 512 amu when mounted

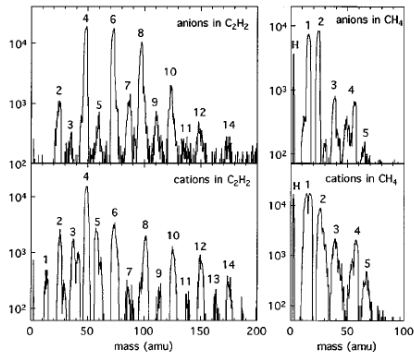


FIG. 4. Comparison of positive and negative ion mass spectra (raw data in counts/s) measured in methane and acetylene plasmas for low mass resolution of the Hidden spectrometer. Plasma parameters: 0.1 mbar, electrode temperature 350 K. Radio frequency excitation at 10 MHz with 550 V amplitude at the electrode, ON/OFF modulation at 1 kHz with 30% duty cycle.

J. Vac. Sci. Technol. A, Vol. 14, 1996

$m/q = -16$ , and no-oxygen!

## Dust formation in Ar/CH<sub>4</sub> and Ar/C<sub>2</sub>H<sub>2</sub> plasmas

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Online at stacks.iop.org/PSSST/18/034010

### Abstract

This paper discusses the growth of nanoparticles in capacitively and inductively coupled radio-frequency plasmas operated in hydrocarbon gases and the back-reaction of particles on the plasma properties. The focus is on the growth mechanism in CH<sub>4</sub>- and C<sub>2</sub>H<sub>2</sub>-containing plasmas, on the role of atomic hydrogen and on the dynamic charging and discharging of particles in pulsed plasmas.

(Some figures in this article are in colour only in the electronic version)

### 1. Introduction

Since Langmuir and his co-workers discovered the existence of small solid particles (dust) in glow discharges [1], the formation of particulates in plasmas has been a well-known phenomenon. Particle formation has been observed in several plasma processes such as etching, sputtering or thin film deposition using reactive gases. In the fabrication of electronic circuits, for example, dust particles are considered to be a main source of contamination. They are regarded in these cases as 'killer particles' as they can cause severe defects in the final product [2]. In other cases, however, the controlled growth of particles is required, for example, for applications in catalysis and pharmacy and for the fabrication of nanocrystalline materials. In the latter case nanoparticles are incorporated into the growing film in order to improve the film properties.

Besides silane, important in PECVD for solar cells, hydrocarbon molecules are frequently used as reactive precursors for functional coatings with widespread technological applications. A prominent example is diamond-like carbon

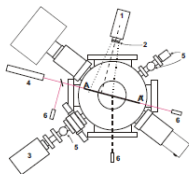


Figure 1. Experimental set-up: 1—CCD camera, 2—632 nm optical filter, 3—mass spectrometer, 4—He-Ne laser (632 nm), 5—pressure gauge, 6—photo diode.

”...five minutes later we added a constant flow rate of 2 sccm CH<sub>4</sub> to the reaction chamber resulting in an increase in the mass spectrometer signal at mass 16 and mass 26...” ... ”... As these particles can survive in the discharge for more than 5 min (up to 20 min in one experiment) they have to be charged negatively...”

Winter *et al.*, Plasma Sources Sci. Technol. 18 (2009) 034010.

Has anyone seen  $\text{CH}_4^-$  ?

Can theory predict it?

# CH<sub>4</sub> ground state

Computational Chemistry, 2014, 2, 31-41  
Published Online April 2014 in Scifires, <http://www.scirp.org/journal/cc>  
<http://dx.doi.org/10.4236/cc.2014.22005>



## On the Accuracy of the Complete Basis Set Extrapolation for Anionic Systems: A Case Study of the Electron Affinity of Methane

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### Abstract

Recent experimental evidence suggests again the existence of the metastable methane anion in plasma swarms. In order to test the reliability of the complete basis set (CBS) extrapolation scheme with augmented correlation-consistent basis sets for anionic molecules, we study the evolution of the electron affinity of methane with benchmark *ab initio* calculations with *aug-cc* basis sets up to *aug-cc-pV6z + diffuse*. Geometry optimizations and vibrational analysis were done at the MP2 level. The electron affinity (EA) was calculated at the MP2 and CCSD(T) levels with and without frozen core and including the extrapolations to the CBS limit. Using the *aug-cc-pVnZ* basis sets it is found that two non-decreasing CCSD(T) CBS limits exist for the EA (0.29 and 0.53 eV) obtained with the  $n = 3, 4, 5$  and  $n = 4, 5, 6$  series, respectively. A new scheme is proposed which can be generalized for very accurate quantum chemical description of molecular anions: the standard *aug-cc-pVnZ* basis sets can be supplemented with extra-diffuse orbitals using a simple even-tempered scheme. This yields a reliable CBS extrapolation method to develop a (discrete approximation of a) continuum anionic state near ionization, viz., one that closely matches the energy of the corresponding neu-

≠ in the ground state

Demonstrated that the negative ion does not exist in its ground state:  $^2A_1$ .



