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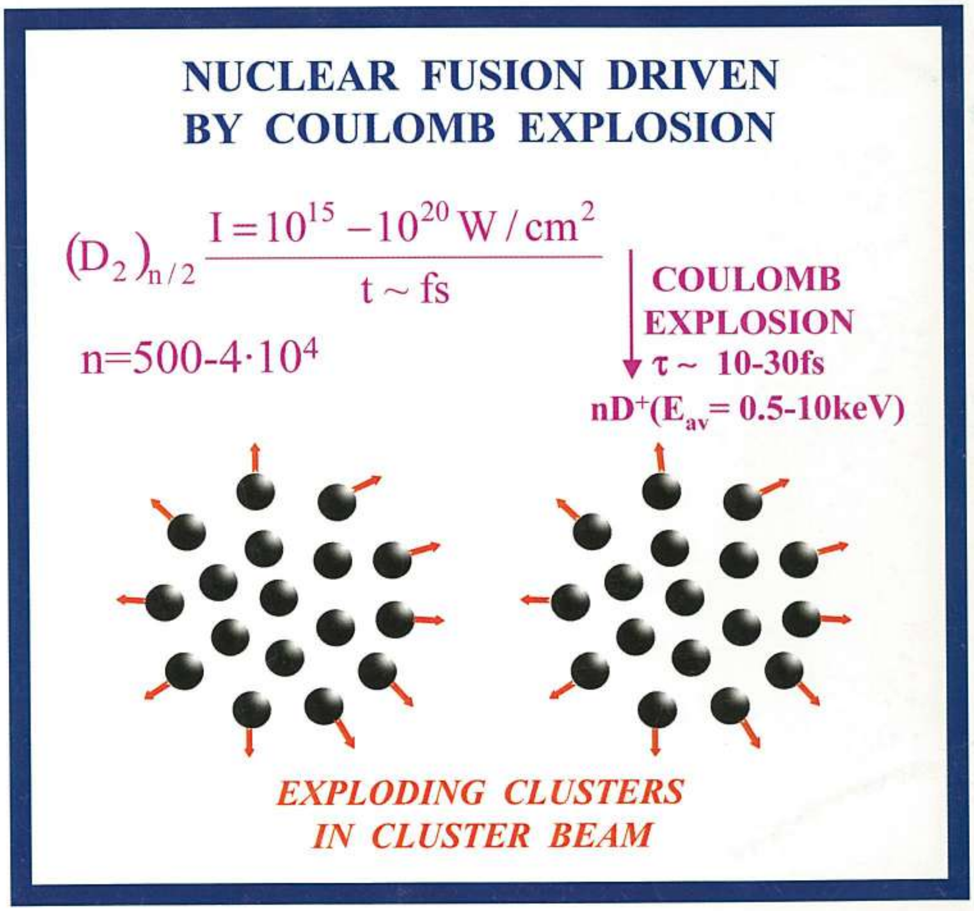

dd nuclear fusion driven by Coulomb explosion of deuterium clusters
(See article by Jortner and Last)

כימיה בישראל - בטאון החברה הישראלית לכימיה

גליון מספר 19, אב התשס"ה, אוגוסט 2005 http://www.weizmann.ac.il/ICS

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המחלקה לדפוס ושכפול, מכון ויצמן למדע, רחובות

דבר המערכת

הכינוס השנתי ה-71 של החברה הישראלית לכימיה, מאורגן השנה ע"י המחלקה לכימיה של אוניברסיטת בן-גוריון בנגב. הכינוס יתקיים ב- 27-28 בפברואר 2006, במלון דוד אינטר-קונטיננטל בתל-אביב. ההודעה הראשונה הופצה בין החברים ומובאת בגליון זה.

הכימיאדה ממשיכה את תנופתה הודות למסירותם של חברי סגל הפקולטה לכימיה בטכניון ולשיתוף הפעולה של החברה הישראלית לכימיה. פעילות זו חשובה ביותר לקידום התעניינות הנוער במקצוע הכימיה, כפי שמתארת ד"ר מירה כ"ץ.

את מאמרם של פרופ' יהושע יורטנר (מדלית החברה הישראלית לכימיה לשנת 2003) ופרופ' איזידור לסט, מאוניברסיטת תל-אביב, ניתן לקרוא כמדע בדיוני. מדובר בו על לייזרים בעוצמה של 10^{20} $\mathrm{Wcm^{-2}}$, שהיא העוצמה החזקה ביותר על פני כדור הארץ, זמנים קצרים עד כדי אטו (10^{-18}) שניות, וטמפרטורות מסדר גודל של ננו קלווין. אלא שבניגוד למדע דמיוני, החישובים שנעשו ע"י הקבוצה מאוניברסיטת תל-אביב, נלקחו ברצינות ע"י קבוצת חוקרים בינלאומית (שכללה 14 מדענים ממדינות שונות) שהוכיחה שניתן להגיע, ע"י פיצוץ קולומבי של צברים של דוטריום ותרכובותיו, למה שיורטנר מגדיר "החלום של היתוך גרעיני בתנאי מעבדה". (ראה תמונת שער).

מדלית החברה הישראלית לכימיה לשנת 2004 ניתנה לפרופ' ראובן פאונץ, שנחשב למוביל במחקר והוראה של כימיה קוונטית בישראל. במאמרו בגליון זה, מביא פרופ' פאונץ כמה נושאים שעסק בהם במשך השנים וכן את תרומתו לסדנאות המפורסמות בכימיה קוונטית, מיסודו של פר-אולוב לוודין, שהחלו ב- 1959 ונמשכות עד עצם היום הזה.

נשיא הטכניון, פרופ' יצחק אפלויג (פרס החברה הישראלית לכימיה לשנת 2002), וד"ר מרים קרני, מדגישים במאמרם את החשיבות של שילוב תיאוריה ונסיון. זאת במסגרת מחקריהם על תרכובות סיליקון. למרות העובדה שסיליקון הוא האלמנט הנפוץ ביותר על פני כדור הארץ (אחרי חמצן), מספר התרכובות שלו (בהשוואה לפחמן) אינו גדול. מסתבר שניתן להסביר זאת בעזרת תאורית הקוונטים ולהוכיח שלמעשה האלמנטים מאותה קבוצה מתנהגים בצורה זהה ורק הפחמן הוא החריג. זאת לדבריהם נקודה חשובה שכדאי להדגיש בקורסים הבסיסיים בכימיה כללית.

תהודה מגנטית גרעינית הפכה לכלי חשוב ביותר במדעי הטבע וברפואה הודות להתקדמות המרשימה בתיאוריה ובטכנולוגיה בתחום. במאמרו מתאר פרופ' לוסיו פרידמן (פרס המדען הצעיר המצטיין של החברה הישראלית לכימיה, לשנת 2004) את הפיתוחים החדשים שלו, שבעזרתם ניתן להגיע לקליטת נתוני NMR במהירות העולה בכמה סדרי גודל על המצוי כיום. הדבר מודגם בכמה ממצאים חדשים, והציפיות לעתיד מבטיחות ביותר.

במדור מן הארכיון מביא בוב וינטראוב את סיפור פיתוח הגלולה למניעת הריון דרך עבודתם של גרגורי פינקוס וקרל ג'רסי. אין ספק שפיתוח זה, שביסודו הבנת המבנה והתפקוד של סטרואידים והסינתזה שלהם, הביאה למהפכה בחיי האדם על פני כדור הארץ.

ממשלת אוסטריה הנפיקה בול לכבוד יום הולדת ה-80 של קרל ג'רסי. הבול מובא בסוף המאמר.

את סיפור השתלשלות הוצאת הבול ניתן לקרוא ב- Autobiography of a Stamp by Carl Djerassi,
Philatelia Chimica et Physica 27 (2), 68, 2005.
http://www.cpossu.org/Djerassistamp.pdf

המחלקה לכימיה באוניברסיטת בן-גוריון בנגב ספגה שלשה אסונות כבדים עם פטירתם בטרם עת של שלשה חברי סגל: פרופ' שלמה אפרימה ופרופ' בלהה שגב, מהמחלקה לכימיה, ופרופ' שמעונה גרש, מהמחלקה להנדסת ביוטכנולוגיה, שהיתה קשורה למחלקה לכימיה מראשית דרכה. בגליון זה הבאנו דברים לזכרם, מתוך הספדים שנאמרו בעת ההלוויות או בימי הזיכרון שלאחר מכן.

Guest Institute:

Harvard University, USA

Plenary Lecturers from Israel:

Reshef Tenne
Weizmann Institute of Science

David Avnir
Hebrew University

מקום:
מרכז הכנסים, מלון דויד אינטר-קונטיננטל, רח' קויפמן 12, ת"א

תאריך:
ימים ב'-ג', כ"ט-ל' בשבט תשס"ו, 27-28 בפברואר 2006

מתכונת הכינוס:
התכנית המדעית תכלול הרצאות מליאה, הרצאות במסגרת
סימפוזיונים בנושאים מובילים בכימיה העכשווית ופוסטרים

שפת הכינוס:

Ben-Gurion University
of the Negev

הכינוס ה-71
של החברה הישראלית לכימיה

The 71st Meeting of the Israel Chemical Society

Organized by the Department of Chemistry, Ben Gurion University

First Circular and Call for Abstracts

שלב הגמר של הכימיאדה השמינית תשס"ה (2004-5)

מירה כ"ץ, הפקולטה לכימיה, הטכניון

תחרות הכימיאדה הארצית הפכה למסורת בפקולטה לכימיה בטכניון. היא מתקיימת בשיתוף החברה הישראלית לכימיה ובעידוד ותמיכת משרד החינוך (המחלקה לנוער שוחר מדע), אשר תומכים שנים במפעל חשוב זה לעידוד המדע בקרב הנוער. השנה הצטרפה לתמיכה גם חברת החשמל לישראל בע"מ. הכימיאדה הפכה למפעל מצליח בקרב בתי-הספר התיכוניים מכל רחבי הארץ, וזוכה להשתתפות תלמידים רבים מכל המגזרים. השנה היו פניות ישירות גם של תלמידים שאינם לומדים כימיה בבית-ספרם. הישג מיוחד שנרשם השנה הוא השתתפות חוזרת של תלמידי כתות י"ב (אשתקד תלמידי כתות י"א), למרות העומס הרב בבחינות הבגרות והמטלות הלימודיות המוגברות.

ביוזמתם ועידודם של פרופ' אהוד קינן דקן הפקולטה לכימיה, ופרופ' גבריאל קוונצל האחראי האקדמי על ה"כימיאדה", הסתיים בהצלחה רבה שלב הגמר של הכימיאדה לשנת תשס"ה, לתלמידי כתות י"א-י"ב בבתי-הספר התיכוניים ברחבי הארץ.

שלב הגמר התקיים במשך יומים (13–14 בחדש אפריל השנה). בשלב זה שהו התלמידים יומיים בפקולטה לכימיה בקרית הטכניון, חיפה. המתמודדים הרצו בנושאים שנבחרו על ידם בפני אורחים וחברים ונבחנו ע"י צוות שופטים שכלל את הפרופסורים: אורי פסקין, יואב אישן ואמנון שטנגר, והמשתלמים אשר שמידט וזוהר אמיתי.

שתי הרצאות מרכזיות, אשר ניתנו ע"י פרופ' אהוד קינן (בנושא:"חומרי נפץ מאולתרים"), ופרופ' נמרוד מוסייב (בנושא: "מכאניקת הקוונטים: דמיון ומציאות"), זכו להצלחה והתעניינות רבה מצד המתמודדים.

טקס הגמר התקיים ביום חמישי 14.4.05 בערב, בהשתתפות מוזמנים ואורחים רבים, כולל משפחות וחברים של המתמודדים, מורים ומנהלי בתי-ספר. את הטקס הנחה פרופ' גבריאל קוונצל. פרופ' אהוד קינן ברך בשם כל בית הפקולטה לכימיה את המשתתפים. את ברכתה של הנהלת הטכניון הביא דקן לימודי הסמכה, פרופ' אלן פינקוס. את ברכת החברה הישראלית לכימיה נשא נשיא החברה, פרופ' שמאי שפייזר. בשם עירית חיפה בירך מר צבי דהרי, מ"מ וסגן ראש העיר. בשם חברת החשמל לישראל בע"מ ברך ד"ר אהוד סוצקובר, הכימאי הראשי של החברה. בנוסף לפרסים, הוענקו גם מכתבי הערכה למורים מצטיינים ע"י ד"ר ניצה ברנע, מפמ"ר כימיה, ותעודות לבתי-ספר מצטיינים מכל רחבי הארץ, ע"י הגב' ריבי לקריץ מנהלת מחלקה לנוער שוחר מדע במשרד החינוך. פרופ' מנחם כפתורי, דקן היחידה לחינוך קדם אקדמי, הביא בדבריו מידע על מחנה הקיץ לנוער, המתקיים בטכניון. פרופ' נמרוד מוסייב סיפר על תכנית המצוינים בטכניון.

רשימת הזוכים בכימיאדה השמינית (שנת תשס"ה) בכתות י"א וכתות י"ב

מקום ראשון	**דן דבירי** (כתה י'), תיכון עירוני ד', תל-אביב; **אורי צוקרמן**, בי"ס מקיף למדעים ולאומנויות, חדרה.
מקום שני	**פנחס שכטר**, תיכון מקיף אורט, קרית-מוצקין; **מעיין זלוואס**, בי"ס להנדסאים אוניברסיטת תל-אביב.
מקום שלישי	**תום קוטלר**, בי"ס להנדסאים אוניברסיטת תל-אביב; **יהונתן גרין**, בי"ס תיכון ראשונים, הרצליה. **ארז שריג**, תיכון למדעים ולאומנויות, ירושלים.

ציון לשבח מטעם חברת החשמל לישראל בע"מ

לכתות י"א	**עידן חריטן**, קרית חינוך בן-גוריון, מדרשת רופין.
לכתות י"ב	**אדוארד חצ'סריאן**, תיכון עירוני קרית-שרת, חולון.

תעודת הערכה למורים מצטיינים

אלול פרידה - תיכון עירוני קרית-שרת, חולון; **גלפרין אדלה** - תיכון הנדסאים אוניברסיטת תל-אביב, ת"א; **דיטל זהבה** - תיכון מקיף אורט, קרית-מוצקין; **די-נור זהר** - תיכון למדעים ולאומנויות, ירושלים; **זעירה אורנה** - בי"ס תיכון אמי"ת גוש דן, גבעת שמואל; **לידמן דניאלה** - תיכון ליאו בק, חיפה; **רייר אלה** - תיכון עירוני ע"ש פנחס אילון, חולון.

תעודת הצטיינות לבתי-ספר התיכוניים:

הנדסאים אוניברסיטת תל אביב; למדעים ולאומנויות, ירושלים; ליאו בק, חיפה; עירוני קרית-שרת, חולון; מקיף אורט, קרית-מוצקין; עירוני ע"ש פנחס אילון, חולון; אמי"ת גוש דן, גבעת שמואל.

EXCURSIONS IN CLUSTER SCIENCE; FROM DYNAMICS OF LARGE FINITE SYSTEMS TO ULTRACOLD CLOUDS

Joshua Jortner and Isidore Last, School of Chemistry, Tel-Aviv University, Tel-Aviv, Israel.

I. PROLOGUE

During the last two decades, the chemical physics group of Tel-Aviv University explored the structure, energetics, spectroscopy and dynamics of clusters, focusing on the energy landscapes, spatial structures and shapes, phase changes, superfluidity, energetics, level structure, electronic-vibrational spectroscopy, size effects, response and nuclear-electronic dynamics of large finite systems [1-22]. Recently, our dynamic studies were extended for the adiabatic nuclear dynamics of multicharged atomic and molecular clusters, which manifest unique fragmentation patterns, such as cluster fission and Coulomb explosion [23-34]. Concurrently, a fascinating analogy was established between Coulomb explosion of multicharged clusters and nuclear dynamics of finite, ultracold gases, i.e., optical molasses, in the temperature domain of T = 10μK–100μK [35, 36]. Cluster science constitutes the art of building bridges, i.e., bridging between the structure, energetics, thermodynamics, response and dynamics of molecular and condensed phase systems in terms of size scaling laws [11-14], bridging between the electron-nuclear dynamics and response of clusters and of nanostructures [37], and bridging between nuclear dynamics of clusters and of ultracold, large, finite, quantum systems [35,36].

