Istituto d'Istruzione Superiore 'Largo Brodolini' - Pomezia (RM)
La Tua scuola, ... il Tuo futuro!

INAIL

La sicurezza in ambito biotecnologico:

un tema in evoluzione

La fisica dell'acqua

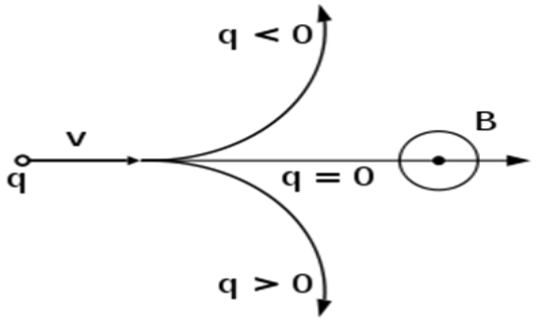
Pomezia 30 maggio 2023

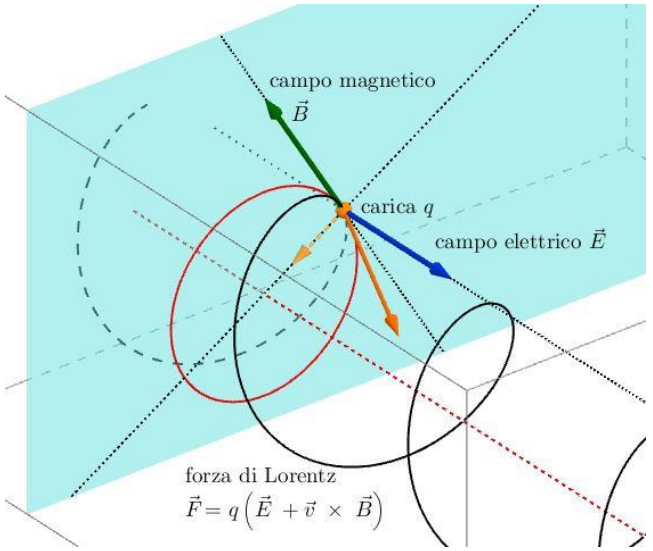
Enrico. D'Emilia (Inail)

Razionale della ricerca

Hendrik Antoon Lorentz (was born at Arnhem) the “father” of ICR

Nobel physics 1902

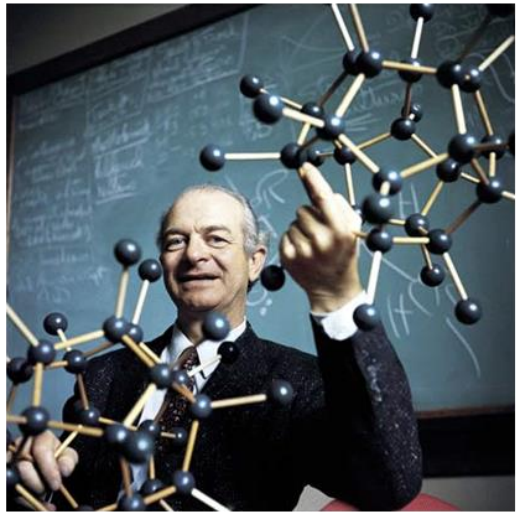




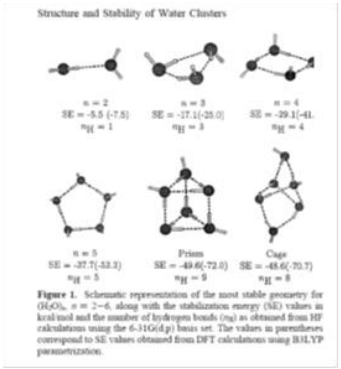
La forza di Lorentz è una forza che agisce su una carica elettrica in movimento all’interno di un campo magnetico; questa forza si esprime con il seguente prodotto vettoriale: dove q indica la carica elettrica puntiforme, v è il vettore velocità con cui si muove la carica elettrica, e B è il campo magnetico cui essa è sottoposta.

$$\mathbf{F}_{mag} = q(\mathbf{v} \times \mathbf{B})$$

Linus Pauling and structure of water



Linus Pauling holding models of water molecules in a classroom at the California Institute of Technology, Pasadena.


Structure and Stability of Water Clusters

n = 2
SE = -5.5 (-7.5)
n_H = 1

n = 3
SE = -17.1(-25.0)
n_H = 3

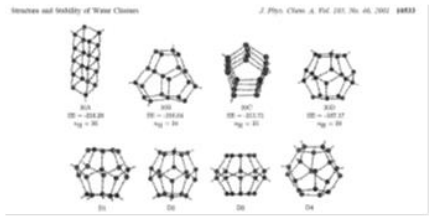
n = 4
SE = -29.1(-41.
n_H = 4

n = 5
SE = -37.7(-52.1)
n_H = 5

Prism
SE = -49.6(-72.0)
n_H = 9

Cage
SE = -48.6(-70.7)
n_H = 8

Figure 1. Schematic representation of the most stable geometry for $(H_2O)_n$, $n = 2$–6, along with the stabilization energy (SE) values in kcal/mol and the number of hydrogen bonds (n_H) as obtained from HF calculations using the 6-31G(d,p) basis set. The values in parentheses correspond to SE values obtained from DFT calculations using B3LYP parametrization.



