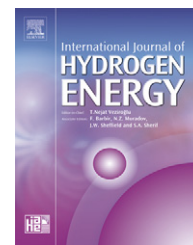


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## Discussion

# A chemist's view of J.M. Calo's comments on: "A new gaseous and combustible form of water" by R.M. Santilli (Int. J. Hydrogen Energy 2006:31(9), 1113–1128)

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## 1. Introduction

The last ten years has seen the emergence of new and revolutionary theories and species within both physics and chemistry. In 2006 the Cplex-isoelectronic theory of pericyclic chemistry and aromaticity was proposed by Cloonan [1,2]. This new electronic theory, which is in line with the Robinson/Ingold electronic theory of organic chemistry and Complexity theory, makes different predictions from the present quantum chemical methods and the empirical evidence, when available, is found to be consistent with the Cplex-isoelectronic theory [1,2]. In 1999 Hadronic Chemistry was proposed by Santilli as a covering theory for quantum mechanism, with a new model for the two electron chemical bond involving the deep overlap of the wavepackets of the valence electrons to form a singlet quasi-particle called the isoelectronium [3,4]. Hadronic Chemistry permits an exact representation of the binding energy of  $H_2$  from axiomatic principles, without ad hoc modifications of the theory, and

predicts new clean energy sources at the level of elementary particles, at the nuclear level and at the molecular level [3,4]. In 2000 Mills proposed the existence of a new form of stable hydrogen, where the electron has less energy than the  $n = 1$  ground state, with strong experimental evidence including solid state NMR spectra [5,6]. This species with fractional quantum energy levels, termed a hydrino, if valid implies a revision of quantum mechanics. In 1998 Santilli proposed, also with strong experimental evidence, the existence of a new chemical species called a magnecule in which atoms/molecules/dimers are held together by opposing magnetic polarization of the orbits [4,7,8]. These new theories and species potentially represent a new era in science.

It is crucial that these new theories and species are tested further, both by the developers and by external researchers, especially in light of their deductions in relation to present theories. Recently Calo, a chemical engineer at Brown University USA, published comments [9] on Santilli's claim for the existence of a magnecule structure derived from

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water via a new electrolyzer [10]. Calo claimed that the reported experimental data was not consistent with a magneclule but rather a mixture of hydrogen, oxygen and water vapour [9]. The objective of this paper is to provide an independent analysis of Calo's comments from a chemist's vista.

## 2. Analysis

Calo claimed, on page 1312, that the fact that the IR spectrum of the HHO gas has the largest absorption in the 2800–3000  $\text{cm}^{-1}$  region is consistent with water vapour. This claim is not consistent with the experimental IR data published in the scientific literature for water vapour [11]. Water vapour at 26.85 °C has the highest absorption coefficient at 3750  $\text{cm}^{-1}$  in the 400–4000  $\text{cm}^{-1}$  IR spectrum followed by the bands at 1525, 1700, 3850, 3825 and 3875  $\text{cm}^{-1}$ . The absorption coefficients in the 2800–3000  $\text{cm}^{-1}$  region are at minimum 736 times weaker than the absorption coefficient at 3750  $\text{cm}^{-1}$  [11]. Even at 326.85 °C the absorption coefficients in the 2800–3000  $\text{cm}^{-1}$  region are still over 250 times weaker than the most intense band in the 3700–3900  $\text{cm}^{-1}$  region [11]. These values were calculated based on approximately 80 published emission and absorption spectra [11]. Furthermore no degree of hydrogen bonding in liquid or solid water will result in the OH stretch moving to a frequency as low as the 2800–3000  $\text{cm}^{-1}$  region and hydrogen bonding is extremely weak to nonexistent in the vapour phase [12]. The only OH that vibrates in the 2800–3000  $\text{cm}^{-1}$  region is the OH function of a carboxylic acid (RCOOH) but there is clearly no evidence for a carboxylic acid in the IR data (C=O stretch not present at  $\approx 1710 \text{ cm}^{-1}$ ) or in the mass spectra [13]. A pressure of 35 psi, as found in the HHO gas, also will not lower the OH stretching band to this region [12].