II. FROM FISSION TO COULOMB EXPLOSION

The fragmentation of multiply charged finite systems driven by long-range Coulomb (or pseudo-Coulomb [35,36]) forces, i.e., nuclei [38], clusters [23-34,39-42], droplets [43,44], and optical molasses [35,36], raises the following interesting questions regarding the energetics and dynamics of dissociation:

(1) How does a finite system respond to a large excess charge or to an effective charge?
(2) What are the topography and topology of the multidimensional energy landscape that guide the system's shape evolution and fragmentation?
(3) What are the fragmentation channels and under what conditions are they realized?
(4) What is the interplay between fission, i.e., instability towards dissociation of the finite system into two (or a small number of) fragments and Coulomb explosion into a large number (~n, where n is the number of constituents) of ionic species?

The ubiquity of fission phenomena of droplets, nuclei, and clusters was traditionally described by the classically liquid drop model (LDM) [38, 44], where a classically charged drop deforms through elongated shapes to form separate droplets. The fissibility parameter X = E(Coulomb)/2E(surface) characterizes the relative contribution of repulsive (Coulomb) and cohesive (surface) energies to the fission barrier, separating between the bound initial states and the fission products. For $X < 1$, thermally activated fission over the barrier prevails. At the Rayleigh instability limit of $X = 1$ the barrier height is zero [38, 44]. Many features of nuclear and metal cluster fission require to account for quantum shell effects. Nevertheless, the simple LDM expression $X=Z^2e^2/16\pi R_0^3=(Z^2/n)/(Z^2/n)_{cr}$, with the proportionality factor $(Z^2/n)_{cr}=16\pi R_0^3/e^2$ (where γ is the surface tension, Z the total charge, R_0 the system's radius and r_0 the constituent radius), provided the conceptual framework for the fission of charged finite systems. All the diverse phenomena of fission were realized for fissibility parameters below the Rayleigh instability limit of $X = 1$, i.e., nuclear fission [45], the fission of metal clusters [42], and of hydrogen-bonded clusters [43]. Beyond the fissibility limit ($X > 1$) barrierless fission and other dissociative channels open up. We have transcended the Rayleigh instability limit ($X = 1$) for Coulomb instability of large finite systems, demonstrating the prevalence of a qualitatively different fragmentation pattern of Coulomb explosion beyond the Rayleigh instability limit [28]. We studied the fragmentation patterns and dynamics of highly charged Morse clusters by varying the range of the pair potential and of the fissibility parameters. The instability of multicharged Morse clusters directly reflects on covalently or dispersion-bound chemical and biophysical finite systems. The Rayleigh instability limit separates between nearly binary or tertiary spatially unisotropic fission for X<1 and spatially isotropic Coulomb explosion into a large number of ionic fragments for X>1 (Fig. 1).

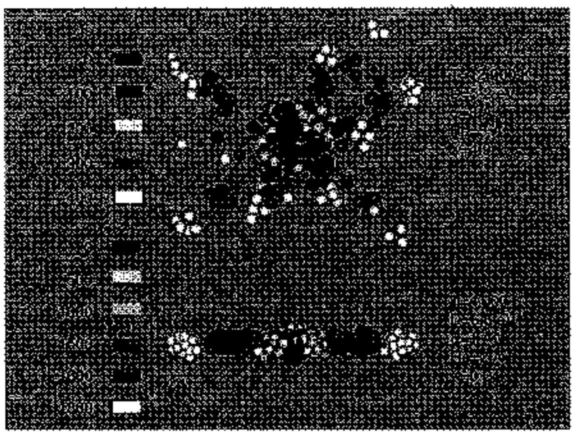

Figure 1. Time resolved nuclear dynamics of the fragmentation of highly charged $(A^+)_{55}$ Morse clusters (mass of A is 100 amu). The two panels show superimposed temporal patterns of the fragmentation, where each color corresponds to a different time for a one-color snapshot, as marked on the two panels. The Morse potential parameters and the fissibility parameter X are marked on the panels. The time t = 0 corresponds to the T jump to the final temperature (see text). Note the dramatic difference between the spatially isotropic Coulomb explosion (for X = 4.9) on the upper panel, and cluster fusion (for X = 0.24) on the lower panel. (See colored figure on back cover).

We explored the Coulomb instability of multicharged [23-34,39-44], or effectively charged [35,36], finite systems (Fig. 2). The majority of the currently available experimental information on the Coulomb instability of nuclei (i.e., X = 0.7 for ^{235}U and X = 0.9 for the recently discovered Z = 114 element [45]), of charged droplets (i.e., X = 0.7 – 1.0 for hydrogen bonded systems [43]), and of multiply charged metal clusters (X = 0.85 ± 0.07 for Na_n^{+z} clusters [42]) pertains to the fission limit, i.e., X < 1 (Fig. 2). How can the Rayleigh limit for the Coulomb instability of a finite system be overcome? The X >> 1 domain can be accomplished either by a marked enhancement of the repulsive Coulomb energy, or by a dramatic reduction of the cohesive surface energy (Fig. 2). The increase of E(Coulomb) can be attained by cluster multielectron ionization in ultraintense (peak intensity $I = 10^{15} - 10^{20}$ Wcm^{-2}) laser fields (section III), while the dramatic decrease of E(surface) can be accomplished in three-dimensional, ultracold optical molasses (section V), where pseudo-Coulomb forces result in isotropic cloud expansion, in analogy with Coulomb explosion [35,36].

The traditional view of Coulomb explosion involves uniform ion expansion. Such is the case for the explosion of multicharged homonuclear clusters (e.g., $(D_2)_{n/2}$ or $(Xe)_n$) with the expansion of (e.g., D^+ or Xe^{q+}) ions retaining a uniform spatial distribution (as is the case for X > 1 in Fig. 1), with an energy distribution being proportional to the square root of the energy, up to a high-energy cut-off. The situation is drastically different for Coulomb explosion of multicharged

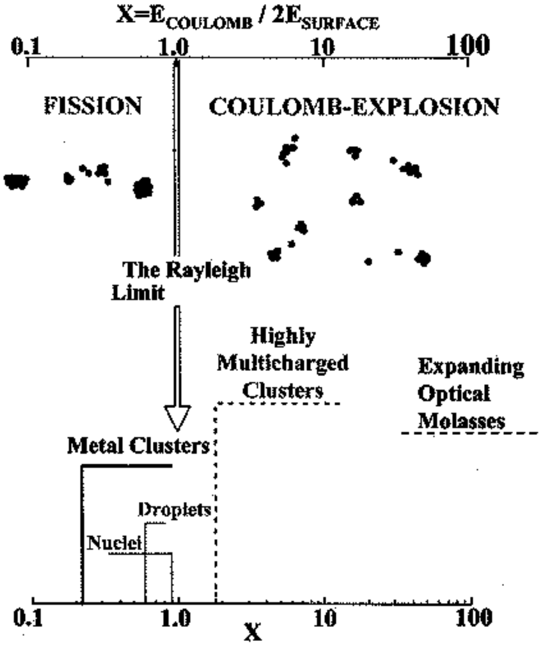

Figure 2. A classification of fragmentation patterns of multicharged and effectively charged large, finite systems.

light-heavy heteroclusters consisting of light and heavy ions, e.g., vertically ionized heteroclusters of hydrogen iodide, $(H^+I^{q+})_n$ or $(D^+I^{q+})_n$ (q = 7–35) [34]. In this case, kinematic overrun effects of the light ions (e.g., H^+ or D^+) will result in thin, two-dimensional shells of these light ions, with the monolayer expansion occurring on the femtosecond time scale (Fig. 3). Such an expanding nanoshell of light ions, corresponding to transient soft matter, is analogous to a 'soap bubble' characterized by negative surface tension and is being driven by Coulomb pressure. This transient halo of an expanding, regular monoionic spherical nanointerface manifests transient self-organization on the molecular level in complex systems [34]. Future experimental interrogations of these novel phenomena will emerge from the exploration of the energetics of the light ions in the Coulomb explosion of multicharged light-heavy heteroclusters, involving a narrow energy distribution with a low-energy cut-off [34]. An exciting experimental approach pertains to the application of ultrafast electron diffraction methods [46] for the exploration of the transient structure of the exploding clusters [34].

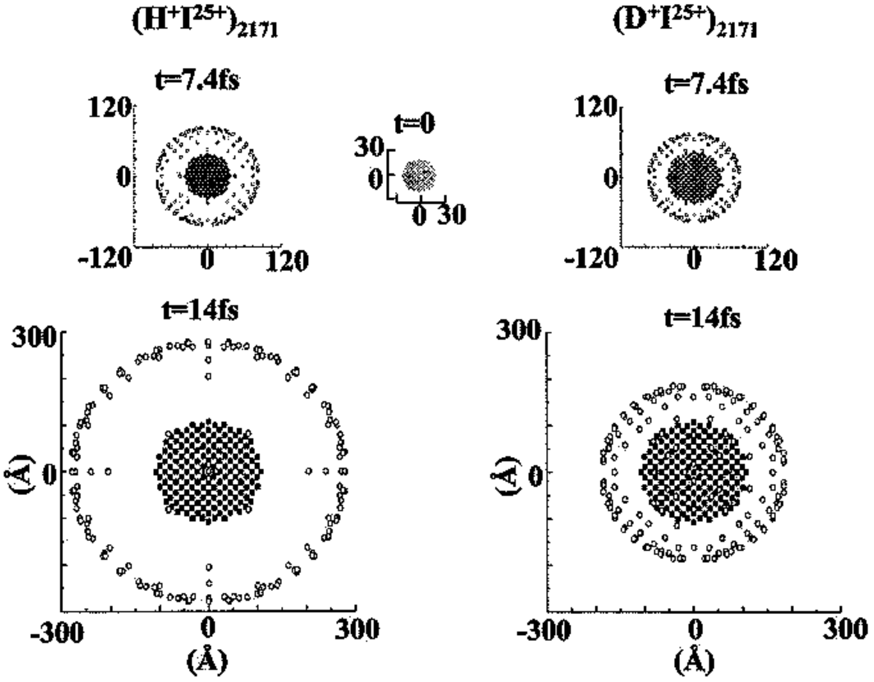

Figure 3. A 2-dimensional picture of the spatial structure of Coulomb expanding $(H^+I^{25+})_{2171}$ light-heavy heteroclusters at t = 0, 7.4 fs and 14 fs, obtained from molecular dynamics simulations. Black squares (■) represent I^{25+} ions, while circles (O) represent H^+ ions. This pictorial representation reveals the formation of narrow expanding shells of the light ions.

III. ULTRAINTENSE LASER – CLUSTER INTERACTIONS

Table top lasers delivering an energy of 1 Joule per pulse on the time scale of ~ 100 fs, can deliver a power of ~ 10^{20} Wcm^{-2}, constituting the highest light intensity on earth. Highly charged molecular clusters can be prepared by the irradiation of a cluster beam by ultrashort (tens of fs) and ultraintense (intensity $I = 10^{15}$–10^{20} Wcm^{-2}) laser pulses (Fig. 4).

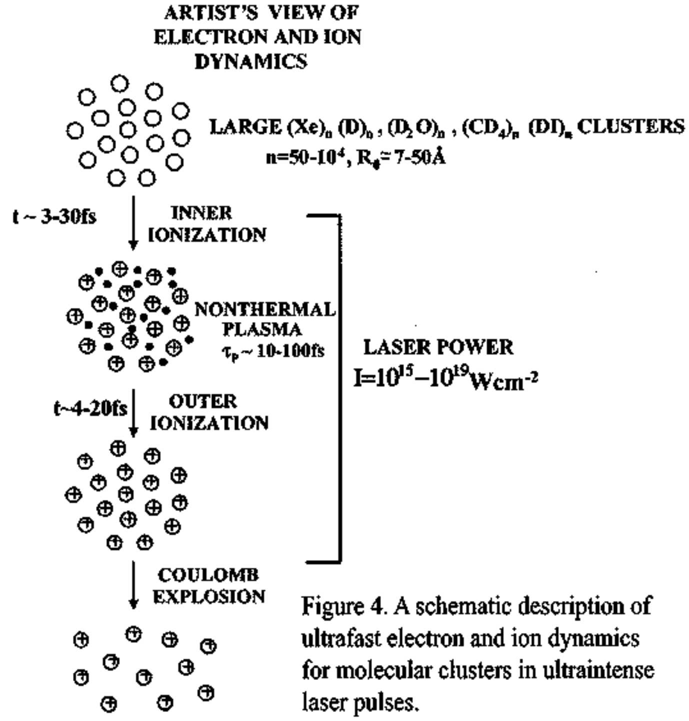

Figure 4. A schematic description of ultrafast electron and ion dynamics for molecular clusters in ultraintense laser pulses.

The extreme cluster multielectron ionization process involves the removal of valence electrons or complete stripping of all the electrons in light first-row atoms or molecules [25-27,29], or the formation of highly charged ions, e.g., up to Xe^{36+}, from heavy atoms [29-31,41]. The compound multielectron ionization mechanism of clusters is distinct from that of a single constituent. It involves three sequential processes of inner ionization (due to the semiclassical barrier suppression mechanism for each constituent with a contribution of impact ionization), the formation and response of a nonequilibrium, high energy (100eV–3keV) nanoplasma within the cluster, and outer ionization (induced by barrier suppression for the entire cluster and by quasiresonance effects) [24,30,31]. Femtosecond [24,30,31] electron dynamics of inner ionization on the time scale of ~ 1–5 fs and of outer ionization on the time scale of ~ 5–20 fs results in multielectron ionization. For the intensity domain of $I = 10^{16}–10^{17}$ Wcm^{-2} the cluster molecules loose all their valence electrons, with the nanoplasma being persistent, while for the highest intensity range of $10^{18}–10^{19}$ Wcm^{-2} both valence and inner shell electrons can be stripped off, with the nanoplasma being completely depleted [31]. The Coulomb instability of a highly charged finite cluster triggers simultaneous and concurrent ultrafast Coulomb explosion [24-29,32,33,41] on the time scales of 10–200 fs (Fig. 4). Analytical expressions for the fs time scales of Coulomb explosion and of (divergent) scaling laws for the energetics of the highly charged ions were derived [25-27,32,33] and were confirmed by molecular dynamics simulations with attosecond time steps describing fs dynamics. Ultrahigh ion energies in the range of 1keV–1MeV are released by cluster Coulomb explosion, as portrayed in Fig. 5 for deuterium containing homonuclear and heteronuclear clusters, where deuteron energies in the range of 1–100keV can be obtained.

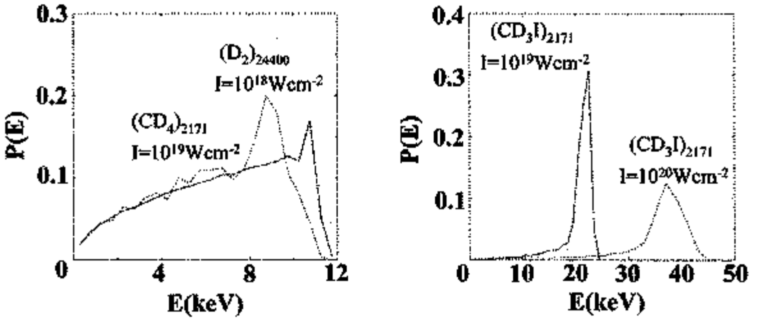

Figure 5. Energy distributions of D^+ ions from Coulomb explosion of $(D^+)_n$ homonuclear clusters ($n = 2.44\cdot10^4$) and deuterium containing heteronuclear clusters $(C^{6+}D_4^+)_n$ ($n = 2171$) and $(C^{+4}+H_3^+I^{q+})_n$ ($n = 2171$, $q = 25$ at $I = 10^{19}$ Wcm^{-2}, and $q = 35$ at $I = 10^{20}$ Wcm^{-2}).

A significant implication of these high ion energies pertains to nuclear fusion reactions of highly energetic D^+ (as well as T^+ or H^+) ions produced by Coulomb explosion of multicharged clusters in extreme multielectron ionization in ultraintense laser fields, which will be addressed in section IV. Cluster dynamics is moving from ultrafast femtosecond to picosecond nuclear dynamics, towards ultrafast attosecond to femtosecond electron dynamics, and towards electron-nuclear dynamics in ultraintense laser fields. 'Pure' electron dynamics constitutes new dynamic processes in chemistry and physics. Ultrafast cluster dynamics is not limited to the dynamics of ions on the time scale of nuclear motion, but is extended to the realm of electron dynamics, which bypasses the constraints imposed by the Franck-Condon principle [47].