Can theory predict it?

Not so far, ups!

## First report on negative methane.

We measured electron detachment cross sections as an advanced laboratory course at UNAM →

- No differences between two measurement methods were measurable.
- No effect from the time of flight.
- Very large size ( $r_p = 3.15 \text{ \AA}$ ).
- Either is something very different or we are (completely) wrong!

Plasma Sources Sci. Technol. 23 (2014) 015018

## Electron detachment cross sections of $\text{CH}_4^-$ colliding with $\text{O}_2$ and $\text{N}_2$ below 10 keV energies

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### Abstract

Negative methane is an interesting molecular anion from a fundamental point of view and also because it can be a source of thermal electrons in low temperature hydrocarbon plasma. Measurements of collisional electron detachment from methane anions colliding with  $\text{O}_2$  and  $\text{N}_2$  in the energy range of 0.3 to 10.0 keV are presented. Single electron detachment was measured with the signal grow-rate method and total electron detachment was measured with the beam attenuation technique. Both techniques were employed in order to study the process of electron detachment over the present energy range. The validity of the geometrical model is discussed.

Keywords: methane anion, collision detachment, lifetime

(Some figures may appear in colour only in the online journal)

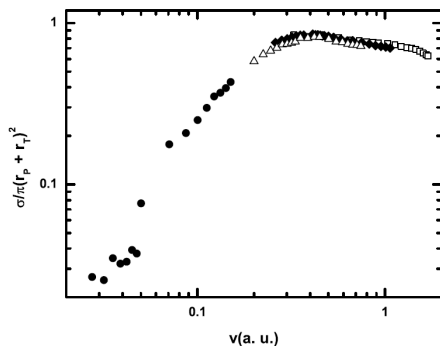
### 1. Introduction

Collision electron detachment (CED) from molecular anions is a process of fundamental interest in cold plasma physics. Detailed knowledge of CED is important in controlling the dielectric strength of gas mixtures because free electrons can be removed from a plasma when the effective electron

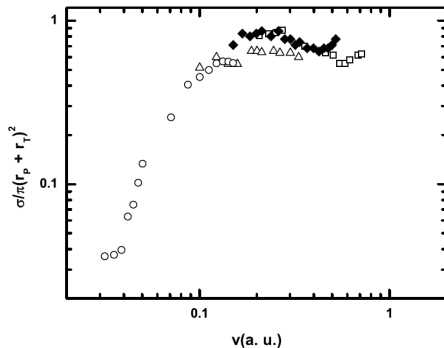
electron detachment may explain the electrical properties of a methane-air flame potential distribution [6].

The present measurements of electron detachment cross sections from  $\text{CH}_4^-$  in collisions with  $\text{O}_2$  and  $\text{N}_2$  at low energies may shed light on the understanding of the details of plasma processes in hydrocarbon atmospheric environments. For instance, a large quantity of heavy negative ions was discovered

## The geometrical model applied to $\text{CH}_4^-$ on $\text{N}_2$ and $\text{O}_2$



Scaled CED cross sections by the geometrical factor for  $\text{N}_2$  target: projectiles are: present data with  $\text{CH}_4^-$ , solid circles. From Sant'Anna et al, squares,  $\text{F}^-$ ; closed diamonds  $\text{Cl}^-$ ; up triangles  $\text{Br}^-$ .



Scaled CED cross sections by the geometrical factor for  $\text{O}_2$  target: Projectiles are: present data with  $\text{CH}_4^-$ , open circles. From Lichtenberg et al squares,  $\text{F}^-$ ; closed diamonds  $\text{Cl}^-$ ; up triangles  $\text{Br}^-$ .

What if...

Are we not seeing something we have in front of our noses?

What if...

Are we not seeing something we have in front of our noses?