Calo also claims on page 1312 that “the 18 peak is most certainly nothing but “conventional” water vapor”. The peak at 18  $m/z$  in the mass spectrum is consistent with  $\text{H}_2\text{O}$  but this is not absolute. The peak at 18  $m/z$  could also have arisen from a fragmentation process [13] and thus  $\text{H}_2\text{O}$  would not exist as an isolated entity in the mixture in this case. The 18  $m/z$  peak could be due either to a  $\text{H}_2\text{O}$  cation or a  $\text{H}_2\text{O}$  radical cation as mass spectroscopy detects both. If the former is involved it would be inconsistent with  $\text{H}_2\text{O}$  as a separate entity in the mixture as a separate water molecule would give rise to a molecular radical cation in the EI method [13]. Furthermore the  $m/z$  ratio has to be determined to four decimal places for any degree of certainty to be assigned to the peak from a molecular formula point of view. If the peaks at 18  $m/z$ , 17  $m/z$  and 16  $m/z$  were due to water as Calo claims, it would form at minimum 12% of the HHO gas, based on the intensities of the peaks in the mass spectrum of Fig. 1, and thus the water would be expected to show bands in the IR spectrum. There are no bands in the IR spectrum consistent with water vapour [11]. Thus the experimental data are not consistent with Calo's claim that the HHO gas is a mixture of ‘hydrogen, oxygen, and water-vapor’. The IR spectrum of the HHO gas is not consistent with  $\text{H}_2\text{O}_2$  [14,15] or  $\text{O}_3$  [16] which are other possible combinations of hydrogen and oxygen. C–H bonds from hydrocarbons

typically appear in the 2800–3000  $\text{cm}^{-1}$  region and are accompanied by bands at approximately 1467, 1450, 1378 and 720  $\text{cm}^{-1}$  [13]. Although the IR spectrum of the HHO gas has some resemblance to a hydrocarbon, the mass spectrum is clearly inconsistent with a hydrocarbon (cyclic or acyclic) [13]. There was also no source of carbon mentioned in Santilli's paper [10]. Hence the bands in the IR spectrum, combined with the MS and GC/MS data, do appear to be anomalous as Santilli claims [10].

Calo claims on page 1312 that the experimental data obtained from bubbling HHO gas through diesel could be interpreted in terms of the removal of the more volatile components from diesel [9]. This is clearly incorrect based on the data presented by Santilli. There is no reduction in the number of the peaks at the start of the TIC for the HHO/diesel system in Fig. 6 compared to the diesel itself in Fig. 5 [10]. The simulated distillation by gas chromatography (SDGC) method elutes compounds according to increasing boiling point and thus the most volatile components will elute first [17–19]. In fact there seems to be on approximation, a similar number of peaks in the chromatogram of Fig. 6 as in the chromatogram of Fig. 5. Thus even if the GC conditions were different in both runs the data are still consistent with no loss of the diesel components due to evaporation. As there is no major degree of evaporation in the HHO/diesel system the increase in the ion abundance in Fig. 6 compared to Fig. 5 provides evidence for an interaction between the diesel and the HHO gas. This could have been confirmed further by comparing the mass spectrum for the peak in Fig. 5 with the highest  $m/z$  ratio to the mass spectrum of the peak in Fig. 6 with the highest  $m/z$  ratio. The SDGC data provides strong evidence for anomalous behaviour in the HHO gas as Santilli claims. Bubbling a gas like  $\text{N}_2$  through an organic liquid such as acetone or methylene chloride does cause evaporation but this is clearly not what is occurring in this diesel/HHO system.  $\text{N}_2$  (argon or helium) are inert whereas the HHO gas is not based on this experimental result. Thus none of the experimental data provided by Santilli is consistent with Calo's claim that the HHO gas is a mixture of ‘hydrogen, oxygen and water-vapor’. The data by Santilli does show anomalous behaviour.

Calo provides an alternative rationale for the “widely varying thermal content” of the HHO gas on page 1310 but he does not apply this rationale to explain why the HHO gas can reach a temperature of 9000 °C [9]. A temperature of 9000 °C is inconsistent with Calo's claim that the HHO gas is a mixture of ‘hydrogen, oxygen and water-vapor’ and is consistent with Santilli's claim of anomalous behaviour from a gas derived from water. Calo has stated on page 1310 that a hydrogen flame in oxygen has a temperature of 3080 K (2807 °C) [9]. The presence of water vapour in a  $\text{H}_2$  and  $\text{O}_2$  mixture cannot account for this temperature difference of over 6000 °C by any known law of science. Calo did not focus on this *unambiguous evidence* for anomalous behaviour in the HHO gas. In fact the presence of water would lower the temperature of the flame due to the heating and evaporation of the water. Calo himself mentioned the effect of the water in absorbing the heat of the flame on page 1310 (right-hand column, 2nd paragraph) and he even did calculations for this under his discussion of the “widely varying thermal content”.