Linus Pauling
Nobel chemistry 1954


112 CHEMISTRY: PAULING AND MARSH PROC. N. A. S.

THE STRUCTURE OF CHLORINE HYDRATE

BY LINUS PAULING AND RICHARD E. MARSH

THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY,* CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIFORNIA

Communicated December 31, 1951

In 1811 Humphry Davy[1] showed that water is a component of the phase that had earlier been thought to be solidified chlorine, and twelve years later Michael Faraday[2] reported an analysis that corresponds to the formula $Cl_2 \cdot 10H_2O$. He surmised that his determination of the chlorine content was low, and later studies have indicated the composition to be close to $Cl_2 \cdot 8H_2O$. Since Faraday's time similar crystalline hydrates of many gases with small molecular volume, including the noble gases and simple hydrocarbons, have been reported. The determination of the structure of ice and the development of an understanding of the nature of the hydrogen bond have strongly suggested that these substances are clathrate compounds, with a tetrahedral hydrogen-bonded framework of water molecules (with O H···O = 2.76 A, as in ice) defining cavities large enough to contain the other molecules.

Only recently have serious steps been taken toward determining the structure of these hydrates. About ten years ago von Stackelberg and his collaborators[3, 4] made x-ray studies of some of these compounds, including the hydrates of xenon, chlorine, bromine, sulfur dioxide, hydrogen sulfide, methyl bromide, methyl iodide, ethyl chloride and chloroform. They reported that most of the crystals have a cubic unit cell with a_0 equal to about 12.0 A. From single crystal x ray photographs of the hydrate of sulfur dioxide they decided on the space group O_h^8, and postulated a structure consisting of a framework of 48 oxygen atoms in a set of general positions x, y, z in the unit cell. With this structure each oxygen atom has neighboring oxygen atoms at a distance of about 2.4 A, and the framework has eight cavities in which the gas molecules could lie. The ideal formula would thus be $M \cdot 6H_2O$. This structure is not acceptable because of the very short O H···O distance of 2.4 A; in addition, the hydrogen bonds lie at angles between 60° and 145°, which differ greatly from the expected tetrahedral angle.

Claussen[5] then proposed a structure based on a larger cubic unit cell, about 17 A on edge, containing 136 water molecules. The oxygen atoms would be arranged to form 16 pentagonal dodecahedra and 8 hexakaidecahedra. This structure leads to the empirical formula $M \cdot 5^2/_3H_2O$ for smaller molecules which occupy all of the polyhedra, and $M \cdot 17H_2O$ for larger molecules which occupy only the hexakaidecahedra. The obvious advantage of such a structure is the presence of hydrogen bond angles of

The inhomogeneous structure of water at ambient conditions

C. Huang[a], K. T. Wikfeldt[b], T. Tokushima[c], D. Nordlund[a], Y. Harada[c,d], U. Bergmann[a], M. Niebuhr[a], T. M. Weiss[a], Y. Horikawa[c,e], M. Leetmaa[b], M. P. Ljungberg[b], O. Takahashi[f], A. Lenz[g], L. Ojamäe[g], A. P. Lyubartsev[h], S. Shin[c,i], L. G. M. Pettersson[b], and A. Nilsson[a,b,1]

[a]Stanford Synchrotron Radiation Lightsource, P.O.B. 20450, Stanford, CA 94309; [b]FYSIKUM, AlbaNova, and [h]Division of Physical Chemistry, Stockholm University, S-10691 Stockholm, Sweden; [c]RIKEN/SPring-8, Sayo-cho, Sayo, Hyogo 679-5148, Japan; [d]Department of Applied Chemistry, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan; [e]Department of Physical Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan; [f]Department of Chemistry, Hiroshima University, Higashi-Hiroshima 739-8526, Japan; [g]Department of Chemistry, Linköping University, S-581 83 Linköping, Sweden; and [i]Institute for Solid State Physics, University of Tokyo, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan

Edited by H. Eugene Stanley, Boston University, Boston, MA, and approved July 7, 2009 (received for review May 7, 2009)

Small-angle X-ray scattering (SAXS) is used to demonstrate the presence of density fluctuations in ambient water on a physical length-scale of ~1 nm: this is retained with decreasing temperature while the magnitude is enhanced. In contrast, the magnitude of fluctuations in a normal liquid, such as CCl_4, exhibits no enhancement with decreasing temperature, as is also the case for water from molecular dynamics simulations under ambient conditions. Based on X-ray emission spectroscopy and X-ray Raman scattering data we propose that the density difference contrast in SAXS is due to fluctuations between tetrahedral-like and hydrogen-bond distorted structures related to, respectively, low and high density water. We combine our experimental observations to propose a model of water as a temperature-dependent, fluctuating equilibrium between the two types of local structures driven by incommensurate requirements for minimizing enthalpy (strong near-tetrahedral hydrogen-bonds) and maximizing entropy (non-directional H-bonds and disorder). The present results provide experimental evidence that the extreme differences anticipated in the hydrogen-bonding environment in the deeply supercooled regime surprisingly remain in bulk water even at conditions ranging from ambient up to close to the boiling point.