IV. NUCLEAR FUSION DRIVEN BY CLUSTER COULOMB EXPLOSION

Eighty years of search for table-top nuclear fusion, driven by bulk or surface chemical reactions, which involved catalytic dissociation or electrochemical productions of deuterium, reflects on a multitude of experimental and conceptual failures [29]. In 1926 the German physicist Fritz Paneth reported on the apparent observation of helium from hydrogen absorbed on powdered palladium, which might have originated from nuclear fusion. A year later this claim was retracted. In 1935 Adalbert Farkas and Ladislaus Farkas, the founders of physical chemistry in Israel, worked on ortho- and parahydrogen and on deuterium chemistry in the Department of Colloid Science at Cambridge University, England, where they found shelter as refugees from Germany. When passing deuterium gas through a palladium tube, they seemed to observe traces of helium, which might have originated from dd (D^++D^+) nuclear fusion. However, a search for neutron emission in this system, conducted by Lord Rutherford at the request of the Farkas brothers, was negative and eliminated any possibility of nuclear fusion. In this category of negative results for nuclear fusion belongs the widely publicized 1989 "cold fusion" controversy, which did not provide any acceptable scientific information.

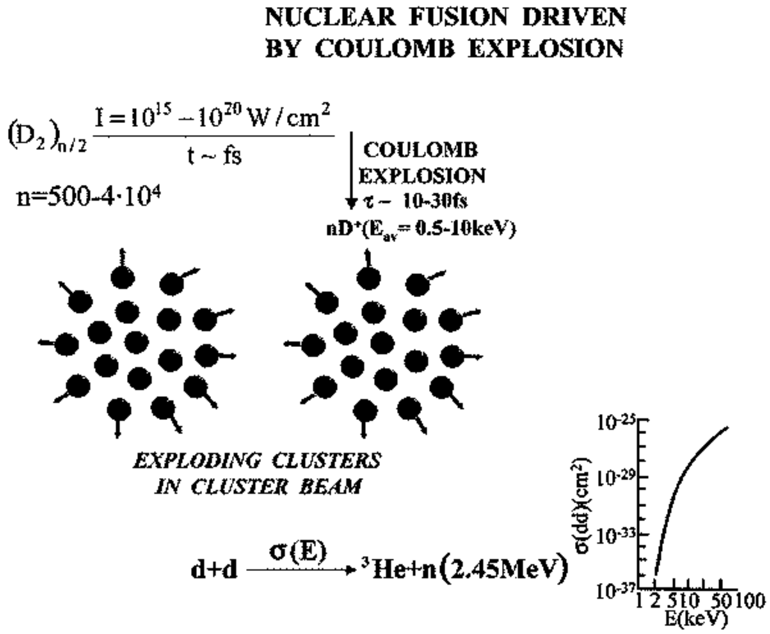

Figure 6. dd nuclear fusion driven by Coulomb explosion of deuterium clusters. Top: Multielectron ionization in ultraintense laser fields ($I > 10^{17}$ Wcm^{-2}) strips the $(D_2)_{n/2}$ clusters of all their valence electrons via consecutive inner and outer ionization. Parallel and concurrent with outer ionization, cluster Coulomb explosion of $(D^+)_n$ clusters occurs. In the size domain of $n = 459–7.6 \cdot 10^4$ the D^+ average energy increases from 0.3keV to 9.0keV. Energetic deuterons (D^+ ions) emerging from different clusters in the cluster beam undergo dd nuclear fusion. Bottom: Energy dependence of the cross sections σ(dd) for dd fusion adopted from the data of reference [48].

These spectacular failures

are not surprising as, to the best of our knowledge, no theoretical evidence is available to support any valid mechanism of nuclear fusion driven by chemical reactions in infinite bulk or surface systems [29]. The fragmentation dynamics of large finite systems involves an alternative avenue for the induction of nuclear fusion by chemical reactions, e.g., the dd (D^++D^+) nuclear fusion reaction $D^+ + D^+ \rightarrow {}^3He^{2+} + n(2.45MeV) + 3.27MeV$, with the production of neutrons (n). Coulomb explosion of extremely multicharged finite molecular systems strives towards the exploration of new areas that are alien to the majority of the chemical physics community. These areas involve nuclear fusion driven by Coulomb explosion of deuterium containing homonuclear and heteronuclear clusters [25-27,29,31-33,49-51]. High-energy Coulomb explosion of an assembly of multicharged, deuterium containing, molecular clusters produces high-energy (1–100keV) deuterons (Fig. 5) in the energy domain of nuclear physics. The high energy deuterons originating from different clusters undergo dd nuclear fusion. During the last four years compelling experimental [49,50] and theoretical [25,26,32] evidence was advanced for nuclear fusion driven by Coulomb explosion (NFDCE) in an assembly of deuterium clusters (Fig. 6). Completely ionized $(D^+)_n$ clusters are produced by multielectron ionization of homonuclear $(D_2)_{n/2}$ ($n = 500–4 \cdot 10^4$, $R_0 = 10–75$Å) clusters in ultraintense laser fields ($I > 10^{17}$ Wcm^{-2}), stripping the clusters from all their electrons (section III). For Coulomb explosion of very large homonuclear deuterium $(D^+)_n$ clusters ($n = 3.8 \cdot 10^4$ and cluster radius $R_0 = 72$Å), the average deuteron (D^+) energy is $E_{av} = 9$keV and the maximal energy is $E_M = 13$keV [25,26,32]. For these deuteron energies the cross section for dd (D^++D^+) nuclear fusion is $\sigma(dd) \simeq 10^{-28}$cm^2 (Fig. 6) [48], being sufficiently high to induce the dd fusion reaction [25,26,32]. Collisions between energetic deuterons, which originate from Coulomb explosion of different deuterium clusters (Fig. 6), result in NFDCE [25,26,32], which was experimentally observed in the Lawrence-Livermore laboratory [49,50]. Our theoretical and computational work [25-27,29-34] proposed and demonstrated that an effective way to produce highly energetic d nuclei (D^+ ions) for nuclear fusion involves multielectron ionization and Coulomb explosion of molecular heteroclusters of deuterium bound to heavy atoms. Highly ionized heteroclusters for high-energy Coulomb explosion involve heavy water clusters $(D^+D^+O^{q+})_n$ ($q = 6–8$), heavy methane clusters $(C^{q+}(D^+)_4)_n$ ($q = 4–6$), or deuterated hydroiodic clusters $(D^+I^{q+})_n$ ($q = 7–35$) in the size domain of $n = 55–4 \cdot 10^3$ ($R_0 = 10–40$Å). A dramatic energy enhancement of deuteron energy from these heteroclusters, as compared to deuterons from homonuclear deuterium clusters, is manifested (Fig. 5). For Coulomb explosion of heteroclusters the heavy multicharged ions (e.g., C^{4+}, C^{6+}, O^{6+}, O^{8+}) act as energetic triggers driving the light

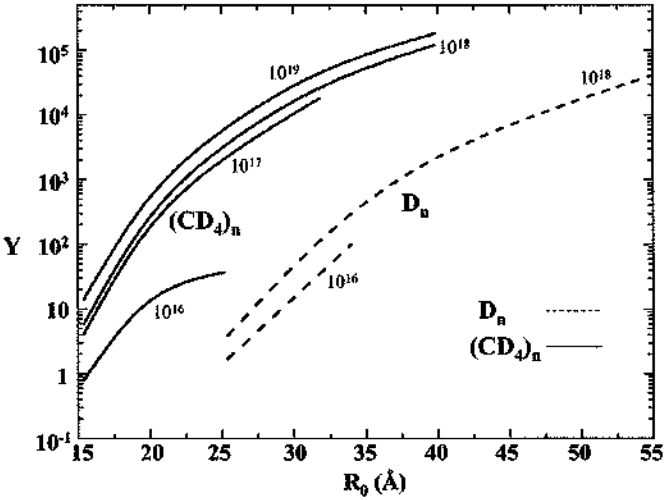

Figure 7. Cluster size dependence of neutron yields per laser pulse for dd NFDCE in an assembly of $(CD_4)_n$ ($n = 55–4213$) heteroclusters (solid curves), and of $(D_2)_{n/2}$ ($n = 55–33573$) homonuclear clusters (dashed curves) in the laser intensity range $I = 10^{16}–10^{19}$ Wcm^{-2}. Data adopted from reference 33. The NFDE for heteronuclear clusters manifests a considerably larger neutron yield than for homonuclear clusters of the same size, exhibiting energetic and kinematic effects, as discussed in the text.

D^+ clusters to considerably higher kinetic energies than for totally ionized deuterium clusters of the same size. In addition, kinematic effects, which manifest a sharp energy maximum in the vicinity of E_M, in the energy spectra of the D^+ ions from heteronuclear clusters, provide a supplementary contribution to the efficiency of the NFDCE [25,27,33,34]. The effects of energetic and kinematic triggering on the energetics of the D^+ ions in Coulomb explosion of multicharged deuterium containing homonuclear and heteronuclear clusters are manifested by the neutron yields for NFDCE (Fig. 7) calculated [26,32,33] under the conditions of the Lawrence-Livermore experiment [49,50]. The neutron yields per laser pulse (Fig. 7) for laser intensities of $I > 10^{17}$ Wcm^{-2} are higher by 2–3 orders of magnitude for Coulomb explosion of $(CD_4)_n$ clusters than for $(D_2)_{n/2}$ clusters of the same size [27,32,33]. This theoretical prediction [27] was confirmed by the experiments of the Saclay group [51], which demonstrated a marked enhancement of neutron yields from dd fusion in an assembly of Coulomb exploding $(CD_4)_n$ clusters, as compared to $(D_2)_{n/2}$ clusters.

An extreme way to attain highly effective energetic and kinematic triggering for driving deuterons to very high energies can be achieved for Coulomb explosion of deuterated methyl iodide $(C^{6+}D_3^+I^{q+})_n$ and hydroiodic acid $(D^+I^{q+})_n$, which produces heavily charged I^{q+} ions in very intense laser fields, i.e., $q = 25$ at $I = 10^{19}Wcm^{-2}$ and $q = 35$ at $I = 10^{20}Wcm^{-2}$ [34]. For such iodine containing heteroclusters (with $n \approx 4213$, $q = 25$ and $R_0 \approx 40Å$) the deuteron energies are $E_{av} = 40keV$, being considerably higher than those for homonuclear $(D_2)_{15000}$ ($E_{av} \approx 2.8keV$) and heteronuclear $(CD_4)_{4213}$ clusters ($E_{av} = 10keV$) of the same size. When the D^+ energy increases by a numerical factor of 3, the cross section for dd fusion and the neutron yield increase by 2-3 orders of magnitude (Fig. 6) [48]. We infer from the data of Fig. 7 and from the foregoing discussion that the neutron yields for Coulomb explosion of deuterium containing homonuclear and heteronuclear clusters with $R_0 = 40Å$ are predicted to be $Y = 10^3$ neutrons/laser pulse for $(D_2)_{15000}$, $Y = 10^5$ neutrons/laser pulse for $(CD_4)_{4213}$, and $Y = 10^8$ neutrons/laser pulse for $(DI)_{4213}$. A semi-quantitative confirmation of these predictions was provided from experiments for Coulomb exploding $(D_2)_n$ and $(CD_4)_n$ clusters [51]. The dream of table-top nuclear fusion in the chemical physics laboratory came true.

IV. PERSPECTIVES

The NFDCE of molecular clusters induced by multielectron ionization and Coulomb explosion involves a "cold-hot" fusion mechanism, where the cluster beam constitutes a cold (or even ultracold) target, while Coulomb explosion of the assembly of clusters provides the high energy required to induce nuclear fusion. Of considerable interest are the perspectives of the NFDCE of deuterium (or tritium) containing homonuclear and heteronuclear clusters for the production of short (100ps–1ns) neutron pulses [26,50], which may be instrumental in the exploration of time–resolved structural studies of biomolecules or large molecules. The utilization of NFDCE of deuterium containing heteronuclear clusters will greatly enhance the intensity of the neutron pulse. In addition, some nuclear fusion reactions involving protons and heavy nuclei, e.g., the $^{12}C^{6+}+H^+ \rightarrow {}^{13}N^{7+}+\gamma$ reaction, are of astrophysical interest for the carbon-nitrogen-oxygen (CNO) cycle in hot stars. The CNO cycle of nuclear fusion, which supplies energy to the hot stars, is catalyzed by $^{12}C^{6+}$, which is regenerated. The $^{12}C^{6+}+H^+$ NFDCE [27] can be induced by multielectron ionization of sufficiently large methane clusters ($R_0 = 120Å$), providing information on the cross sections and dynamics of elemental nuclear processes in astrophysics.

Some novel and fascinating phenomena relating to cluster size effects and dynamics pertain to the nuclear dynamics and phase changes in finite, ultracold, gases in the temperature domain of

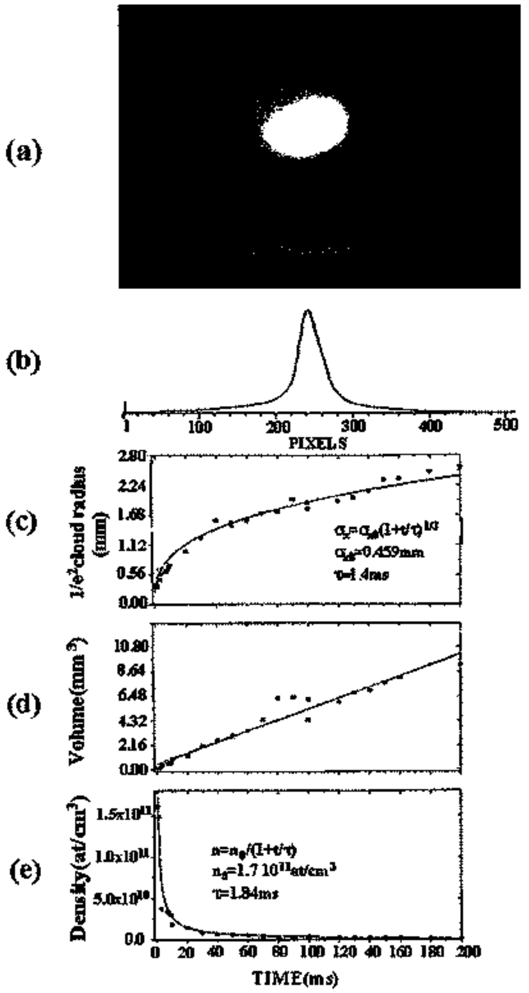

Figure 8. Nuclear dynamics of the spatial extension of optical molasses of Rb, as reported in reference 35. (a) A photograph of the irradiated cloud at t = 0. (b) Distribution of excited atoms in an irradiated cloud at t = 0. (c) Time dependence of the radius of the irradiated cloud. Characteristic expansion time τ = 1.4ms. (d) Time dependence of the volume of the irradiated cloud. (e) Time dependence of the density of the irradiated expanding cloud. Characteristic expansion time τ = 1.8ms.

T = 100nK–100μK, involving gases in magneto-optical traps, optical molasses and Bose-Einstein condensates [36]. A striking analogy was established between the nuclear dynamics of ultracold optical molasses (T = 10–100 μK) and Coulomb explosion of multicharged atomic clusters [35,36]. The optical molasses involve a cloud of trapped, laser irradiated, neutral atoms, e.g., Rb, in a magnetic trap (Fig. 8) which is characterized by a density of $\rho = 10^{11}$–10^{13} atoms/cm^3 and by an interatomic distance of $r_0 \approx 10^4$Å. When the magnetic trap is suppressed, the cloud expands via the radiative trapping force, which prevails between radiation–emitting and reabsorbing atoms [35]. An isomorphism was established [35,36] between the radiative trapping force and the electrostatic Coulomb force, with the effective charge characterizing the radiative trapping force being $\sim 4 \cdot 10^{-5}$e, with e being the electron charge. The theory of the dynamics of cluster Coulomb explosion of multicharged molecular clusters [23,25,32,33] was applied for the expansion of optical molasses [35,36]. While the Coulomb explosion time of $(Xe^+)_n$ clusters is 10^{-13}s [23], the expansion time of optical molasses of Cs atoms was predicted to be 10 orders of magnitude longer, i.e., $\sim 10^{-3}$s [35]. This estimate is in accord with experiments (Fig. 8) [35,36]. These studies, together with the exploration of superfluidity of helium–4 clusters [22], bridge between the dynamics of clusters and ultracold, large finite quantum systems.