On page 1309 Calo fails to see that the use of 'water evaporation' on page 1114 (right column, 1st paragraph) is clearly a typing error. The abstract, the introduction and the theoretical section in Santilli's paper clearly states that a 'new electrolyzer' is used to generate the HHO gas and not a water vaporizer (or evaporator). Santilli is attempting to show that the mechanism by which the HHO gas is formed is different from the conventional electrolysis of water or the evaporation of liquid water to the water gas state. This is stated clearly on page 1114 (left column, 4th paragraph) and also in the theoretical section [10]. Furthermore Calo attempts to calculate the amount of energy required for water vaporization using the 55 SCF value quoted by Santilli. This starting point for the calculation is incorrect as the HHO gas has a specific weight of 12.3 g/mol and not 18 g/mol as per water vapour. If the HHO gas was hydrogen and oxygen as Calo claimed he should have used the equation  $\text{H}_2\text{O g (2 volume)} \rightarrow \text{H}_2 \text{ (2 volume)} + \frac{1}{2}\text{O}_2 \text{ (1 volume)}$  in this case. Calo also continues to do his calculation on evaporation but at the end of page 1309 admits that this calculation was meaningless to begin with. The above equation was used by Santilli on page 1113 with the correct input but with an incorrect output as Calo correctly points out. The incorrect output from the above equation did lead to Santilli making incorrect deductions from the specific weight of the HHO gas. Calo also correctly points to the typing errors on page 1115 (i.e.  $\text{HBN}_2$  and  $\text{P}_2$ ). These are clearly typing or formatting errors as they are out of context with the rest of the paper.

Calo stated on page 1310 that 'I cannot even begin to speculate on what adhesion of a gas to another gas means, since adhesion requires the interaction of a species with a bulk phase' [9]. This is not technically correct as the term adhesion is not confined to the field of adhesives and sealants but is a broad term within science. Adhesion also means an intermolecular force of attraction between two different molecules. This can be seen in the following quote from the general and physical chemistry section of Chemical Abstracts 1885 "the author has more particularly studied the phenomena of cohesion and adhesion of liquids, a subject of interest to the chemist as dealing with the attraction of homogeneous and heterogeneous molecules" [20]. A further example is also found in the general and physical chemistry section of Chemical Abstracts 1887 "solution results from the tendency towards equilibrium of three forces, attraction of water for water, and of salt for salt (cohesions), and attraction of salt for water (adhesion)" [21]. Robinson, in his electronic theory of organic chemistry, developed concepts based on scientists who used the term adhesion in relation to the chemical bond and dipoles [22]. London used the term cohesion in his theory of molecular forces [23]. Furthermore adhesion in the field of adhesives and sealants relates to the interaction of species at their surfaces [24] and not at their bulk phase as Calo states [9]. In fact the surface can be chemically different from the bulk of the material in some cases. Thus Santilli's use of the term adhesion is technically correct.

Calo states that the abscissa in Fig. 1 should be ' $m/e$ —mass to charge ratio'. This is not technically correct. It should be  $m/z$  not  $m/e$  based on the current IUPAC standard and most journals' criteria. The ' $m/e$ ' was typically used in the older literature and the ' $e$ ' really refers to an electron stemming

from Thomson's work on the electron. This change from  $m/e$  to  $m/z$  can be seen by comparing the 7th edition (2005) of Ref. [13] to the 4th edition (1981). Furthermore the ' $m/z$ ' value is nearly always equal (or approximately equal) to mass as the charge species are usually +1 in the EI method. In fact the  $m/z$  value is used by chemists on a regular basis to determine the molecular weight of a compound to four decimal places. This method of determining molecular weight is accepted in peer reviewed scientific journals and used as proof of structure [25,26]. In Figs. 10–12  $m/z$  is clearly seen on the x-axis.