~ coffee enters the scene ~

What if...

Are we not seeing something we have in front of our noses?

~ coffee enters the scene ~

What if negative methane happens to be isoelectronic to Na and not to Ne?  
Jacques Vigué.

## Sodium has very long lived metastable states...



### NIST Atomic Spectra Database Levels Data

Na I 430 Levels Found

Z = 11, Na isoelectronic sequence

Data on Landé factors are not available for this ion in ASD

Some data for neutral and singly-charged ions are available in the [Handbook of Basic Atomic Spectroscopic Data](#)

| Primary data source                 |                                                                                                                                 |
|-------------------------------------|---------------------------------------------------------------------------------------------------------------------------------|
| <a href="#">Sansone et al. 2008</a> | Identifications and values of core-excited energy levels of the $2p^3$ and $3s$ configurations are from <a href="#">Kramida</a> |

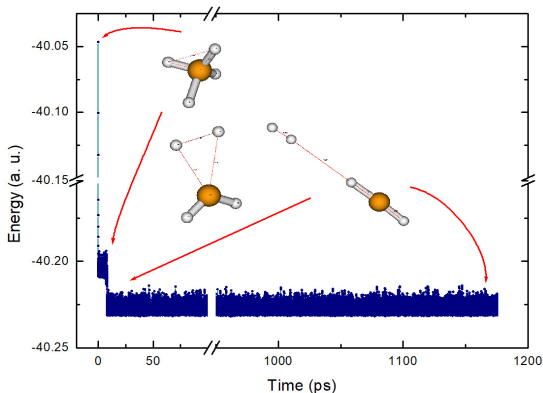
| Configuration | Term    | J     | Level (eV)  | Uncertainty (eV) |
|---------------|---------|-------|-------------|------------------|
| $2p^6 3s$     | $^2S$   | $1/2$ | 0.000000000 |                  |
| $2p^6 3p$     | $^2P^o$ | $1/2$ | 2.102297177 | 0.000000005      |

Sodium has 11  $e^-$ . Note:  $2p^6 3s$

|                                          |              |                                  |                                          |                                      |
|------------------------------------------|--------------|----------------------------------|------------------------------------------|--------------------------------------|
| $2p^6 19f$                               | $^2F^o$      | $5/2, 7/2$                       | [5.10138254]                             | 0.00000025                           |
| $2p^6 19g$                               | $^2G$        | $7/2, 9/2$                       | [5.10138725]                             | 0.00000025                           |
| $2p^6 20p$                               | $^2P^o$      | $1/2$<br>$3/2$                   | [5.10195472]<br>[5.10195795]             | 0.00000025<br>0.00000025             |
| $2p^6 20d$                               | $^2D$        | $3/2$<br>$5/2$                   | [5.10501280]<br>[5.10501280]             | 0.00000025<br>0.00000025             |
| $2p^6 20f$                               | $^2F^o$      | $5/2, 7/2$                       | [5.10505805]                             | 0.00000025                           |
| $2p^6 20g$                               | $^2G$        | $7/2, 9/2$                       | [5.10506202]                             | 0.00000025                           |
| <b>Na II (<math>2p^6 \ ^1S_0</math>)</b> | <b>Limit</b> | <b>---</b>                       | <b>5.13907696</b>                        | <b>0.00000025</b>                    |
| $2p^6 3s^2$                              | $^2P^o$      | $3/2$<br>$1/2$                   | 30.7692<br>30.9327                       | 0.0006<br>0.0015                     |
| $2p^6 (2p^+ ) 3s 3p (2p^+ )$             | $^4S$        | $3/2$                            | 32.7002                                  | 0.0005                               |
| $2p^6 (2p^+ ) 3s 3p (2p^+ )$             | $^4D$        | $7/2$<br>$5/2$<br>$3/2$<br>$1/2$ | 33.0525<br>33.0956<br>33.1388<br>33.1752 | 0.0005<br>0.0005<br>0.0005<br>0.0005 |

And incredible long-lived metastable states way above the ionization limit.