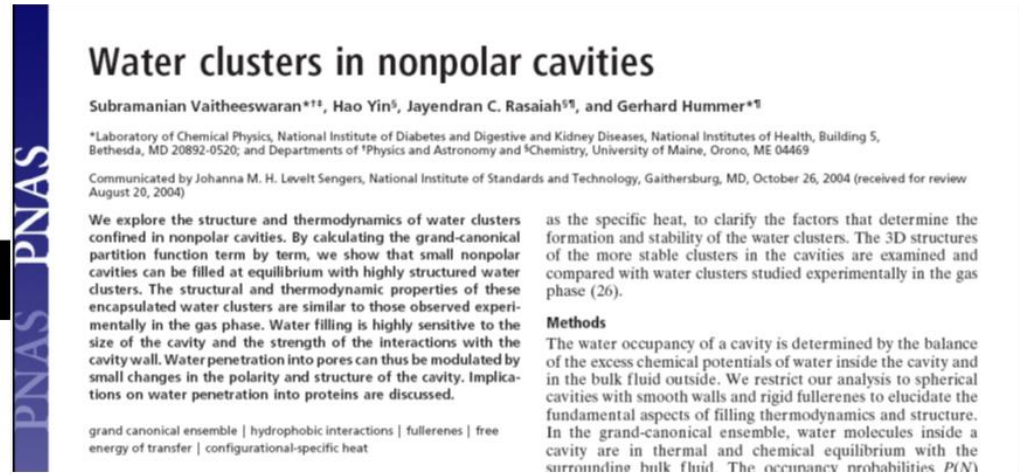
density fluctuations | liquid–liquid hypothesis | small angle X-ray scattering | water structure | X-ray spectroscopy

Liquid water shows many anomalies in its thermodynamic properties such as compressibility, density variation and heat capacity (1–4). In the low-temperature regime, below the freezing point, these properties deviate strongly from normal and mostly focused on the supercooled region and given contradictory results where both positive (10–12) and zero enhancement (13, 14) at low Q have been reported. With the development of third-generation synchrotron light sources the ability to perform SAXS has been greatly advanced and measurements can now be performed in a large Q-range with high accuracy and reproducibility (15).

Results

Fig. 1*A* shows the normalized structure factor, $S(Q)$, derived from the SAXS intensity in ambient water (H_2O) as function of Q for temperatures from 7 to 74 °C in the full Q-range of interest, 0.04–0.78 $Å^{-1}$ (see *SI Methods*). All scattering curves show an enhancement approaching $Q \to 0$ after experiencing a minimum ≈0.4–0.5 $Å^{-1}$, which to first approximation directly indicates the presence of density heterogeneities. In particular, the enhancement becomes *smaller* with increasing temperature in strong contrast to expectation from simple thermal density fluctuations.

To address whether the enhancement at low Q can be related to and reproduced by thermal fluctuations in common water models, we have performed molecular dynamics (MD) simulations using the extended simple point charge (SPC/E) potential (see *SI Methods*). The SAXS signal at low Q is given by the Fourier transform (FT) of the longer intermolecular correlations in real space from the simulation. To model SAXS data it is thus essential to use large simulation boxes (here 40,000 molecules) and also to average over long simulation runs (here longer than 0.3 ns) to reduce artificial oscillations in Q space. Fig. 1*B* shows the SPC/E oxygen–oxygen partial structure factor, $S(Q)$ (see *SI*



Water clusters in nonpolar cavities

Subramanian Vaitheeswaran*[†‡], Hao Yin[§], Jayendran C. Rasaiah[§¶], and Gerhard Hummer*[¶]

*Laboratory of Chemical Physics, National Institute of Diabetes and Digestive and Kidney Diseases, National Institutes of Health, Building 5, Bethesda, MD 20892-0520; and Departments of [†]Physics and Astronomy and [§]Chemistry, University of Maine, Orono, ME 04469

Communicated by Johanna M. H. Levelt Sengers, National Institute of Standards and Technology, Gaithersburg, MD, October 26, 2004 (received for review August 20, 2004)

We explore the structure and thermodynamics of water clusters confined in nonpolar cavities. By calculating the grand-canonical partition function term by term, we show that small nonpolar cavities can be filled at equilibrium with highly structured water clusters. The structural and thermodynamic properties of these encapsulated water clusters are similar to those observed experimentally in the gas phase. Water filling is highly sensitive to the size of the cavity and the strength of the interactions with the cavity wall. Water penetration into pores can thus be modulated by small changes in the polarity and structure of the cavity. Implications on water penetration into proteins are discussed.

grand canonical ensemble | hydrophobic interactions | fullerenes | free energy of transfer | configurational-specific heat

as the specific heat, to clarify the factors that determine the formation and stability of the water clusters. The 3D structures of the more stable clusters in the cavities are examined and compared with water clusters studied experimentally in the gas phase (26).