During the last decade, cluster science explored new fascinating scientific territories, bridging between cluster electron-nuclear dynamics and nuclear dd fusion, and bridging between cluster dynamics and ultracold quantum clouds.

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Joshua Jortner held the position of the Heinemann Professor of Chemistry at Tel-Aviv University (1973-2003). He served as the first Chairman of the Deparment of Chemistry, Deputy Rector, Acting Rector and Vice-President of Tel-Aviv University (1965-1972). He holds honorary doctorates from Universities in Israel, France and Germany and among his awards are the Israel Prize, the Wolf Prize in Chemistry and the Medal of the Israel Chemical Society. He is a member of the Israel Academy of Sciences and Humanities, and a foreign member of 13 Academies of Sciences and Learned Societies in the USA, Europe and Asia. Jortner's scientific work in physical and theoretical chemistry, which contributed to the elucidation of the dynamics of complex systems from large molecules and clusters to biomolecules, is summarized in over 700 scientific articles and 23 books. He contributed to shaping the scientific research and public service in Israel. He served as the President of the Israel Academy of Sciences and Humanities (1986-1995) and as the first Chairman of the Israel National Science Foundation (1986-1995). He acted as science advisor to three Prime Ministers of Israel. On the international level Jortner served as the President of the International Union of Pure and Applied Chemistry (1998-2000). He is currently immersed in scientific research and in international scientific collaborations. His current public service activities span issues of science and public policy.

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His main work experience: 1954-1957 Lecturer at the Karaganda Mining Institute (Kazakhstan); 1958-1974 Senior Research Fellow at the Institute of Chemistry of the Academy of Science (Ufa, Russia); 1964-1977 part-time Associate Professor at the Bashkirian State University (Ufa); 1974-1977 Senior Research Fellow at the Institute of Geophysics (Ufa); 1979-1996 Research Fellow at the Soreq Nuclear Center; as of 1996 he is at the Tel-Aviv University. His main research activities include: solid dielectrics theory, radiometric chemical analysis, quantum chemistry, chemical reaction dynamics, atmospheric optics, and intense laser light interaction with matter.

SOME TOPICS IN QUANTUM CHEMISTRY

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INTRODUCTION

The molecular orbital method in its most general formulation chooses the trial wavefunction in the form of an antisymmetrized product of n functions, each of which depends on the space and spin variables of only one electron. It is obvious from the form of the total Hamiltonian, which contains terms involving the relative coordinates of two electrons, that this formulation cannot yield the exact wavefunction. However, it serves as a very good starting point in the investigation of the general properties of atoms and molecules. It gives a natural link to the older concept of orbit in describing the structure of the atom. In the case of molecules it gives a simple description of the excitation and ionization processes, while the correlation with chemical properties is best achieved by means a unitary transformation leading to equivalent orbitals, which correspond to inner shells, lone pairs and bond orbitals, respectively.

Inherent in the general formulation (product form) is the neglect of correlation between the electrons. The antisymmetrization partly corrects for this error by introducting quite a strong correlation between electrons with parallel spins. If we wish to improve the wave function, while retaining the molecular orbitals as basis functions in the treatment, we have three possibilities:

(a) Introduction of a correlation factor which explicitly contains the inter electronic distance.

(b) Expansion of the wave function in terms of configurations which can be obtained by distributing the electrons in different ways over the molecular orbitals (configuration interaction method).

(c) Alloting different molecular orbitals for different spins, i.e. lifting the restriction that the same molecular orbital should be associated with α and β spin functions.

I. The alternant molecular orbital method

The idea of different orbitals for different spins starts with Slater.[1] He pointed out that the potential experienced by the $1s\alpha$ electron is different from the one experienced by the $1s\beta$ electron. Löwdin[2] generalized this approach for alternant systems. Coulson and Rushbroke[3] defined that conjugated systems are alternant when one can divide the atoms into two sets in such a way that no two atoms which belong to the same set are neighbors to each other. Benzene, naphtalene, and anthracene are alternant systems while fulvene is not. Coulson and Rushbroke showed that the molecular orbitals of alternant systems (using the simple Hückel approach) are paired: to each orbital ψ_i in the occupied set corresponds an orbital in the empty set (ψ_i') in such a way that the coefficients belonging to one set are the same in both orbitals, while coefficients belonging to the other set differ only in sign.

$$\begin{aligned} \psi_i &= \sum_{\mu} C_{\mu i}\varphi_{\mu} + \sum_{\nu} C_{\nu i}\varphi_{\nu} \\ \psi_i &= \sum_{\mu} C_{\mu i}\varphi_{\mu} - \sum_{\nu} C_{\nu i}\varphi_{\nu} \end{aligned} \qquad (1.1)$$

In the molecular orbital description the ground state of the system can be represented by a single determinant in which each of the orbitals ψi occurs twice (once with α spin, and once with β spin):

$$U=A\psi_1(1)\alpha(1)\ldots\psi_n(n)\alpha(n)\psi_1(n+1)\beta(n+1)\ldots\psi_n(2n)\beta(2n) \qquad (1.2)$$

Here A is the antisymmetrizer operator. The wavefunction U is a proper spin eigenfunction, it represents a singlet state. (For the sake of simplicity we are dealing here with an even number of atoms).

Löwdin[2] suggested to generalize the wavefunction U in the following way:

$$V=Au_1(1)\alpha(1)\ldots u_n(n)\alpha(n).v_1(n+1)\beta(n+1)\ldots v_n(2n)\beta(2n) \qquad (1.3)$$

In this function orbitals $u_1 \ldots u_n$ are associated with α spin, while orbitals $v_1 \ldots v_n$ are associated with β spin (different orbitals for different spins). He proposed to consctruct the orbitals u and v by the following transformation:

$$\begin{aligned} u_i &= \cos(\vartheta_i)\psi_i + \sin(\vartheta_i)\psi_{i'} \\ v_i &= \cos(\vartheta_i)\psi_i - \sin(\vartheta_i)\psi_{i'} \end{aligned} \qquad (1.4)$$

For $\vartheta_i = 0$, $i = 1 \ldots n$ the orbitals u_i and v_i become $\psi_1 \ldots \psi_n$ and the wavefunction V becomes equal to U. There is a new problem with the wavefunction V: it is not a singlet eigenfunction. Löwdin suggested to get the singlet eigenfunction by the use of the spin projection operator: Os so the new wavefunction has the following form $V' = OsV$. One can derive the energy expression corresponding to the projected wavefunction, the energy depends on the non-linear parameters $\vartheta_1 \ldots \vartheta_n$. We can minimize the total energy with respect to the parameters and one obtains an improvement as compared with the single determinant description. The method was summarized in my first book - Alternant Molecular Orbital Method[4]. It turned out to be very successful for alternant systems. I generalized the method later for arbitrary systems.[5] The problem is how to obtain the best pairing of orbitals in the general case. For alternant systems the pairing is dictated by the special property of the alternant systems. The method was less succesful for the general case.

II. The construction of spin eigenfunctions

If one uses a spin-free Hamiltonian as in most molecular calculations, the Hamiltonian commutes with the square of the total spin operator S and therefore the wavefunction has to be a proper eigenfunction of this operator and can be classified according to the eigenvalues (S=0 singlet, S=1 triplet, and so on). When one uses a single determinant with doubly occupied orbitals as in the simple molecular orbital method then the wavefunction is a proper spin eigenfunction corresponding to S=0.

In the previous section we met with the problem how to construct proper spin eigenfunctions in the more general case. There are four general methods how to obtain proper spin eigenfunctions:

(a) the branching diagram method
(b) the Serber construction
(c) the projection operator method
(d) the valence bond type spin coupling

In the branching diagram method one constructs the spin eigenfunction stepwise. In each step one either adds or subtracts the spin of the last electron in such a way that the new function is again an eigenfunction of the total spin. An interesting property is the fact that many functions belong to the same spin eigenvalue (spin-degeneracy). The spin degeneracy can be represented by the branching diagram given in Fig.1. In Fig.2 we have a pictorial representation of the five spin eigenfunctions which belong to the spin eigenvalue S=1/2.

In the Serber construction one builds up again the many electron spin eigenfunctions but here one uses two electron spineigenfunctions as building blocks (they can be either singlet or triplet).

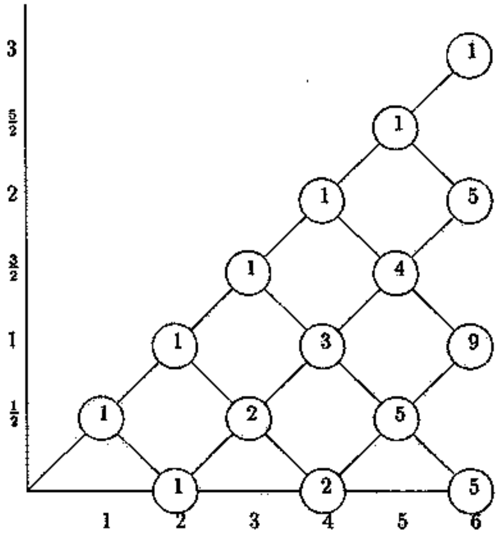

Fig.1 Branching diagram

The two previous methods can be considered as synthetic procedures. In the projection operator method one starts from a trial spinfunction which is an eigenfunction of the S_z operator. It could be considered as a linear combination of spin eigenfunctions. The method works in an analytic way, it selects the proper eigenfunction by annihilating the unwanted components. Löwdin[2] constructed a projection operator which when applied to a trial function yields the proper spin eigenfunction.

The last method uses building blocks which are two-electron spin eigenfunctions but each of them corresponds to a singlet state. This type of construction is very convenient when building many electron functions according to the valence bond procedure.

The four methods of construction, their use in the building of many electron wavefunctions and many other properties have been considered in the author's book: Spin eigenfunctions[5] . This book published in 1979 turned out to be very useful. Recently a shortened and updated version, which also contains many exercise problems, has been published by the author in 2000[6]. It grew out of a graduate course given in the Technion.

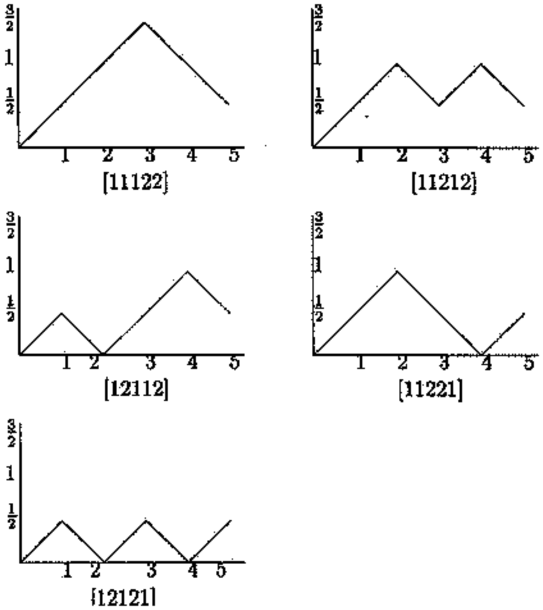

Fig.2 Spin eigenfunctions for N-=5 , S=1/2

III. The use of the symmetric and of the unitary group in quantum chemistry

Let us consider the five spin eigenfunctions corresponding to N=5 and S=1/2. Their pictorial representation is given in Fig. 2. If one performs any permutation of the spin variables, the resulting function is still a spin eigenfunction, but it is a linear combination of the five functions.

The spinfunctions generate an irreducible representation of the symmetric group. It can be shown that the representation corresponds to those Young tableaux which have only two rows. One can even establish a one-to-one correspondence between the spin eigenfunctions and the Young tableaux. In Fig. 3 we have the five tableaux arranged according to the one-to-one correspondence with the five spin eigenfunctions obtained in the branching diagram method.

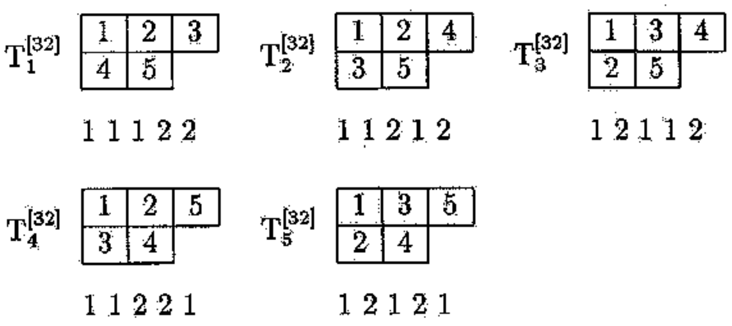

Fig. 3 Standard Young tableaux and Yamanouchi symbols for [32] of S_5

In the spin eigenfunction book I treated quite extensively the representations of the symmetric group generated by the spin eigenfunctions. One can also show that the correct spatial eigenfunctions (which are essential in the energy expression) also generate a representation of the symmetric group. These correspond to those Young tableaux which have not more than two columns. If one uses a spin free Hamiltonian, then the energy depends only on the spatial part, but in order to satisfy the antisymmetry principle, they have to belong to these irreducible representations of the symmetric group. Matsen advocated an approach (Spin-free quantum chemistry) in which one uses only the spatial functions with the correct permutational symmetry.

In 1994 I received an invitation from Prof. D.J. Klein to write a monograph on the use of the symmetric group in quantum chemistry. In this book [7] I treated again the construction of spin eigenfunctions and the representations of the symmetric group generated by these functions.

A separate chapter treated Matsen's approach in detail (Spin-free quantum chemistry). In the last chapter (Spin-coupled functions) I drew attention to a very promising approach started by J. Gerratt and co-workers[9]. They use a linear combination of spin eigenfunctions. They optimize simultaneously both the orbitals and the spin coupling coefficients. The simultaneous optimization of the orbitals (through their expansion coefficients) and the search for the best combination of spin eigenfunctions gives a great flexibility and still retains visuality. It is very interesting to follow what happens with the orbitals and the spin-coupling coefficients upon dissociation. When the nuclei are well separated the orbitals are similar to atomic orbitals, and the mode of spin coupling is characteristic of the separated fragments. When the atoms become closer the orbitals deform, they have more contributions from neighboring atoms. The spin-coupling coefficients change first very slowly but they undergo a rapid change when the fragments approach a certain distance. The method is represented very clearly in the article of Gerratt, Cooper, Karadakov and Raimondi.[9]

The unitary group approach

The latest development in spin free quantum chemistry has been the use of the unitary group for the calculation of the matrix elements of the Hamiltonian in the configuration interaction treatment. Moshinsky[10] realized the importance of the unitary group in the theory of the nucleus and in spectroscopic calculations. Matsen[11] advocated the use of unitary group in spin free quantum chemistry. The latest developments in the representation theory of the unitary group culminated in the work of Gel'fand[12], who was able to give expicit formulas for the representation of the elementary generators of the unitary group. Paldus[13] made a breaktrough when he realized that Gel'fand's formulas become considerably simpler when one restricts the representations to only those which are physically allowed. The next great improvement was achieved by Shavitt[14] who introduced the graphical unitary group approach. Using these methods it became possible to perform configuration interaction calculation involving many million configurations.

An alternative approach has been developed by Duch and Karwovski[15]. They use the same model Hamiltonian as the one used in the unitary group approach, but they base the calculation of the matrix elements of the Hamiltonian on the representation of the symmetric group. A similar successful treatment was presented by Sarma and Rettrup[16].

Matsen invited me to participate in the writing of a monograph on the unitary group in quantum chemistry[17] In the symmetric group book I devoted one chapter to the latest developments of the unitary group approach and another chapter to the representation of the symmetric group approach in the configuration interaction treatment

IV. The teaching of quantum chemistry

I started at the University in Szeged, Hungary in 1938. I was interested from the beginning to learn about the structure of atoms and molecules and I knew that I have to learn quantum mechanics in order to achieve this goal. Unfortunately nobody taught quantum chemistry (or even quantum mechanics) there, at that time. I had to learn it from books, among them one of the best was by Hellmann: Einführung in die Quantenchemie. He was an excellent scientist, he had to leave Germany in the thirties, went to the Soviet Union and he became a very successful scientist. (Hellmann-Feynman theorem). Some of his colleagues were not happy about his success, they denounced him to the KGB and he was executed as a German spy.