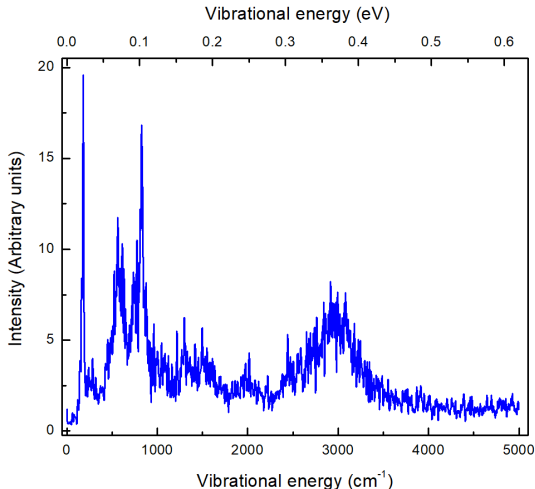
## $\text{CH}_4^-$ energy as a function of time



Energy evolution of the excited quartet state of  $\text{CH}_4^-$  at 300 K. The deep about 8 ps indicates the appearance of the  $\text{CH}_2^-:\text{H}_2$  exciplex. Metastability with respect to the separate  $\text{CH}_2^-$  ( $S = 3/2$ ) +  $\text{H}_2$  ( $S = 0$ ) fragments was found.

## $\text{CH}_4^-$ energy as a function of time

Infrared spectrum obtained from the Fourier transform of the velocity autocorrelation function after thermalization was achieved (10 ps) at 300 K. Features of independent  $\text{CH}_2^-$  and  $\text{H}_2$  roughly appear. The peak at  $180\text{ cm}^{-1}$  is unique to  $\text{CH}_4^-$ .



## The model on negative methane.

- No differences between two measurement methods were measurable: because  $\exists$  only one state.
- No effect from the time of flight: because is very stable.
- Very large size: as predicted.
- And everything was consistent with the experiment on cross sections.

Phys. Rev. Lett., 124, 056001 (2020)  
and the pandemic hits (lockdown starts in march 2021)!

PHYSICAL REVIEW LETTERS 124, 056001 (2020)

### Solving the $\text{CH}_3^-$ 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  $\text{CH}_3^-$  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  $\text{CH}_3^-$ . Here we find  $\text{CH}_3^-$  as being a metastable species in its lowest quartet spin state, a  $\text{CH}_3^-:\text{H}_2$  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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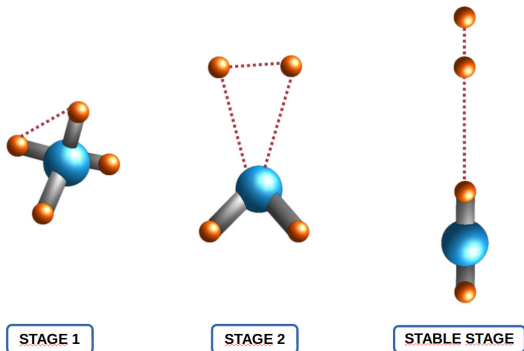
**The  $\text{CH}_3^-$  puzzle.**—Methane has ten electrons in a noble gaslike configuration so that electron capture by this very stable molecule is considered impossible. Nonetheless, electron attachment in methane has consistently been evidenced by several groups over five decades [1–10] though the 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

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  $\text{CH}_3^-$  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 Trempa and Neut [1] and by Sharp and Dowell [2], who used a beam technique and found that dissociative electron attachment in  $\text{CH}_4$  took place over the 2–13 eV range of electron energies with  $H^-$  and

## $\text{CH}_4^-$ energy as a function of time



The extra electron is captured in an excited state with a tetrahedral geometry (Td) of the methane molecule. This state is temporal (stage 1) and instantly evolves into an intermediate configuration (stage 2). The configuration continues to evolve reaching a final state (stable stage) after 8 ps, unfolding into an exciplex with linear geometry.

## In conclusion:

- 1  $\text{CH}_4$  captures an  $e^-$  in a excited state that evolves to an linear exciplex (excited complex):  $\text{CH}_2^-\text{:H}_2$
- 2 It is very stable - analogue - to  $\text{Na}^*$  six-times fold above its ionization energy.
- 3 Therefore,  $\text{CH}_4^- \exists$  and is very stable.
- 4 This a new fundamental peace of knowledge of an important molecule.

## In conclusion:

- ❶ Negative ions are opportunity for advancing fundamental knowledge.
- ❷ There are many questions in terms of practical applications.
- ❸ In the XXI century, nobody expected to find an unknown spectrometric species at  $m/q = -16$ .

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- ❸ In the XXI century, nobody expected to find an unknown spectrometric species at  $m/q = -16$ .
- ❹ ... and is not  $O^-$ !!!

Mercy beacoup!

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