Methods

The water occupancy of a cavity is determined by the balance of the excess chemical potentials of water inside the cavity and in the bulk fluid outside. We restrict our analysis to spherical cavities with smooth walls and rigid fullerenes to elucidate the fundamental aspects of filling thermodynamics and structure. In the grand-canonical ensemble, water molecules inside a cavity are in thermal and chemical equilibrium with the surrounding bulk fluid. The occupancy probabilities $P(N)$

nature COMMUNICATIONS

ARTICLE

Received 8 Apr 2013 | Accepted 5 Aug 2013 | Published 13 Sep 2013

DOI: 10.1038/ncomms3401

Evidence of two distinct local structures of water from ambient to supercooled conditions

A. Taschin[1], P. Bartolini[1], R. Eramo[1,2], R. Righini[1,3] & R. Torre[1,4]

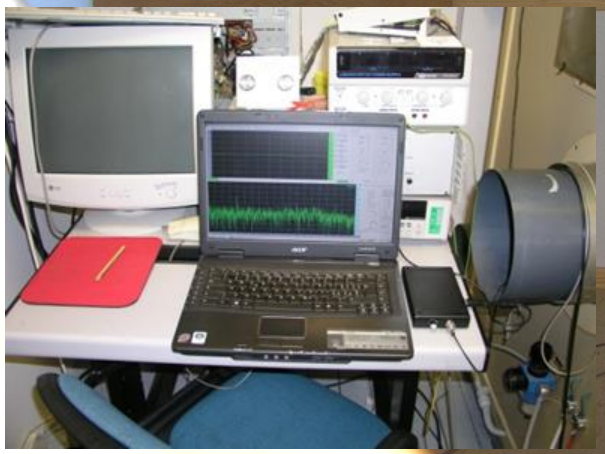
Valutazione dell'interazione CEM con molecole biologiche