I returned to the University in 1948 and taught there for 8 years in the Theoretical Physics Deparment. I was the first to teach a quantum chemistry course for the chemistry students. I also gave some lectures about the subject in Budapest. After the communist takeover we have been "asked" to give lectures about prominent Soviet Scientists. I choose Hellmann and spoke enthusiastically about his great achievements. At that time I did not know (and extremely fortunately for me, nobody in the audience knew it either) what happened to him. Otherwise I am not sure that I could write this text.

In 1956 the Hungarian revolution broke out and I took the opportunity to come to Israel. We left under dramatic circumstances, leaving all our belongings there. We crossed the border at night (my wife was expecting a second child, the first was two and half years old at that time).

We arrived safely in Austria and I contacted immediately the Israeli Embassy. We were on our way in a few days. We arrived in Haifa on December 21, 1956. I did not know anybody there. I went to the Technion to look up in Chemical Abstracts the references to my papers written in Hungary. David Ginsburg was the Head of the Department, and he accepted me first as a Research Fellow. In half a year I started to teach quantum chemistry in Hebrew (Arza Ron and Asher Mandelbaum have been among my first students).In preparing my lectures in Hebrew I used the lecture notes of Aaron Katzir prepared by Joshua Jortner.

In 1959 I was invited by Per-Olov Löwdin to participate in the first Summer Institute organized by him in Sweden. I gave there a seminar, Löwdin invited me to come to Uppsala for a year and since then I was one of the main lecturers in his Summer and Winter Institutes (the latter were in Florida). I participated in 35 Institutes, these Institutes became an important tool in teaching modern methods in quantum chemisty. Thousands of researchers participated in them over the years, coming from several countries.

When I came to Israel in 1956 I was also interviewed by Aaron Katzir (Katchalsky). He offered me a position to come to the Weizmann Institute. At that time there was no teaching there and I chose the Technion because I am very fond of teaching. Many years later the Graduate School of the Weizmann opened and they invited me to give courses in Quantum chemistry. For six years I gave a course there, I had excellent participants, many of them later became leading scientists. For one Semester I also gave a quantum chemistry course in the Bar–Ilan University.

When Charles Coulson and Joshua Jortner arranged the first Pesach School in Quantum Chemistry in Jerusalem, they invited me to give there some lecture courses. It was a great experience with many outstanding lecturers. While I was in Hungary (1955) I participated in the first Summer School in quantum chemistry organized by Coulson (Oxford). I admired Coulson's approach to quantum chemistry, he had great influence on my work. In one of the evening seminars he spoke about the alternant molecular orbital method. He also expressed great interest in the using of different spin functions.

Acknowledgments: I would like to acknowledge the great influence of Charles Coulson and Per-Olov Löwdin on my work, I treasure their memory. I am also indebted to Prof. Al Matsen, who introduced me first to the symmetric group and later to the unitary group. Finally I am very grateful to all of my graduate students, some of them became excellent scientists.

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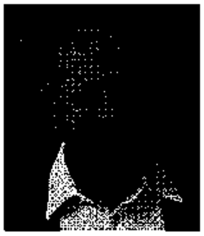

Ruben Pauncz was born in Hungary in 1920. He is a graduate of the University of Szeged. He returned to the university in 1948 and taught for 8 years (Departrment of Theoretical Physics). He emigrated to Israel in 1956 and joined the Department of Chemistry at the Technion. He became Professor in 1962 and taught there until his retirement in 1985.

In his Sabbatical leaves he spent a year in Uppsala (Sweden), two years in Gainesville (Florida), half a year in Basel. He had shorter leaves at the University of Waterloo (Canada), University of North Carolina, Chapel Hill, University of of California, Santa Barbara, University of Texas, Austin. Kahlbaum Lecturer, Basel 1986, Löwdin Lecturer, Uppsala 1991. Visiting lecturer, University of Aarhus (1968) and Boulder, Colorado (1965)

He received a Doctorate Honoris Causa from the University of Szeged in 1996. He is a member of the International Academy of Quantum Molecular Science (1968), exterior member of the Hungarian Academy of Sciences (1995), and member of the European Academy of Sciences and Letters (1998).

His research interests include the electronic correlation problem, the alternant molecular orbital method, construction of spin eigenfunctions and the use of symmetric and unitary group in quantum chemistry.

THE FASCINATING WORLD OF LOW-COORDINATION SILICON COMPOUNDS

Theory and Experiment in Synergy

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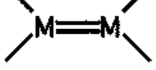
Silicon is the closest element to carbon in the Periodic Table, both belonging to group 14, but, the structural rules, chemical behavior and physical properties of their compounds are very different. These differences are most pronounced for low-coordination compounds. Doubly- and triply-bonded carbon compounds e.g., alkenes, benzenes, butadienes, allenes, acetylenes etc. are among the most important building blocks of organic chemistry. In contrast, until the 1970s only transient compounds with double bonds to silicon were known,[1] leading to the consensus that "compounds containing double bonds to silicon or other heavier main group elements must be unstable".[2] This statement was refuted in 1981 by the landmark syntheses and X-ray crystallography characterization of the first stable disilene, $Mes_2Si{=}SiMes_2$ (Mes=mesityl),[3] and silene, $Me_3SiSi{=}C(OSiMe_3)Ad$ (Ad=1–adamantyl).[4] This important breakthrough was followed by the syntheses and isolation of other stable silenes and disilenes and of compounds with heteroatom-silicon double bonds (as well as double bonds to other group 14 elements).[5] Yet, only recently have other important low-coordination silicon building blocks been synthesized. Thus, the first tetrasilabutadiene and trisilaallene were synthesized only in 1997[6] and in 2003,[7] respectively, and the first silicon analogue of acetylene, i.e., disilyne ($RSi{\equiv}SiR$), was synthesized only in 2004.[8] On the other hand, a stable silyne ($RSi{\equiv}CR'$) is still unknown and its synthesis remains a major challenge. Thus, low-coordination silicon chemistry is still a field in its infancy and presents many challenges for the future.

While the field of low-coordination silicon chemistry was evolving, computational chemistry reached maturity mainly due to the pioneering work of J. A. Pople and his group[9] and to the fast development of computers. Consequently, theory played a major role in the development of low-valent silicon chemistry - a field were theory works in concert and synergism with experiment.

Our group has been involved in the last 15 years both in theoretical and in experimental study of low-coordination silicon chemistry. In this manuscript we will describe some of the properties of low-coordination silicon compounds with emphasis on their unique structures and will demonstrate the benefits of a close collaboration between experiment and theory for the development of this important field of chemistry.

A. Disilenes

Unlike ethylene (**1**, M=C) which is planar, disilene, $H_2Si{=}SiH_2$ was predicted by theory[10] to have a trans-bent structure with pyramidal silicon atoms (**2**, M=Si). The degree of bending ranges between θ=13 - 34°, depending on the theoretical method used.[10] The experimental values observed later for substituted disilenes range between 0-18°.[11] Calculations carried out in our group, shown in Figure 1, reveal that the potential energy surface (PES) for pyramidalization at the silicon atoms



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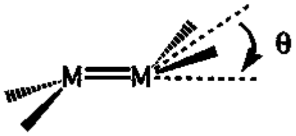

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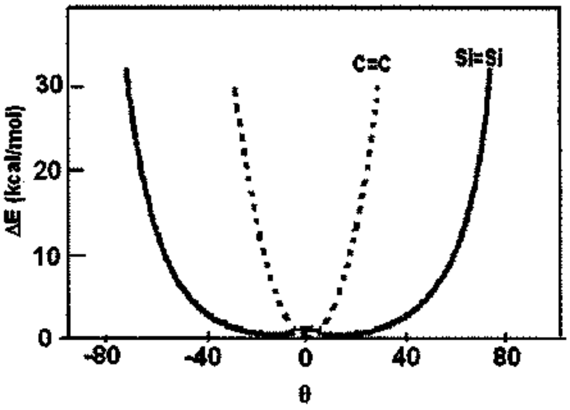
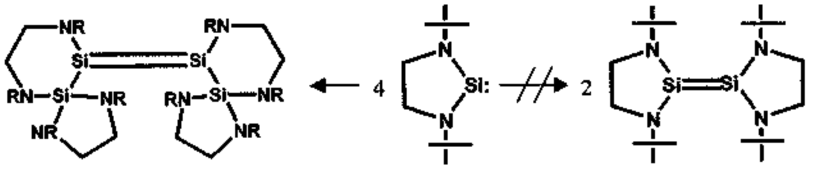


Figure 1. Calculated energy for pyramidalization of the H_2M groups in $H_2M{=}MH_2$, M=C, Si.[12a]

in disilene is very flat and the energy required even for large bending angles is only few kcal/mol (e.g., bending θ to 60° requires only ca. 6 kcal/mol)[12a]. The analogous PES for pyramidalizing the carbon atoms in ethylene is much steeper (Figure 1), and therefore deviations from planarity are rare.

As the PES for pyramidalization in disilenes is so flat, substituents are expected to strongly affect their structures. Calculations indeed predict that with electropositive substituents (e.g., Li, BeH, BH_2 and SiH_3) disilenes are planar[10b]. In contrast, electronegative and particularly π-donating substituents induce very large deviations from planarity as shown in Figure 2; e.g., in $H_2Si{=}SiHNH_2$, $\theta_H = 64.1°$![10b]. Electronegative substituents also cause considerable elongation of the Si=Si double bond and consequently its weakening (Figure 3).[10b] Thus, the calculated dissociation energy (DE) of the Si=Si bond in $H_2NHSi{=}SiHNH_2$ to the two corresponding silylenes is only 20 kcal/mol compared to 57 kcal/mol for $H_2Si{=}SiH_2$ (Figure 3). These bold theoretical predictions which we made some 15 years ago were recently tested when in a collaboration with West, **3** was isolated and its structure indeed confirmed the theoretical predictions. **3** is highly bent (θ=32°), it is twisted about the Si-Si axis by 82° and its Si-Si bond length is 2.29 Å significantly longer than a regular Si=Si bond (ca. 2.14Å) and close to that of a Si-Si single bond (2.35 Å). The calculated DE of **3** is only 27 kcal/mol.[13]



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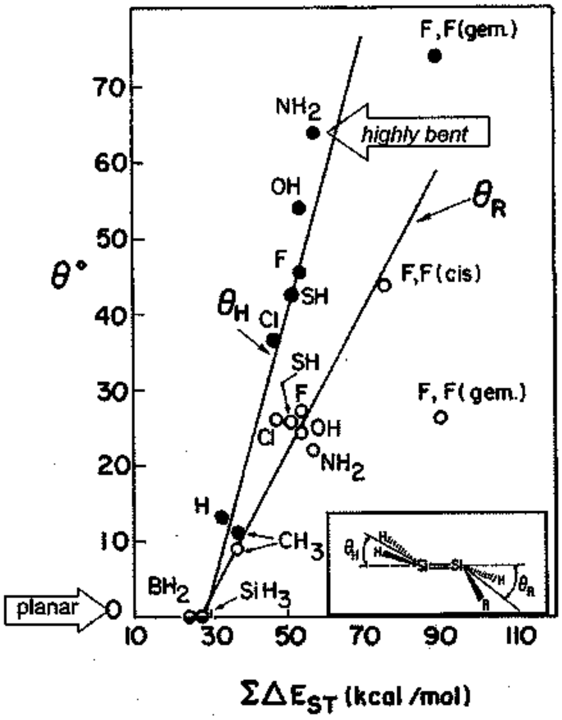


Figure 2. Pyramidalization angles in substituted disilenes $H_2Si{=}SiHR$ as a function of $\Sigma\Delta E_{ST}$ of the corresponding silylene fragments. [10b]

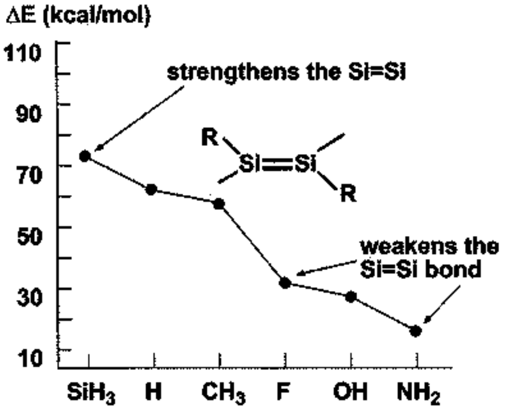
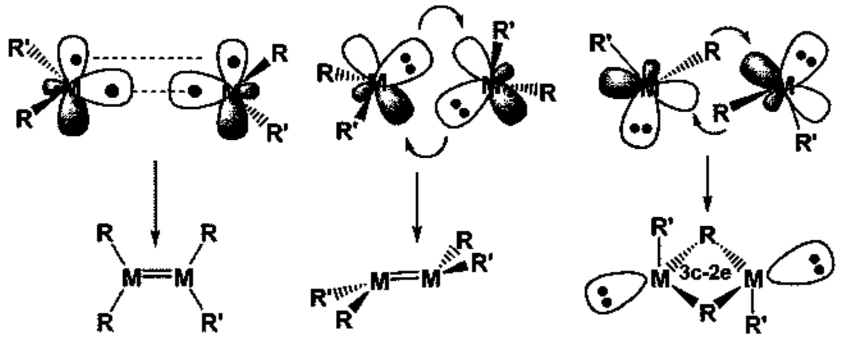


Figure 3. Dissociation energies of HRSi=SiRH to two HRSi: fragments as a function of the substituent R.

Theory finds a linear correlation between the degree of pyramidalization of the doubly-bonded silicon atoms, the Si=Si bond length and its bond dissociation energy with the sum of the singlet-triplet energy gap ($\Sigma\Delta E_{ST}$) of the two divalent R_2Si: fragments that formally compose the disilenes (Figure 2).[10b] The larger is $\Sigma\Delta E_{ST}$ the larger is the bending angle θ (Figure 2) and the longer and the weaker is the Si=Si bond. A surprising prediction of theory is that $(H_2N)_2Si{=}Si(NH_2)_2$ **cannot** exist (i.e., it is not a minimum on the PES), being less stable than two $(H_2N)Si$: fragments.[12] This prediction was later supported by an experiment in which dimerization of silylene **4** failed to form disilene **5** (a cyclic analog of $(H_2N)_2Si{=}Si(NH_2)_2$), producing instead tetramer **3** discussed above (eq. 1).

An insightful theoretical model, shown in Scheme 1, was suggested[14,15] to account for the different structures of ethylene and disilene. $R_2M{=}MR_2$ are formally composed of two R_2M: units (Scheme 1). For M=C, these are carbenes which are generally ground state triplets (or singlets with a small singlet-triplet (S-T) energy gap)[16a] and they dimerize to planar alkenes. In contrast, for M=Si, these are silylenes which are ground state singlets with a relatively large ΔE_{ST} (21 kcal/mol for H_2Si,[16b] and considerably larger ΔE_{ST} values for silylenes substituted with π-donor substituents[10b,13]). Dimerization to a planar structure requires that the silylenes are first excited to the triplet state, demanding twice the energy of ΔE_{ST}. A lower energy path is dimerization via a non-linear approach utilizing two donor-acceptor interactions in which the lone-pair of one silylene donates electrons into the empty 3p(Si) orbital of the second silylene, yielding a trans-bent structure (Scheme 1b). The following rules were suggested for homopolar M_2R_4 molecules:[15] (a) a trans-bent doubly-bonded structure **(2)** will be more stable than a planar structure **(1)** when ΔE_{ST} of the R_2M: fragment is larger than 0.25 of the total M=M bond energy ($E_{\sigma+\pi}$) (Scheme 1b); (b) when ΔE_{ST} is larger than 0.5 $E_{\sigma+\pi}$ a direct M-M link is less favored and a bridged structure **6** will be more stable than **2** (Scheme 1c).