Calo's analysis of the "gas chromatograph" and "Gas Chromatographer" issue is not accurate. Calo claims that Santilli is "attempting to refer to a gas chromatograph not a gas chromatographer". Santilli is clearly not referring to a gas chromatograph or even a gas chromatogram, based on his choice of words and the structure of the sentence. Santilli clearly refers to the scans being reproduced in Fig. 1 [10]. Namely the reference to 'scans' relates to the magnetic scanning or magnetic focusing involved in producing the mass spectrum [13]. GC does not invoke scans only MS does. Santilli has clearly misplaced the term mass spectrometer with gas chromatographer. These typing errors were either missed by the reviewers or they occurred during formatting at the printers.

Calo states on page 1311 that there is absolutely no  $m/z = 2$  and 5 in Fig. 11. Calo is clearly incorrect here. The 2 and 5 are marked in the spectrum of Fig. 11 although their intensity is very low and very close to the baseline. What is not clear from Santilli's paper is whether Figs. 10 and 11 are from the same mass spectrum or involve separate spectra. Calo also fails to explain the origin of the anomalous peak at  $m/z = 5$ . The presence of peaks due to air in the mass spectrum in Figs. 11 and 12 are feasible as Calo suggests, although some of the crucial areas in the mass spectrum are not visible to confirm this. However, these peaks are not to be found in the mass spectrum of Fig. 1 and is consistent with Figs. 11 and 12 arising from GC/MS and Fig. 1 from MS. Air can arrive at the MS via the GC column and is well documented in GC/MS. Calo is correct in stating that the baseline in the mass spectrum of Fig. 1 is not good. Calo is also correct that a negative peak ( $m/z = 34$ ; Fig. 1) should not exist in a mass spectrum. Santilli stated on page 1118 "even if the species is formed by the spectrometer" in relation to  $m/z = 5$ . This shows that Santilli does understand how MS works despite Calo's claim. Calo in most cases attaches absolute formulae to the  $m/z$  ratios. Calo states that  $m/z = 33$  is 'probably just'  $\text{HO}_2^+$ . Objectively it is consistent with  $\text{HO}_2^+$  or  $\text{HO}_2^+$  radical cation, or other species who's  $m/z$  add up to 33 such as  $\text{H}_3\text{NO}$ . It is also consistent with a magnecule. Calo claims that  $16m/z$  and  $17m/z$  are  $\text{O}^+$  and  $\text{OH}^+$  and are 'PRODUCED' from water vapour. It is consistent with water vapour but these species could arise from other structures and from fragmentations [13]. These peaks may also be radical cations as opposed to cations. They could correspond to  $\text{CH}_4$ ,  $\text{CH}_5$  or  $\text{NH}_4$  (cation or radical cation) for example or a magnecule. The  $m/z$  ratios need to be calculated to four decimal places before any degree of certainty is attached to its structure. If they arise from water, the water itself may have arisen from a fragmentation process as discussed above. Calo's assertion that 'how could the HHO gas not contain water vapour...it is produced from

liquid water and thus is undoubtedly saturated with water vapor' is not technically correct. A reaction/process which goes 100% to completion cannot contain any reactant/starting material by definition. Furthermore the HHO gas may have been purified, this paper dealt only with the analysis of the HHO gas and not its production. Thus it cannot be stated that the HHO gas is 'undoubtedly' contaminated with water vapour. The peak at  $m/z = 35$  in Fig. 1 is of very low intensity and this is one possible reason why it may be absent in other spectra. The GC column may also affect the observation of the peak through a decomposition or a chemical alteration process. These possibilities were not mentioned by Calo.

Calo's claim that  $H_2$  and  $O_2$  are transparent to IR radiation is not precise.  $H_2$  absorbs in the near IR and both absorb when sufficiently long path lengths, as well as their liquid states, are used due to collision induced vibrational bands, electrical quadrupole transitions and magnetic dipole rovibrational transitions [27–31]. The path length is not reported and thus an exact analysis of Figs. 2 and 3 is not possible. Juxtaposition with Fig. 4 does prove that the HHO gas contains something other than  $H_2$  and  $O_2$  and is unsymmetrical as Santilli claims [10]. The Raman spectrum is required to confirm the existence or absence of  $H_2$  and  $O_2$  in the HHO gas.