Camera schermata

Cella elettrolitica

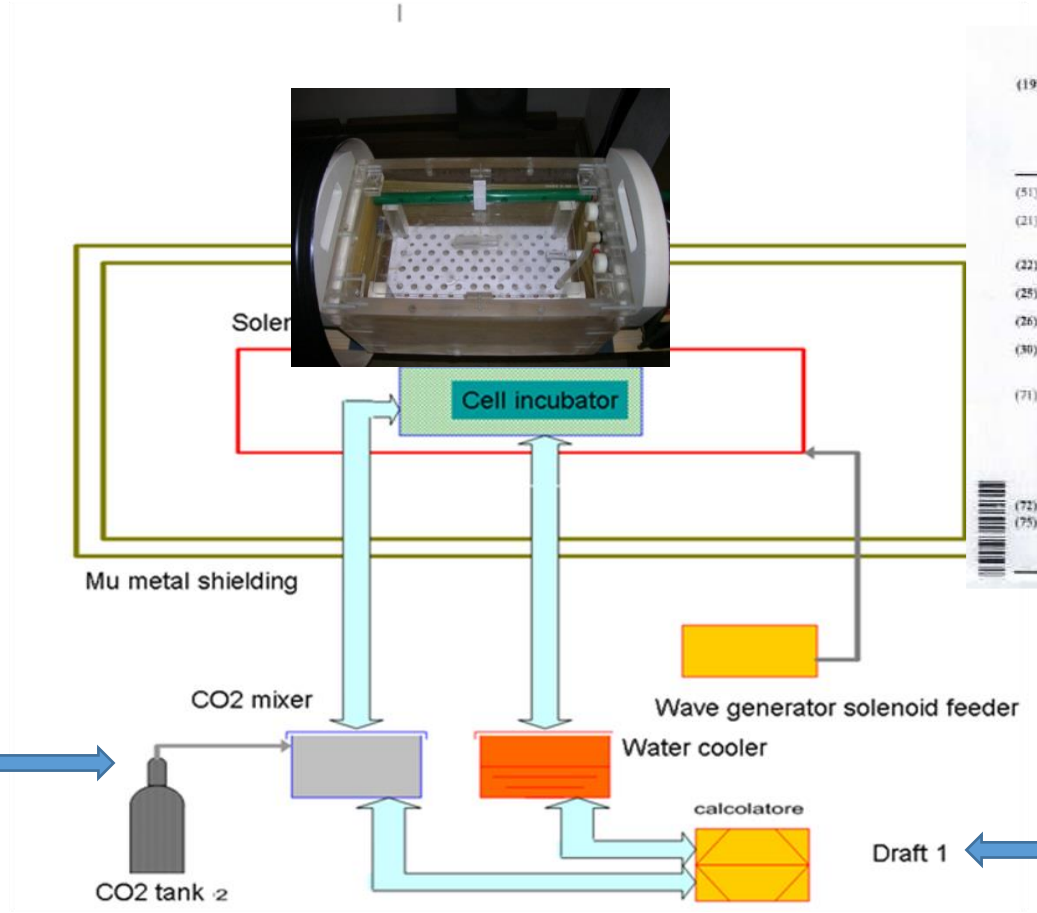
Cella incubazione

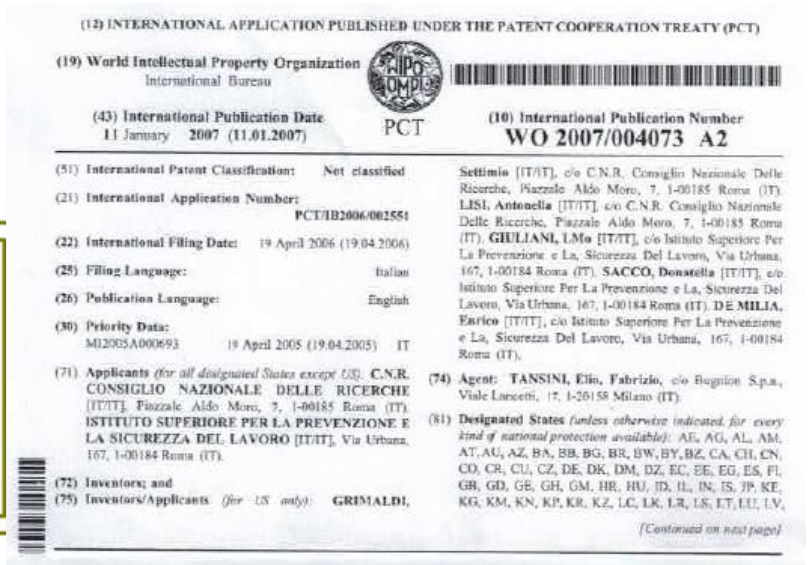
Apparati di controllo e misura esterni



Valutazione dell'interazione CEM con linee cellulari

Schema impianto trattamento cellulare





(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

PCT

(43) International Publication Date
11 January 2007 (11.01.2007)

(10) International Publication Number
WO 2007/004073 A2

(51) International Patent Classification: Not classified

(21) International Application Number:
PCT/IB2006/002551

(22) International Filing Date: 19 April 2006 (19.04.2006)

(25) Filing Language: Italian

(26) Publication Language: English

(30) Priority Data:
MI2005A000693 19 April 2005 (19.04.2005) IT

(71) Applicants (for all designated States except US): C.N.R. CONSIGLIO NAZIONALE DELLE RICERCHE [IT/IT]; Piazzale Aldo Moro, 7, I-00185 Roma (IT). ISTITUTO SUPERIORE PER LA PREVENZIONE E LA SICUREZZA DEL LAVORO [IT/IT]; Via Urbana, 167, I-00184 Roma (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): GRIMALDI, Settimio [IT/IT], c/o C.N.R. Consiglio Nazionale Delle Ricerche, Piazzale Aldo Moro, 7, I-00185 Roma (IT). LISI, Antonella [IT/IT], c/o C.N.R. Consiglio Nazionale Delle Ricerche, Piazzale Aldo Moro, 7, I-00185 Roma (IT). GIULIANI, LMo [IT/IT], c/o Istituto Superiore Per La Prevenzione e La, Sicurezza Del Lavoro, Via Urbana, 167, I-00184 Roma (IT). SACCO, Donatella [IT/IT], c/o Istituto Superiore Per La Prevenzione e La, Sicurezza Del Lavoro, Via Urbana, 167, I-00184 Roma (IT). DE MILIA, Enrico [IT/IT], c/o Istituto Superiore Per La Prevenzione e La, Sicurezza Del Lavoro, Via Urbana, 167, I-00184 Roma (IT).

(74) Agent: TANSINI, Elio, Fabrizio, c/o Bugnion S.p.a., Viale Lancetti, 17, I-20158 Milano (IT).

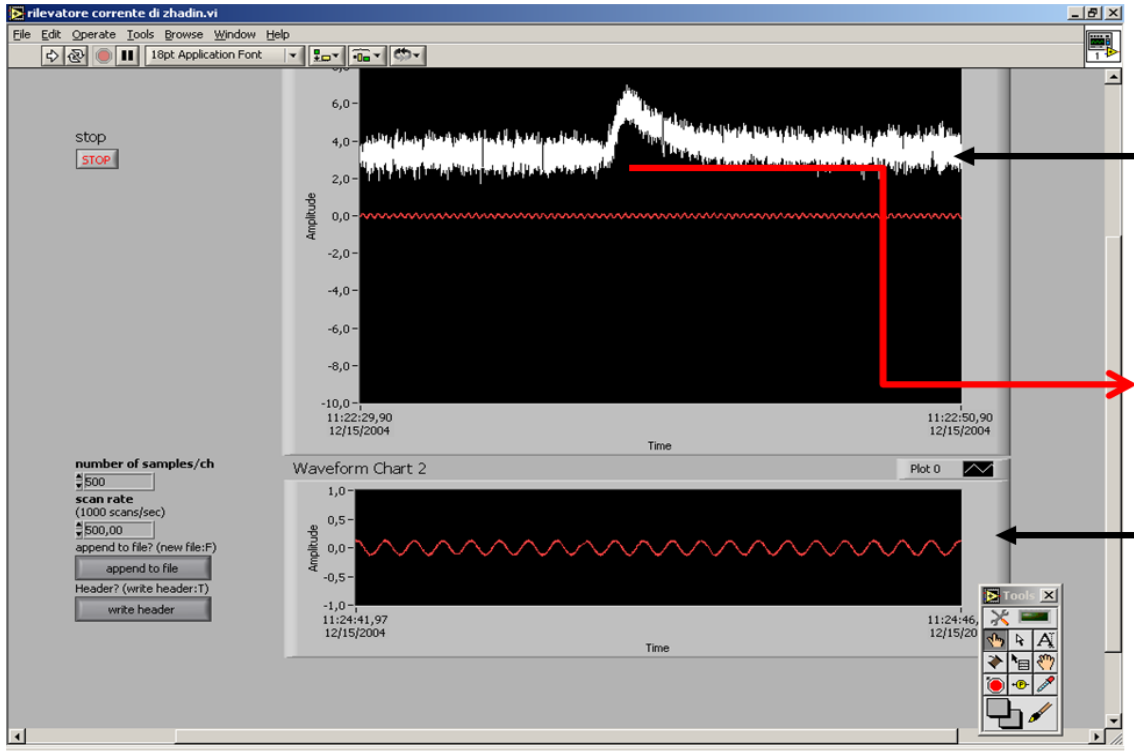
(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV,