1 **2** **6**

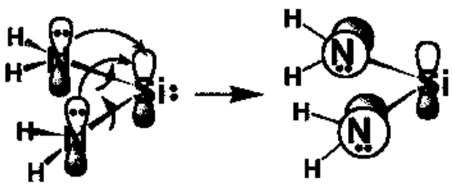
$\Delta E_{ST}(MR_2) < 1/4E\sigma{+}\pi$ $\Delta E_{ST}(MR_2) > 1/4E\sigma{+}\pi$ $\Delta E_{ST}(MR_2) > 1/2E\sigma{+}\pi$

(a) (b) (c)

Scheme 1

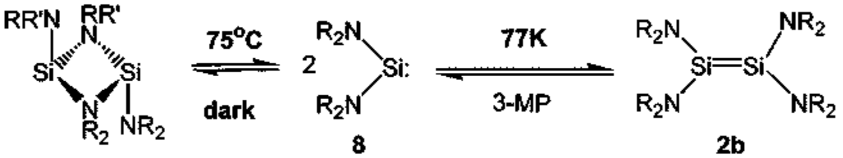
The relationship between ΔE_{ST} and the various M_2R_4 structures is beautifully demonstrated for $R{=}NR'_2$, for which the unusual bridged structure **6**, in which the silicon atom is only tri-coordinated, is predicted by theory to be the most stable structure. Is **6** indeed a viable structure? Can it be observed experimentally? For C_2H_4, **6** is not a minimum on the PES. An artificially constrained **6**, M=C, R=R'=H is by 173 kcal/mol less stable than ethylene **1**! However, for M=Si; R=R'=H, **6** is by only 28 kcal/mol less stable than **2**, and it is by 22 kcal/mol more stable than two H_2Si: fragments.[12a] The electronic structure of **6** consists of two sets of 3-center-2-electron Si-R-Si bonds, and two lone-pair orbitals with high s-character which reside on each of the Si atoms (see **6**). The surprising high stability of such bridged silicon compounds can be attributed to the low energy of the 3s-orbital of silicon, favoring low-valency.

With suitable substituents, i.e., those increasing ΔE_{ST} of the silylene fragments, **6** may become even more stable than **2** (Scheme 1). Indeed, for R'=H and R=NH_2 both **2** and **6** are calculated to be minima on the PES, but, the bridged isomer **6** is by 10 kcal/mol more stable than the trans-bent doubly-bonded conformer **2**.[12a] When R and R' are both amino groups, the singlet state of $(H_2N)_2Si$: is highly stabilized by conjugation between the lone-pairs on the nitrogen and the empty 3p-orbital on Si (see **7**) resulting in a very high ΔE_{ST} of 57 kcal/mol[17] and as predicted by the model in Scheme 1, $(H_2N)_2Si{=}Si(NH_2)_2$ is not a minimum on the PES,[18] while **6**, M=Si, R=R'=NH_2 is by 16 kcal/mol more stable than two molecules of $(H_2N)_2Si$:[18].



7, ΔE_{ST}= 57 kcal/mol **7a**, ΔE_{ST}= 22 kcal/mol

The importance of N (lone-pair)-3p(Si) conjugation and its effect on ΔE_{ST} and the stability of **2** is nicely demonstrated by rotation of the amino groups by 90° (∠HNSiN=90°, see **7a**), so that the 2p(N) and 3p(Si) orbitals are out of conjugation. This rotation reduces ΔE_{ST} to 22 kcal/mol making the corresponding constrained $(H_2N)_2Si{=}Si(NH_2)_2$ a relatively stable structure with DE(Si=Si) of 55 kcal/mol.[17]



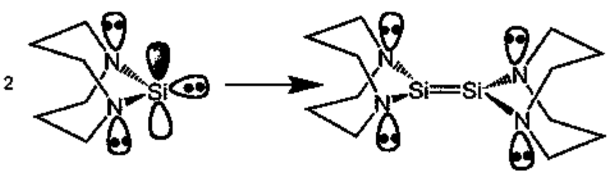
6b **8** **2b**

R=CH(CH$_3$)$_2$ λ_{max} =439 nm

Scheme 2

When substituents are introduced on the amino groups, i.e., R=R'= Me_2N **(a)**, R=R'= *i*-Pr_2N **(b)**, or R=R'= $(H_3Si)_2N$ **(c)**, the corresponding silylenes are no longer planar and the nitrogen lone pairs are twisted away from the 3p(Si) empty orbital by 23°, 26° and 30°, respectively, reducing 2p(N)-3p(Si) conjugation and consequently ΔE_{ST} is reduced to 52, 44 and 47 kcal/mol, respectively. Accordingly, theory predicts that for these substituents both isomers of R_4Si_2, **2** and **6**, are minima on the PES and should therefore be amenable to experimental observation.[17,18]

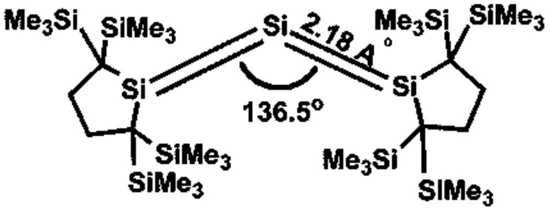
To test our theoretical predictions new experiments were carried out in collaboration with the group of Kira.[18] These experiments fully support the theoretical predictions demonstrating, by sophisticated labeling experiments (with R=CH(CD$_3$)$_2$), that indeed both **2b** and **6b** can be obtained by dimerization of (*i*-Pr_2N)2Si: depending on the reaction temperature as shown in Scheme 2.[18,19] It should be noted however, that **2b** (R=R'= *i*-Pr_2N) is predicted by calculations to have a very unusual geometry, very different from what we expect for a Si=Si doubly- bonded compound. The Si-Si distance of 2.47Å is dramatically longer than a regular Si=Si bond (2.14 Å in $Me_2Si{=}SiMe_2$) and it even exceeds that of a single Si-Si bond (e.g., 2.37 Å in $(Me_2N)_3Si\text{-}Si(NMe_2)_3$). **2b** is also strongly pyramidalized around the Si atoms (θ=43°) and the torsion angle between the two NSiN planes is 55°.[17]



9 10

Following the theoretical prediction (see above) that a diaminosilylene constrained to a conformation in which the nitrogen's lone-pairs are in a nearly perpendicular plane to the empty 3p(Si) orbital has a small ΔE_{ST}, we predict that bicyclic silylene **9** (ΔE_{ST} = 38 kcal/mol) should dimerize to a strongly bonded tetraaminodisilene **10** having a much stronger Si=Si bond (DE=41 kcal/mol) than in simple alkyl-substituted tetraaminodisilenes (e.g., **2**, R=R'=*i*-Pr_2N, DE=4 kcal/mol).[17] This is a clear demonstration of how stereoelectronic effects of the amino substituents control the Si=Si bond energy. This theoretical prediction is awaiting experimental testing.

Before theory pointed to the possible existence of bridged structures such as **6**, experimentalists ignored this possibility. For example, it was suggested that in the dimerization of $(C_5Me_5)FSi$: the corresponding disilene is formed.[20] However, our calculations that predicted that a bridged structure of type **6** is also an option[21] lead to a reexamination of the experimental NMR which actually fits structure **6**, R=F, R'=C_5Me_5 and not structure **2** (i.e., the NMR[20] exhibits a single ^{29}Si NMR resonance split to a triplet ($J_{Si\text{-}F}$=341 Hz)[20]).[21] Experimentalists now agree that $(C_5Me_5)FSi$: dimerizes to a bridged structure **6** and not to the classic doubly-bonded structure **2**.



13

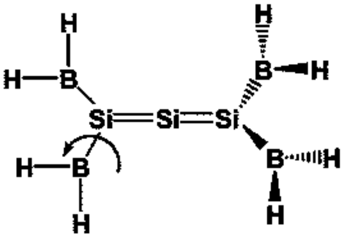
B. Trisilaallenes

Trisilaallene and its higher congeners, trigermaallene and tristannaallene, provide another interesting example of the unique structures that are formed by higher group 14 elements.

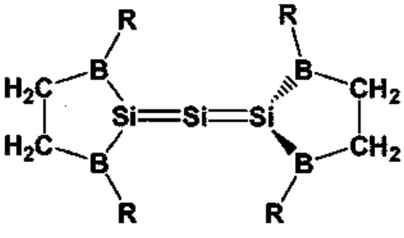
Allene $H_2C=C=CH_2$ is linear and the terminal CH_2 groups are mutually perpendicular **11**. In contrast, theory predicts that a linear trisilaallene is not a minimum on the PES, and the global minimum on the Si_3H_4 PES is a highly bent structure, **12**, R=H, with a SiSiSi angle of 69°, a long Si=Si bond of 2.27 Å and two planar terminal Si atoms with dihedral angles $\angle H^1Si^1Si^3H^{1'}$= 0° and $\angle H^1Si^1Si^3H^{2'}$=115° (in **11** the analogus dihedral angles are 90° and -90°). This highly bent structure **12** is by 21 kcal/mol lower in energy than the constrained linear trisilaallene.[22] This theoretical prediction was recently verified by the synthesis of the first trisilaallene, **13**,[7] whose X-ray structure reveals a bent structure with a bending angle of 136.5°. The considerably wider bending angle in **13** relative to that calculated for Si_3H_4 is due to the steric repulsion between the bulky substituents present in **13**.

Heavier trimetallaallenes, are also highly bent, i.e., trigermaallene,[23a] 1,3 – digermasilaallene[23a] (both with the same substituents as in **13**) and tristanaallene (R= *t*-Bu_3Si)[23b] show bending angles of 123°, 126° and 156°, respectively. Thus, only allene is linear, while all the heavier allene-analogs are strongly bent.

Can one restore the allenic-type structure for a trisilaallene? We have recently tackled this question computationally.[22]



14



15

Are steric effects effective? In **12**, R=Me the bending angle is widened only slightly to 74°, and the energy required for linearization is reduced to

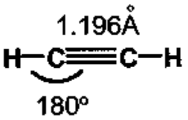
17 kcal/mol. Even with bulkier substituents such as *t*-Bu the SiSiSi angle opens to 108°. In **13** the SiSiSi angle is only 136°. So, it is clear that steric effects alone cannot solve the problem. Silyl substitution has a profound effect on the central bending angle α, and in **12**, $R=SiH_3$ α is widened to 127° and the energy required for linearization is reduced to only 4.7 kcal/mol. Furthermore for $R=SiH_3$, the bending potential is considerably flatter than for R=Me or R=H, making linearization more feasible. Very bulky silyl substituents e.g., $t\text{-}Bu_3Si$ or $(Me_3Si)_3Si$ may thus induce a linear allenic – type trisilaallene.

The computational results for silyl substitution hint that the goal of creating a D_{2d}- trisilaallene might be achieved with other electropositive substituents. Indeed, calculations show that substitution of trisilaallene with four H_2B groups achieves the goal, yielding a classic D_{2d} allenic-type structure, **14**, with a linear SiSiSi skeleton, planar terminal Si atoms, and perpendicular BSiB terminal planes. The Si=Si bond length in 14 is 2.21 Å considerably shorter than in 12, R=H. The 2p(B)-π(Si=Si) conjugation plays a crucial role in the linearization of **14**. The calculations show that a slight rotation of the boryl groups which reduces the 2p(B) - π(Si=Si) conjugation induces bending of the SiSiSi skeleton[22]. To prevent rotation around the Si-B bonds (e.g., due to bulky substituents on the boron atoms), trisilaallene **15** was suggested as a potential synthetic target.[22] These theoretical predictions are now awaiting experimental testing.

C. Disilynes (RSi≡SiR) and silynes (RSi≡CR')

One of the contemporary major challenges of organosilicon chemistry is the synthesis of triply-bonded silicon analogs of acetylene. Synthesis of the first homonuclear RSi≡SiR was achieved last year,[8] but the heteronuclear, RSi≡CR', is still a major synthetic target. In view of this situation theoretical studies were and still are the main source of information on this group of interesting compounds. Using theoretical methods, the structures, the nature of bonding and the stability of heavier group 14 acetylene analogs were predicted. Furthermore, calculations were used to develop strategies for stabilizing these compounds with the aim to direct experimentalists towards their successful synthesis. Some of the theoretical predictions were already verified by subsequent experimental achievements.[8]

For both, HSi≡SiH and HSi≡CH, theory predicts that the linear $D_{\infty h}$ acetylene-like structure **16** is not a minimum on the PES. Instead trans-bent structures shown in **17** and **18** were located as minima.[10a,24] The trans-bent disililyne and silyne are by ca. 20 and 8 kcal/mol, respectively, **more** stable than the analogous linear conformers.[10a,24] In contrast, a trans-bent HC≡CH structure (with fixed HCC angles at 125°) is by ca. 30 kcal/mol less stable than the analogous linear structures.[24]



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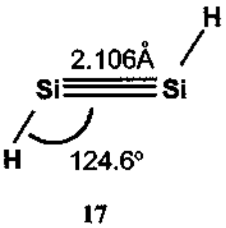

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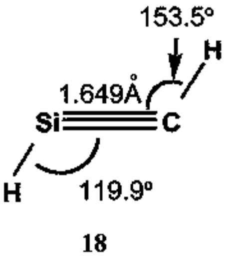

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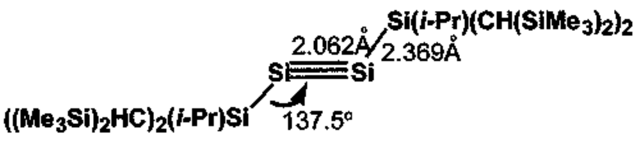
The theoretical prediction that disilynes have a trans-bent structure was recently verified by the isolation and characterization by X-ray crystallography of the first disilyne, **19**, showing a trans-bent structure with a SiSiSi angle of 137.5°.[8]

The inherent preference for bending raises fundamental questions about the nature of the Si≡C or Si≡Si bonding. Is it a real triple bond? Why do these molecules prefer to be bent



19

while acetylene is linear? These questions regarding the nature of the M-M bonds in formally triply-bonded compounds of groups 13 and 14 arose a vigorous debate. [10a,25]

A detailed study of the nature of bonding in HSi≡CH, HSi≡SiH and HC≡CH was reported by Shaik, Apeloig and coworkers,[24] who analyzed these M-M' bonds using new valence bond (VB) techniques which allow to dissect the total M-M' bond energy to energetic contributions of the σ – and π-bonds. According to this study the M-M' bond order (BO) in **17** and **18** is 2.5, intermediate between that of a formal double bond (BO=2.0) and triple bond (BO=3.0). So the question that was asked is why do **17** and **18** bend and by doing so reduce the bond order? The VB analysis shows that upon bending the energy of the π-bonds in HSi≡CH, HSi≡SiH and HC≡CH, is reduced by 34, 24 and 60 kcal/mol, respectively, while the σ-bond is strengthened by 53, 42 and 34 kcal/mol, respectively, leading upon bending to an overall **stabilization** of the M-M' bonding in **17** and **18** by 29 and 8 kcal/mol, respectively, but to an overall weakening by 26 kcal/mol of the C-C bonding in *trans*-bent HC≡CH. Consequently, **17** and **18** are *trans*-bent, while HC≡CH is linear. Thus, the structures of disilynes and silaacetylenes are dominated by the σ-bond and the π-bonds have a smaller effect, while in acetylene the π-bonds are dominant.[24]

The elusiveness of triply-bonded silicon compounds is due primarily to their low kinetic and thermodynamic stability in unimolecular (isomerization) and bimolecular (e.g., dimerization) reactions. Thus, $H_2C{=}Si$: is by 33-37 kcal/mol more stable than HC≡SiH, and a small barrier of only 3-7 kcal/mol separates the two isomers (Figure 4).[10a,26] So even at low temperatures HC≡SiH is expected to isomerize rapidly to $H_2C{=}Si$:. Indeed, only $H_2C{=}Si$: was detected and identified by various spectroscopic experiments attempting to prepare HC≡SiH.[27] With this theoretical background at hand it became clear that in order to detect a silyne, RC≡SiR', it should be stabilized relative to the isomeric RR'C=Si:. This triggered a computational study in our group which showed that ClSi≡CH and HOSi≡CH are by only ca. 5 and 1 kcal/mol less stable than the corresponding silavinylidenes, and FSi≡CH is more stable than FHC=Si: by 10 kcal/mol (Figure 4).[28] Furthermore, the barrier that separates these three silaacetylenes from the corresponding silavinylidene isomers is increased substantially to 15, 24 and 25 kcal/mol for R=Cl, OH and F, respectively (Figure 4), making these silynes possible candidates for detection and identification.[26] This computational prediction was tested in a collaborative study with the group of H. Schwarz (Berlin) leading to the first unequivocal identification of FSi≡CH and ClSi≡CH using a sophisticated neutralization-reionization mass spectroscopy experiment.[29]

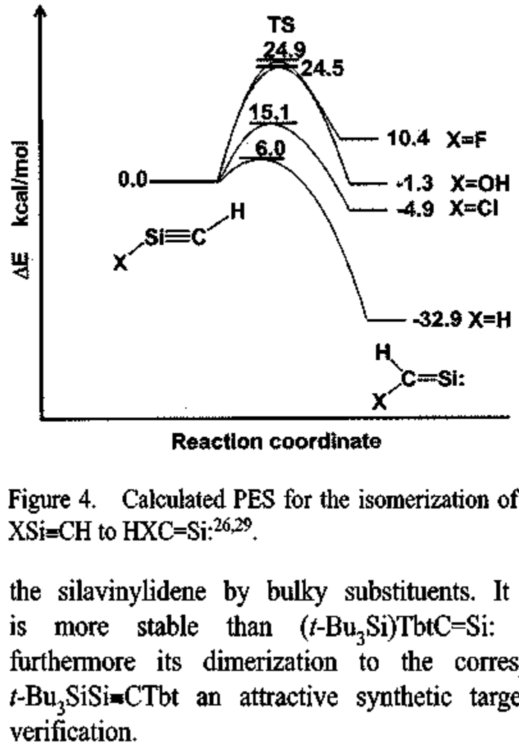
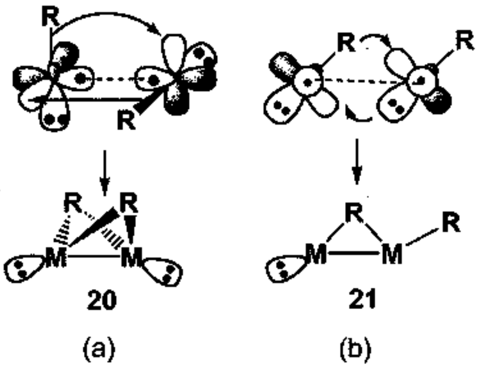


Figure 4. Calculated PES for the isomerization of XSi≡CH to HXC=Si:[26,29].