Calo's assertion on page 1311 that Santilli concludes that conventional O and OH radicals are present in the HHO gas combined with his assertion also on page 1311 that the  $m/z = 33$  peak is probably just  $HO_2^+$ , because how could any chemical species be of nonmolecular nature, and his assertion that magnecules are pseudoscience, shows that Calo has no knowledge of Santilli previous work and terminology used in the field of magnecules. In fact Calo has not referenced or discussed any of Santilli previous work in this area. Santilli for example states that he uses the term atom whether or not it is ionized [4]. Calo for example does not comment on the fact that each peak from the TIC of Magnegas showed a large number of fragments in the mass spectrum yet no or few IR signals were found for these peaks [4,7,8]. Furthermore none of these mass spectra could be assigned to known molecules in the database. He also did not comment on the fact that the IR bands for these peaks mutated and any molecule assigned by IR had a molecular weight dramatically lower than the highest  $m/z$  observed in the mass spectrum [4]. This is truly anomalous behaviour and provides strong evidence for magnecules.

Calo fails to discuss the effect a sufficiently strong magnetic field could have on electrons. Santilli clearly states on page 1122 that 'an external magnetic field sufficient to create the polarization of atomic orbitals into toroids' is used. The effect of magnetism on the electron is seen in the ability to run MS in the negative mode via magnetic focusing [32]. A given nucleus in NMR spectroscopy would exhibit similar signals if the applied magnetic field had no effect on the electrons in the molecules [33]. The effect of a magnetic field on the electron is also seen in ESR spectroscopy [34] and in Faradays law of induction [35]. Calo also fails to recognize that magnecules are feasible within quantum electrodynamics [4,7,8,10]. Thus there is ample experimental and theoretical grounds for the existence of magnecules. Calo's discussion of magnecules in terms of conventional free radicals [36] is not precise and to expect them to behave similarly has no basis.

Magnecules by definition involve atoms, many of which are radicals, dimers and ordinary molecules *bonded together by opposing magnetic polarities*. In fact a free radical in the true or conventional sense may never exist in the formation of magnecules as the strong magnetic field is always present i.e. a free radical may never be a true intermediate in the formation of a magnecule. Furthermore the term radical also relates to a group (symbol R) in organic compounds e.g. R-OH and thus is not restricted to a species with an unpaired electron, although not recommended by the IUPAC nomenclature since 1993.

Calo has provided no reference to back up his claim in relation to the global oxygen levels. He has not stated whether the oxygen level is continuously monitored, on a day by day and hour by hour basis. He has not stated who monitors it and how accurate the data is. He has not stated whether the oxygen level is the same at sea and land and at all points on land and at all times. He has not stated that if combustion of fossil fuels increased and photosynthesis on land and sea decreases the overall level of oxygen would decrease. In fact if photosynthesis stopped completely, it is estimated that after 5000 years all oxygen would be consumed by respiration, combustion, weathering, etc. [37]. He also has not discussed the relevancy of air currents in distributing oxygen from one region to another and the rate of diffusion of oxygen as a function of concentration and temperature. He also has not addressed in detail the comments made by Santilli in relation to oxygen levels [4,8].

Santilli on page 1121 clearly and correctly states [10] that the first publication cannot realistically be expected to explain a new concept in its full entirety and there is no reason why data in relation to this new concept cannot be published even if it cannot be fully explained. Many facts have been published in the scientific literature without a rationale been provided. Products from organic chemistry reactions are routinely published without any solid evidence provided for the mechanism by which they are formed. In the case of magnecules the difficulties in full structural elucidation has been well documented [4,7,8].

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### 3. Conclusion

In conclusion the IR data combined with the mass spectra and GC/MS data, the ability to achieve a temperature of 9000°C and to interact with diesel (SDGC data) are inconsistent with Calo's claim that the HHO gas contains only 'hydrogen, oxygen and watervapor'. The data are consistent with anomalous behaviour for a gas obtained from water and thus the existence of magnecules is feasible. These results must also be viewed in light of Santilli's previous experimental evidence for magnecules [4,7,8,10]. Furthermore Santilli has stated that further data on the HHO gas will be published [10]. There is ample experimental and theoretical grounds for magnecules including quantum electrodynamics. New ideas and theories must be rigorously tested, especially when revolutionary, but only with pure logic and objectivity and via the true scientific method. Objectively Calo's analysis of the HHO gas does not fulfill these criteria.

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