[Continued on next page]

Valutazione interazione CEM con molecole

Glutammic acid

$$\omega_{cyclotron} = 2\pi\nu_{cyclotron} = \frac{qB}{M}$$



Baseline current

Applied sin field

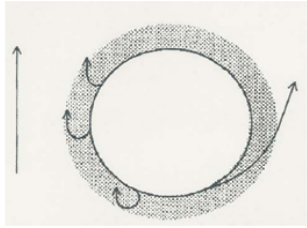


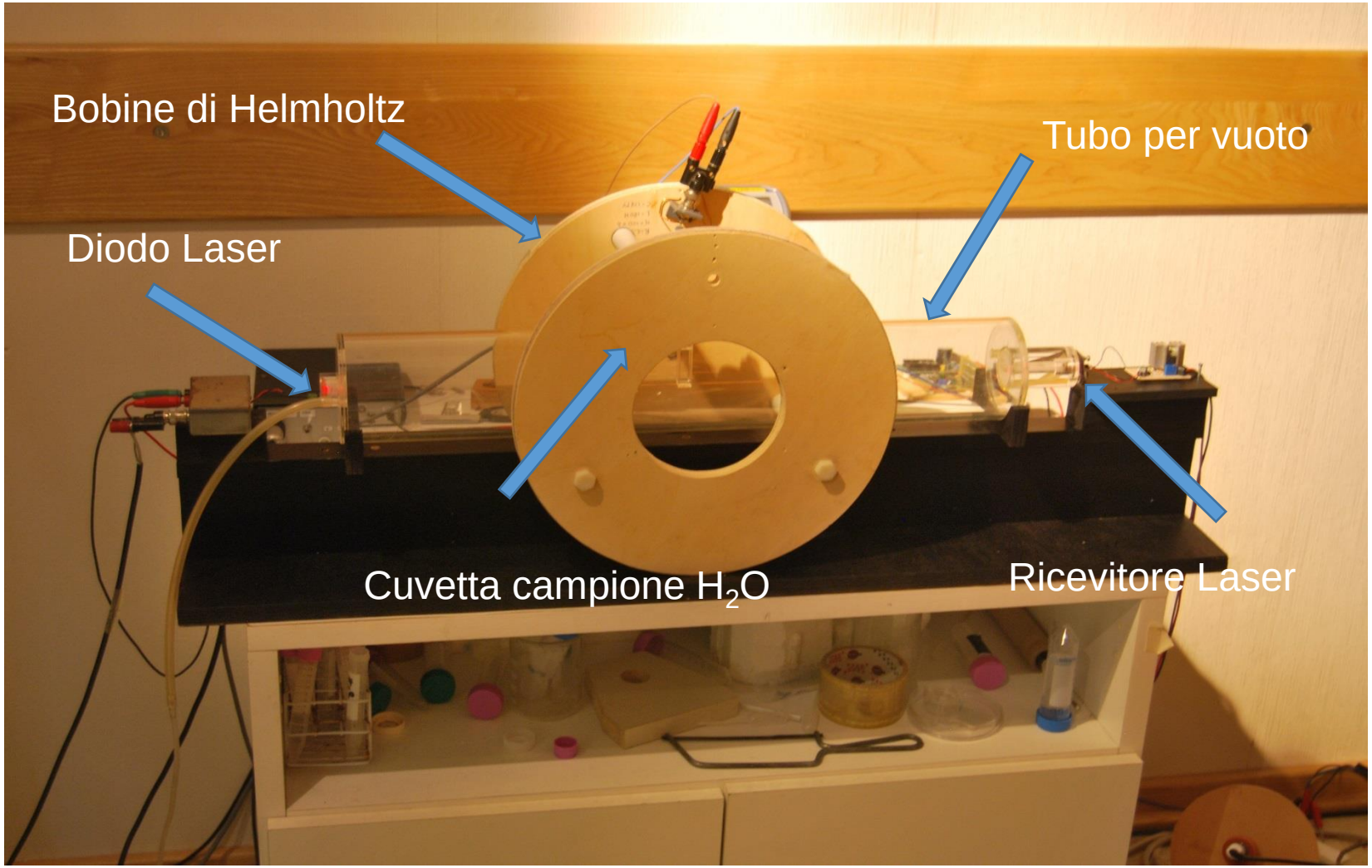
Fig. 2 Se B_{ss} è ridotto, le velocità di deriva degli ioni di glutammato in uscita dalle orbite ciclotroniche sono piccole e vengono deflesse lungo la direzione del campo elettrico all'intorno della regione di frontiera. Se B_{ss} è grande, gli ioni raggiungono l'ampia regione non coerente dell'acqua senza essere deflessi e penetrano nel serbatoio generale degli ioni.

Experimental parameters → 4.17Hz
48uT Bo 48nT B

Biomagn Res Technol. 2008 Jan 25;6:1.