Another possible strategy to reverse the stability order of these isomers is to destabilize the silavinylidene by bulky substituents. It was predicted computationally that $t\text{-}Bu_3SiSi{\equiv}CTbt$ is more stable than ($t\text{-}Bu_3Si$)TbtC=Si: (Tbt=2,4,6-tris[bis(trimethylsilyl)methyl]phenyl), and furthermore its dimerization to the corresponding disilatetrahedrane is endothermic, making $t\text{-}Bu_3SiSi{\equiv}CTbt$ an attractive synthetic target.[30] This theoretical prediction awaits experimental verification.

The H_2Si_2 PES is much richer and more complex than that of H_2CSi, revealing novel unusual structures.



20 21

(a) (b)

Scheme 3

Three isomers, the butterfly shaped dibridged isomer **20**, the monobridged structure **21** and the silylidene, $H_2Si=Si$: (**22**) are predicted to be more stable than the trans-bent HSi≡SiH by 17, 7 and 5 kcal/mol, respectively. The most stable H_2Si_2 isomer is the dibridged **20**.[10a,31] These theoretical predictions were verified experimentally. **20** and **21** were detected and identified specrtoscopically both in the gas phase and in a matrix.[32] The bonding in **20** can be modeled by two donor-acceptor interactions between the Si-H bonds and the empty 3p-orbitals on the silicon atoms (Scheme 3a). The bonding in **21** is modeled by one donor-acceptor interaction of the Si-H bond with the empty 3p-orbital of the second silicon atom and a donor-acceptor interaction between the lone-pair on one silicon atom with the empty 3p-orbital of the second silicon atom (Scheme 3b).[10a,14,33] The high stability of the bridged H_2Si_2 isomers is attributed to the stabilizing effect of the high s-character lone-pairs on Si.

Substituents have a significant effect on the Si_2R_2 PES. When $R=CH_3$[34] or SiH_3, the bridged structures are no longer minima on the PES. $R_2Si=Si$ is the only isomer that is more stable (by 8 and 6 kcal/mol for $R=CH_3$ and SiH_3, respectively[35]) than the triply-bonded isomer. With bulky R substituents, such as Si(Bu-*t*)$_3$[35a], SiDep$_3$[35a] (Dep=2,6-$Et_2C_6H_3$), Tbt (2,4,6-tris[bis(trimethylsilyl)methyl]phenyl)[35b] and Me(*t*-Bu$_3$Si)$_2$Si[36a] the triply-bonded structures were calculated to be more stable than $R_2Si=Si$ by 10, 12, 23 and 33 kcal/mol, respectively. Disilynes even with bulky substituents are however calculated to be very reactive, and the dimerization of e.g., RSi≡SiR, R= SiDep$_3$ is highly exothermic, by 80 kcal/mol.[35a] However, with the bulkier substituents, Tbt or Me(*t*-Bu$_3$Si)$_2$Si the dimerization of the corresponding RSi≡SiR disilynes is endothermic by 58[36b] and 50[36a] kcal/mol respectively, suggesting that these compounds can be isolated. These computational predictions were recently verified by the successful synthesis of RSi≡SiR, R=*i*-Pr((Me$_3$Si)$_2$CH)$_2$Si (**19**) which was isolated and characterized by X-ray crystallography[8] and RSi≡SiR, R= Me(*t*-Bu$_3$Si)$_2$Si which was isolated and identified by NMR and trapping reactions.[37] A recent study in our group allows to predict computationally the ^{29}Si NMR chemical shifts of disilynes,[38] providing experimentalists guidance in their continuing attempts to synthesize novel disilynes.

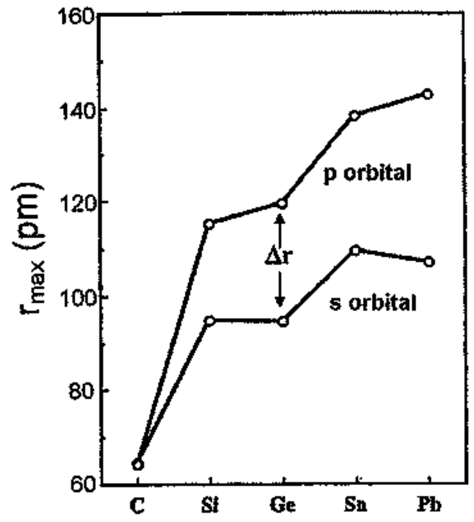


Figure 5. Radial extensions of the ns- and np valence orbitals of C, Si, Ge, Sn and Pb.[39]

Conclusions

In this review we have shown that although silicon is the closest neighbor to carbon in the Periodic Table of elements the rules that control the molecular and electronic structures of silicon compounds are very different from that of carbon. Typical examples are: $R_2Si=SiR_2$ that are pyramidal at silicon rather than planar and $R_2Si=Si=SiR_2$ and RSi≡SiR which are strongly bent in contrast to their carbon analogs that are linear. Organosilicon compounds also adopt unusual structures, e.g., bridged structures which do not exist in organic molecules, forming a rich arena of new molecules and interesting fundamental questions regarding chemical bonding.

The key to the different behavior of carbon and silicon (and higher congeners) is the significantly larger difference in the radial extension of the s and p valence orbitals of silicon relative to that of carbon, i.e., $\Delta r = (r_p - r_s) = 0.2$ pm in C and 20 pm in Si (Δr increases successively in moving down the Periodic Table, Figure 5).[39] So, thes-p radial extension in carbon (and other first row elements) is unique and very different from that of other main group elements. A large difference in s-p radial extension makes hybridization at silicon (and higher group 14 congeners) less effective and these atoms therefore benefit from low-coordination structures having lone-pair electrons in orbitals with high s-character.[10a,40] It can therefore be concluded that **the heavier main-group elements, Si to Pb, actually exhibit 'normal' chemical behavior while carbon should be considered the 'unusual' member of group 14 elements rather than the prototype.**[40] This conclusion holds also for the other elements of the first-row of the Periodic Table such as nitrogen and oxygen. This realization has not yet penetrated most text books of general chemistry and it is an important lesson to be remembered by all who teach an introductory course in chemistry.

Finally, we hope that we have demonstrated the vast potential of modern computational chemistry in predicting properties of novel unknown molecules and in directing experiments towards their synthesis and experimental study. In modern chemistry, theory and experiment should work in concert and the synergism created benefits both disciplines.

Acknowledgment

We wish to thank all the group members, students and postdocs, at present and in the past, whose innovative studies have established the pedestals for this manuscript. Special thanks are due to Dr. Dmitry Bravo-Zhivotovskii who has made critical contributions to the experimental studies in our laboratory, work which we did not have the space to describe in this manuscript.

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Prof. Yitzhak Apeloig

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He received the Technion Prize for Academic Excellence, was elected several times by Technion students for the Distinguished Teacher Award and is a Alexander von Humboldt - Lise Meitner Senior Research Awardee and a Japan Society for the Promotion of Science Senior Visiting Professor Awardee.

He is the receipient of the 2002 Israel Chemical Society Prize.

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SINGLE-SCAN 2D NMR

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1. Introduction

Few branches of spectroscopy match in either breadth or depth the impact achieved by nuclear magnetic resonance (NMR) [1]. Originated as an unexpected by-product of the quantum mechanics revolution [2], NMR remained mostly a curiosity of the molecular beam community until Bloch, Purcell and their coworkers demonstrated the possibility of observing its manifestation in bulk [3]. This in turn triggered the use of nuclear spins as tiny "spies" capable of characterizing the structure of organic molecules [4], a feature that transformed NMR into one of the cornerstones of modern chemical and pharmaceutical research. Over the years NMR undertook many other unforeseen applications: it became a common research tool in solid state chemistry and condensed matter physics; it afforded one of the few methods available for determining the structures of proteins and nucleic acids in their native solution state; and it expanded into medicine both as an imaging as well as a spectroscopy tool to study metabolism, diagnose malignancy, angiograph non-invasively, and reveal brain function [1, 5-9]. A feature that distinguishes modern NMR from the few other techniques that might claim comparably wide impact areas of applicability is the fact that, broadly speaking, one common protocol underlies most of its very different applications. This protocol is multidimensional Fourier transform NMR, nD FT NMR, initially carried out along two axes [10, 11] but eventually extended to the correlation of multiple spectral - and in the case of imaging, to the correlation of multiple spatial [9, 12] - domains. nD NMR seeks to measure, spread and correlate NMR evolution frequencies. This is not generally carried out by exciting spectral lines but rather by manipulations in their Fourier conjugate: the time-domain space. For instance the basic scheme that started the 2D NMR revolution [10, 11, 13]

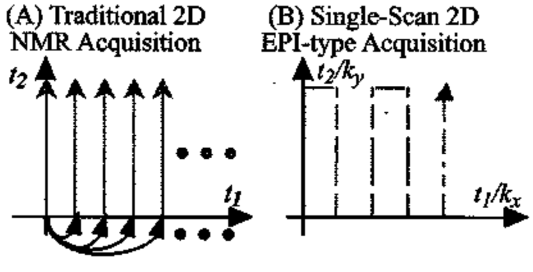
$$\textit{Preparation - Evolution } (t_1) \textit{ - Mixing - Acquisition } (t_2) \qquad (1)$$

provides a time domain set from which correlations between indirect- and direct-domain Bohr frequencies Ω_1, Ω_2 can be extracted following a discrete version of the Fourier analysis

$$I(\nu_1, \nu_2) \propto \int_{\text{all } t_2\text{'s}} dt_2 \left[\int_{\text{all } t_1\text{'s}} dt_1 S(t_1, t_2) e^{-i\nu_1 t_1} \right] e^{-i\nu_2 t_2} \qquad (2)$$

This expression may appear as a simple extension of 1D time-domain NMR to two dimensions, yet this similarity is deceiving and belies the insight involved in the transition from one- to multi-dimensional spectroscopy. Indeed the extraction variable against which data are transformed in 1D pulsed NMR is the physical acquisition time, of which Nature has given us only one [13, 14]. Such acquisition time becomes t_2 in 2D NMR spectroscopy, leaving the problem of how to sample points in the remaining time-domain axis. The answer to this riddle was provided by Jeener, who proposed acquiring complete 2D NMR frequency correlation sets by relying on a parametric incrementation of t_1 in N_1 steps of duration Δt_1 (Fig. 1A). Although in appearance a very simple solution it is actually hard to emphasize the scientific insight of this contribution, whereby a 2D correlation between evolving coherences is extracted from a series of statistically independent experiments. In its stead, perhaps more indicative and meaningful is it to note the ca. 27,000 references arising from a contemporary data base search on the topic of multidimensional magnetic resonance, or the fact that in a very brief survey of its first 100 years the Nobel Foundation devoted a central spot to describing the impact of 2D NMR [15].

In spite of the unambiguous gains resulting from upgrading NMR from one spectral dimension to two, a fundamental drawback also became associated to this transition. As each of the t_1 points to be sampled


(A) Traditional 2D NMR Acquisition

(B) Single-Scan 2D EPI-type Acquisition

Figure 1. (A) Traditional Jeener/Ernst approach to the acquisition of 2D NMR spectra, based on the acquisition of numerous independent $S(t_2)$ signals as a function of an incremented t_1 time parameter (dashed arrows). (B) Mansfield's approach to ultrafast MRI based on the continuous scanning of a 2D time-domain data within a single acquisition, using multiple manipulations of the interactions being correlated. In either case, the resulting temporal evolution obtained from the spins needs to be Fourier analyzed in order to extract the spectral correlations sought.

along the indirect time-domain constitutes an independent acquisition, 2D NMR will demand tens or hundreds of transients in order to adequately sample the t_1 domain-even if the sensitivity is acceptable within a single scan. Such complication is built-in into the scheme illustrated in equation (1), and gets exponentially compounded when porting the 2D NMR principle to higher dimensions. The slow nature of multidimensional spectroscopy was found particularly confining in what eventually became the most widespread of all forms of bidimensional NMR, 2D FT MRI, an experiment where the spins' positions along orthogonal orientations become correlated by the action of external magnetic field gradients [16-18]. Yet in this case the availability of intense signals combined with the unparalleled flexibility with which MRI interactions could be manipulated enabled the eventual development of so-called ultrafast acquisitions techniques, capable of yielding complete 2D MRI data sets within a 0.1-1 sec timescale (Fig. 1B). Principal among these methods stands echo planar imaging, EPI [12, 19], and its daughter techniques [20]. This proposition was originally judged as "ahead of its time" [21] yet eventually it became a cornerstone of magnetic resonance, contributing with the advent of functional MRI to what has arguably become the most exciting area in contemporary magnetic resonance.

Given the benefits that could be reaped from EPI, the question naturally arises of whether it is possible to extend its underlying principles to other, non-MRI types of NMR experiments. And yet except for a few rare cases where the interactions to be correlated can be controlled independently and with nearly ideal efficiency [22-24], one is forced to conclude that the spin physics underlying EPI techniques could not be directly exported into conventional high-resolution spectroscopy. Indeed EPI extends the principle in equation (1) by coupling into it the possibility of "walking" through the time domain [19, 25, 26]; that is, by introducing numerous periodical switchings and/or reversals of the interactions being correlated so as to sample a large region of the 2D time-domain space within a single continuous scan (Fig. 1B). And although of a reliability beyond arguments, it is clear that such "walk in space" approach is simply beyond the realm of the practical when relying on stochastic mixing processes like those involved in 2D Overhauser spectroscopy [13], or repeatable only very few times when dealing with J-mediated coherence transfers like those involved in homo- or hetero-nuclear 2D correlation sequences.

Still, challenged and inspired by these MRI-derived acquisition concepts, we sought for over a decade for a principle capable of reinstating the multiplexing advantages of 1D FT spectroscopy to multidimensional NMR - as well as potentially onto other forms of MR and non-MR time-domain spectroscopies. Very recently one such principle finally crystallized [27, 28], which in analogy to the ultrafast MRI term, proposed for imaging techniques capable of concluding their data acquisitions within sub-second timescales, we have coined "ultrafast NMR". This principle provides a general scheme for completing the acquisition of nearly arbitrary high-resolution multidimensional experiments within a single scan-regardless of whether their dimensions are 2, 3 or higher; regardless of whether they involve internal spin interactions, gradient-driven ones, or a combination thereof. The goal of the present description is to present a brief summary of this new principle, and overview some of its potential applications.