Valutazione dell'interazione CEM con l'acqua

Sistema espositivo

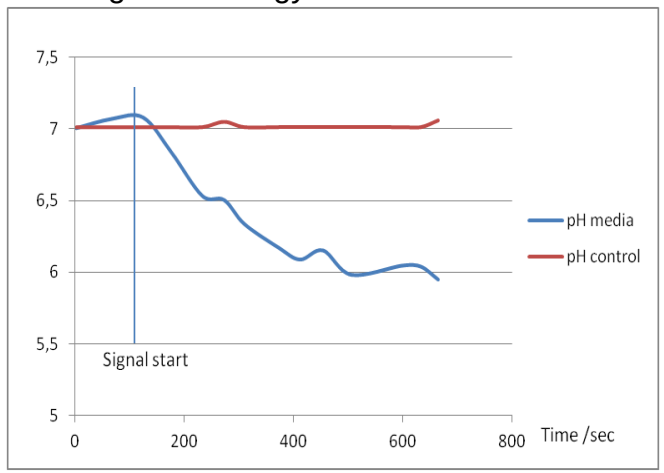


Valutazione dell'interazione CEM con l'acqua

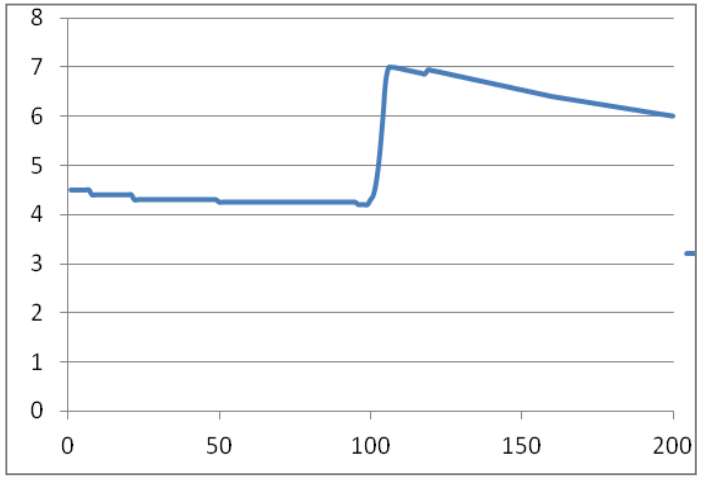
LORENTZ FORCE IN WATER: EVIDENCE THAT HYDRONIUM CYCLOTRON RESONANCE ENHANCES POLYMORPHISM.

E. D'Emilia , **L. Giuliani**, A. Lisi, M. Ledda, S. Grimaldi, L. Montagnier and A.R. Liboff

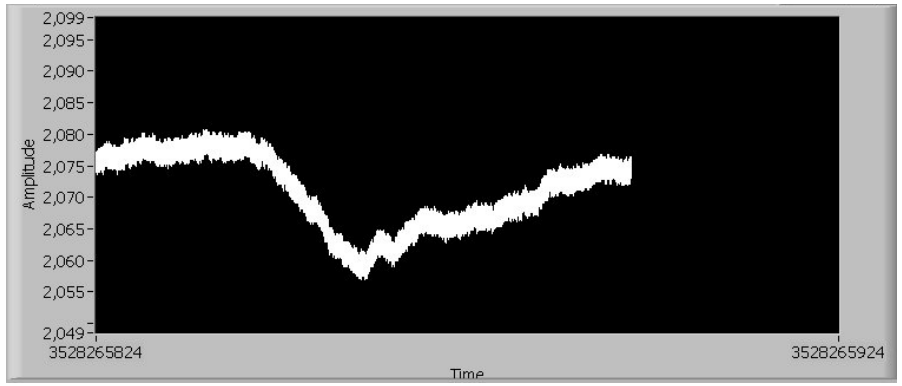
Electromagnetic Biology and Medicine . 2014 Jul 14:1-6



Ph trend



Conductivity increasing



Laser beam deviation

WEAK-FIELD H3O+ ION CYCLOTRON RESONANCE ALTERS WATER REFRACTIVE INDEX

Grimaldi S; Lisi A; Ledda M; **D'Emilia E**; Liboff A; **Giuliani L**; Foletti, A

*Electromagn Biology Med*icine 2017;36(1):55-62. Epub 2016 Jul 1.

Pubblicazioni

Non ionising radiation as a non chemical strategy in regenerative medicine: Ca(2+)-ICR "In Vitro" effect on neuronal differentiation and tumorigenicity modulation in NT2 cells.

Ledda M, Megiorni F, Pozzi D, **Giuliani L**, **D'Emilia E**, Piccirillo S, Mattei C, Grimaldi S, Lisi A.
PLoS One. 2013 Apr 9;8(4):e61535. doi: 10.1371/journal.pone.0061535. Print 2013.

Lorentz force in water: Evidence that hydronium cyclotron resonance enhances polymorphism.

E. D'Emilia , **L. Giuliani**, A. Lisi, M. Ledda, S. Grimaldi, L. Montagnier and A.R. Liboff
Electromagnetic Biology and Medicine . 2014 Jul 14:1-6.

Exposure to extremely low-frequency magnetic field affects biofilm formation by cystic fibrosis pathogens.

Di Bonaventura G, Pompilio A, Crocetta V, De Nicola S, Barbaro F, **Giuliani L**, **D'Emilia E**, Fiscarelli E, Bellomo RG, Saggini R.

Future Microbiol. 2014;9(12):1303-17. doi: 10.2217/fmb.14.96.

Copper ion fluxes through the floating water bridge under strong electric potential.

Giuliani L, D'Emilia E, Lisi A, Grimaldi S, Brizhik L, Del Giudice E.

Electromagn Biol Med. 2015;34(2):167-9. doi: 10.3109/15368378.2015.1036078.

The trail from quantum electro dynamics to informative medicine.

Foletti A, Ledda M, Grimaldi S, **D'Emilia E, Giuliani L**, Liboff A, Lisi A.

Electromagn Biol Med. 2015;34(2):147-50. doi: 10.3109/15368378.2015.1036073.

Nonpulsed sinusoidal electromagnetic fields as a noninvasive strategy in bone repair: the effect on human mesenchymal stem cell osteogenic differentiation.

Ledda M, **D'Emilia E, Giuliani L**, Marchese R, Foletti A, Grimaldi S, Lisi A.

Tissue Eng Part C Methods. 2015 Feb;21(2):207-17. doi: 10.1089/ten.TEC.2014.0216. Epub 2014 Oct 7.

Weak-field H3o+ Ion Cyclotron Resonance Alters Water Refractive Index

Grimaldi S; Lisi A; Ledda M; **D'Emilia E**; Liboff A; **Giuliani L**; Foletti, A

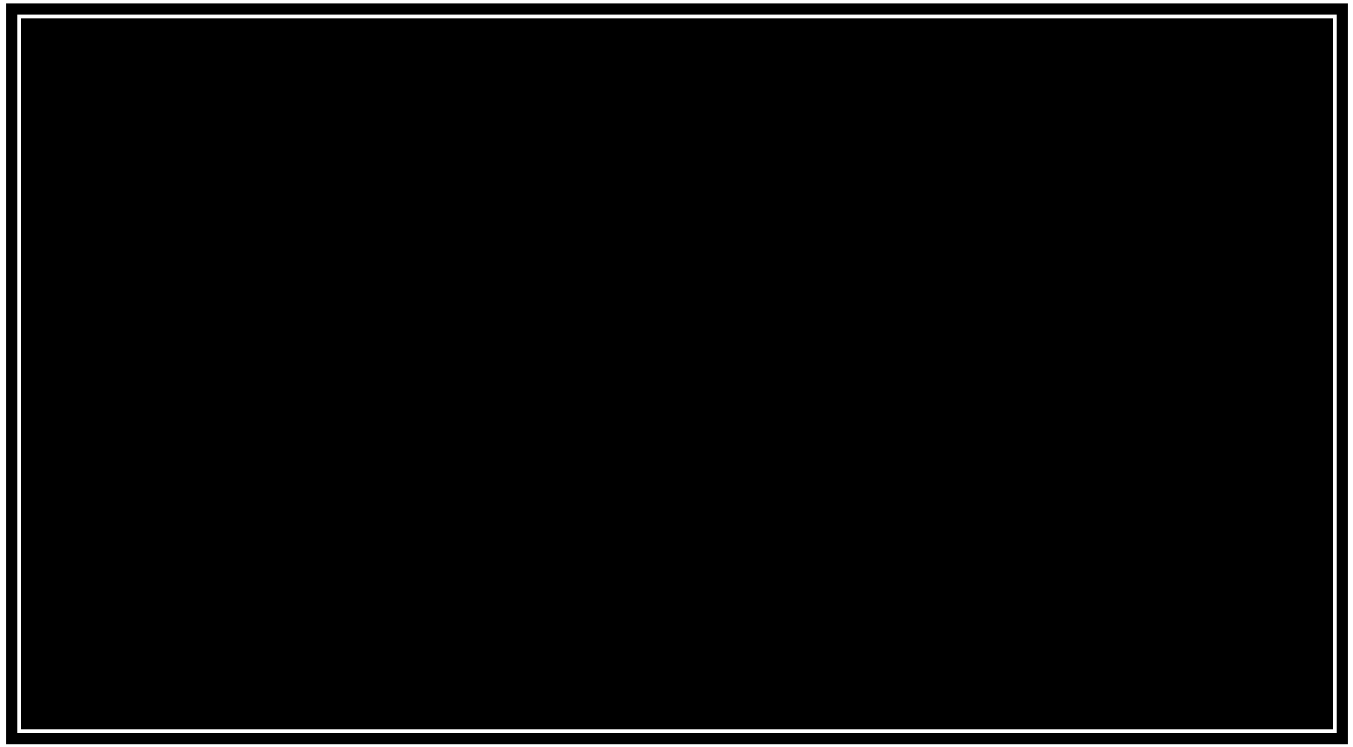
*Electromagn Biology Med*icine 2017;36(1):

Esperimento acqua sottoposta a intenso campo elettrico

ELECTROMAGNETIC BIOLOGY MEDICINE 2015;34(2):167-9. doi:10.3109/15368378.2015.1036078.

Copper ion fluxes through the floating water bridge under strong electric potential.

Giuliani L, ***D'Emilia E***, *Lisi A, Grimaldi S, Brizhik L, Del Giudice E*.



Thanks to Emilio Del Giudice,
Settimio Grimaldi, Antonella Lisi
for their research collaborations.

THANK YOU SO MUCH