2. Spatial Encoding and the Acquisition of 2D NMR Spectra Within a Single Scan

The Principle

The main aspect distinguishing ultrafast from both traditional 2D NMR as well as from EPI-type acquisitions is a departure from the homogeneous encoding of the spin interactions. Instead, indirect-domain evolution frequencies are imparted in a heterogeneous fashion whereby spins positioned at different coordinates within the sample[1] are allowed to evolve over different extents of time prior to the mixing period. A suitable read-out of the heterogeneous evolution thus encoded can then provide the full 2D NMR information being sought, within a single continuous data acquisition. Given present-day NMR hardware it appears that the simplest way to achieve this partitioning of the sample is by activating a magnetic field gradient $G = \partial B_0/\partial r$, discriminating spins according to their spatial coordinate r. A scheme such as the one illustrated in Fig. 2 can then be used to collect the indirect-domain spectral correlations. Such generic sequence assumes that the initial spin evolution is triggered by a frequency-incremented RF pulse, superimposed on top of an excitation gradient $G_e\,\hat{r}$. An important demand placed on this excitation module is that at its conclusion, the evolution phase of the excited spin packets should end up reflecting the effects of internal Ω_1 couplings, but not those of the ancillary G_e gradient. Numerous strategies have already been devised for imparting such internal kind of spatial encoding [27-32], and it is likely that further optimizations will arise in the near future. In broad terms all these spatial encoding strategies involve the application of either discrete or continuous frequency-shifted selective RF pulses, in combination with alternating gradients designed so that their effects are eventually "echoed away" at the conclusion of the irradiation. The common, important point of all these encoding alternatives is that at their conclusion, the combined use of frequency-shifted RF pulses and of spatially dependent resonance frequencies end up imparting on the spins an r-dependent purely internal evolution phase of the kind

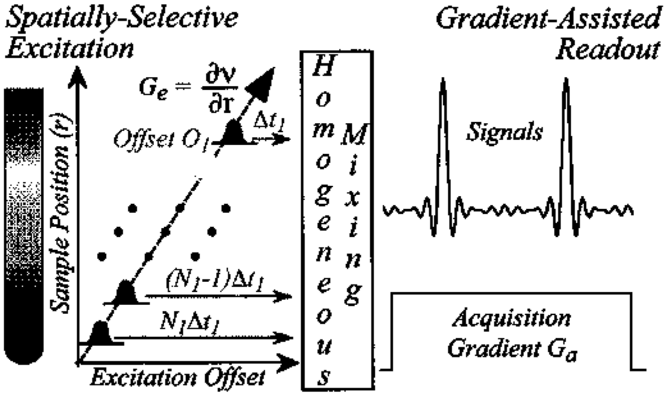


Figure 2: Starting point of the single-scan 2D NMR protocol: A time- and frequency-incremented RF irradiation applied in combination with a suitable gradient imposes an r-dependent evolution of the Ω_1 spin interactions to be measured (Left). Following a homogeneous mixing process this spatial encoding is preserved as either a phase- or an amplitude-modulation (Center), to be subsequently decoded by the application of a second acquisition gradient which reads out the Ω_1 frequencies as site-specific echo signals (Right).

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[1] Or perhaps in the case of anisotrpic media, spins oriented at unequivalent angles with respect to the magnetic field.

$$\phi_e(t) = C\Omega_I(r-r_o) \qquad (3)$$

Here C is a spatio-temporal ratio under the experimentalist's control relating a spin's displacement $r-r_o$ against the extent of its evolution time t_I, and Ω_I is the rotating-frame internal frequency we are attempting to measure. Equation (3) amounts to a "winding" of the spin coherences, a pattern analogous to the one that would arise if a gradient along direction $\hat{r}$ were applied following a hard $\pi/2$ pulse. Analogous but not identical, since unlike what happens when applying a gradient the pitch of the resulting winding will now be site-dependent. In fact it will be governed by the indirect-domain interaction Ω_I conforming the observable that we are attempting to measure.

When inserted at the beginning of a generic 2D NMR experiment such winding will be preserved by the homogeneous mixing process (Fig. 2), and will consequently lead to no observable macroscopic signals when considering the sample as a whole. If, however, the signal detection is now implemented while subjecting the sample to an acquisition field gradient $G_a\hat{r}$ possessing the same geometry as $G_e\hat{r}$, this spiral of magnetizations imparted by the Ω_I will eventually be unwound. The moment at which this Ω_I - dependent unwinding occurs is easily observable, as only at its juncture will spin-packets located at different positions throughout the sample cease interfering and lead to a macroscopic overall signal. This in turn implies that the spatial encoding of the spins interactions and this subsequent gradient-assisted readout provides a way to monitor the indirect domain Ω_I evolution frequencies that affected the spins; not via the Fourier analysis of an evolving coherence as in usual time-domain spectroscopy, but via the displacement observed in the position of a site-specific echo created by interfering spins located at

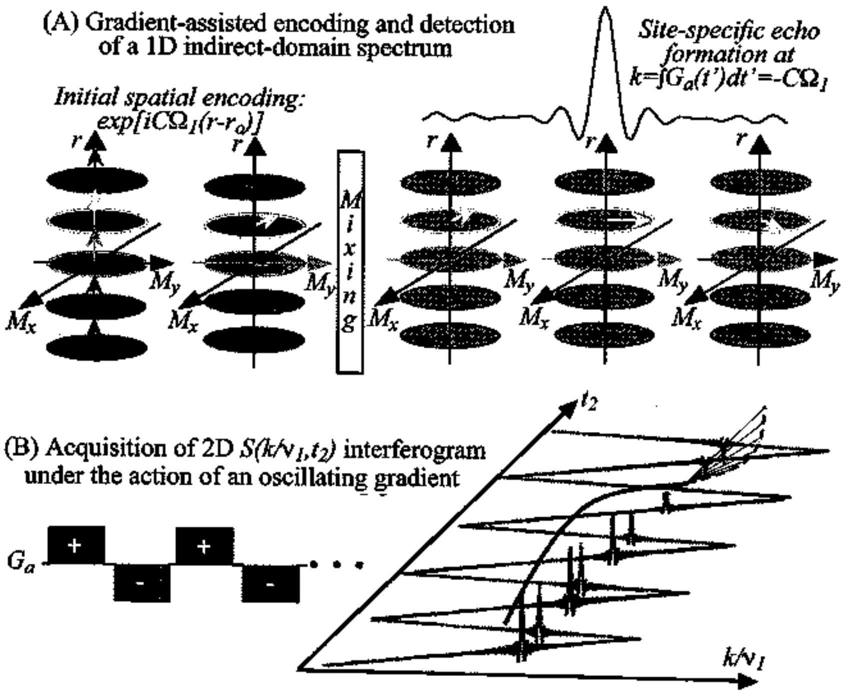

Figure 3: (A) Simplified representation of how the combination of a spatial encoding before the mixing process and a gradient-assisted decoding thereafter (as shown in Fig. 2) allows one to read out the indirect-domain spectral information. (B) Extension of the single gradient-driven refocusing illustrated in (A), to a multiple gradient echo recording capable of yielding a mixed-domain $S(k/\nu_I, t_2)$ interferogram within a single scan.

different positions throughout the sample. A graphical depiction of this unusual feature - whereby the time-domain signal becomes equivalent to its indirect domain frequency spectrum - is illustrated in Fig. 3A, which analyzes the fate of magnetizations throughout a portion of an ultrafast acquisition assuming a simplified "five-slices" sample.

Although this new approach may be capable of reading out an indirect-domain NMR spectrum, it may not be a priori clear of where would its eccentricity pay off in terms of facilitating the acquisition of multidimensional NMR spectra. What brings this about is the realization that unlike what happens with a conventional time-domain encoding, which is a unidirectional process that needs to proceed monotonically and over a relatively long period of time in order to properly characterize the spin evolution frequencies, the gradient-driven readout depicted in Fig. 3A can be concluded very quickly. Moreover, this is a process that can be done and undone numerous times over the course of the data acquisition, simply by reversing back and forth the currents generating the G_a gradient while collecting the data. This in turn enables the repetitive monitoring of the indirect-domain spectrum numerous times as a function of an acquisition time t_2, leading to a mixed frequency/time-domain interferogram from which the 2D NMR spectrum can be retrieved by 1D FT. All of this, from an experiment that can effectively be concluded within a single scan (Fig. 3B).

2D NMR Examples

Having surveyed the principles underlying single-scan 2D NMR, we dwell in this Paragraph onto some of its potential applications. The first question usually arising in this regard concerns whether the strategy just described can find potential uses in biomolecular NMR. The answer to this is "yes"; Fig. 4 for instance compares a conventional 2D HSQC spectrum collected on an ^{15}N-labeled Ubiquitin sample, with an ultrafast counterpart collected within four scans (the extra scans needed in part for the sake of phase cycling away the otherwise intense solvent signal remaining). As can be appreciated both sets convey similar information and at comparable qualities - at least at this level of sample concentration. This in turn opens interesting vistas regarding the possibility of employing real-time 2D NMR as a new tool to follow dynamic biomolecular processes.

A second area where the short acquisition times involved in ultrafast 2D NMR could find interesting applications is that of in vivo spectroscopy; both because of the possibilities that this would open regarding

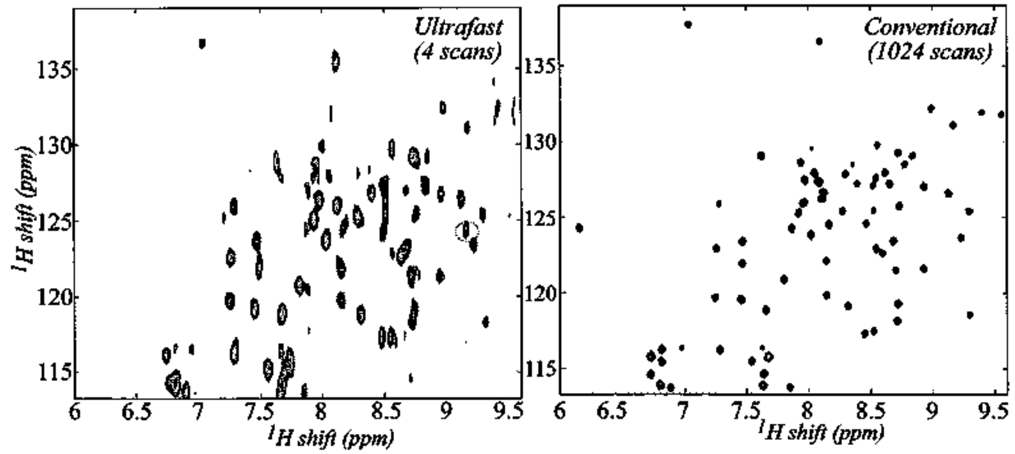

Figure 4: Comparison between ultrafast and conventional 2D HSQC NMR spectra recorded at 18.8 T on a 3.25 mM ^{15}N-enriched Ubiquitin sample dissolved in 93/7 % H_2O/D_2O (courtesy of Boaz Shapira, unpublished).

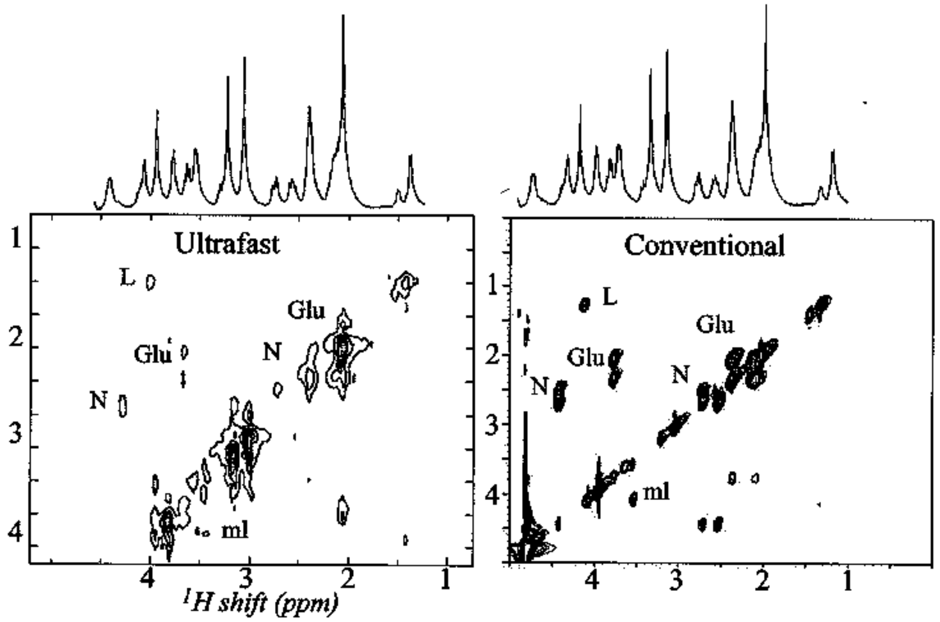

Figure 5: Comparison between ultrafast and conventional 2D TOCSY NMR spectra recorded on a 9.4 T microimaging system on a brain phantom [33]. Shown are principal cross-peaks assigned to Lactate (L), N-acetyl aspartate (N), Glutamate (Glu), myo-Inositol (mI).

the tracking of metabolic processes, as well as due to the opportunities that would arise if experiments where 2D spectroscopy and 3D imaging scans could be combined while acquisition times remain within patient-compatible levels. Fig. 5 illustrates that also in these areas there is a potential for ultrafast 2D NMR, at least judging by the comparisons made on phantom and/or model systems [33].

In addition to speeding up known applications of 2D spectroscopy, ultrafast 2D NMR could help support

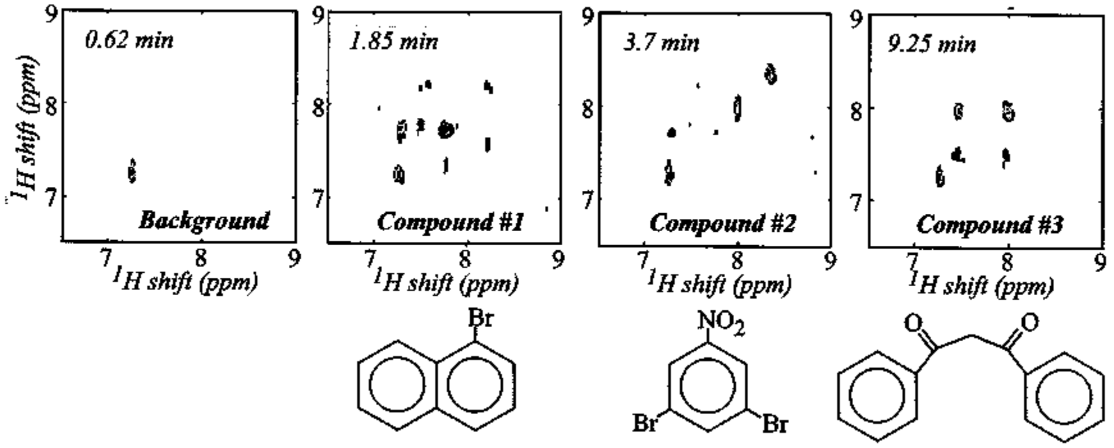

Figure 6: Real-time identification via 2D ultrafast TOCSY ^{1}H NMR of a mixture of three compounds being continuously separated under standard on-flow LC conditions. In the actual experiment 2D NMR spectra were constantly acquired 32 seconds apart over a 15 minute elution period [34]; the Figure concentrates on spectra corresponding to the drawn compounds appearing at the indicated elution times.

certain new technologies that are beyond the realm of the hitherto possible. One such option involves implementing 2D analyses of samples subject to a continuous flow through the NMR sample coil - a flow which could originate from either continuous sample separation requirements as in the case of liquid chromatography, or simply as a result of the desire to impart the highest possible rate of throughput to a chemical/physiological characterization. Under suitable sample sensitivity conditions the ultrafast protocol could make such a continuous flow scenario compatible with real-time 2D NMR acquisitions; Fig. 6 illustrates this with a series of 2D TOCSY NMR spectra collected using a home-built prototype on a chemical mixture, subject to a continuous chromatographic separation of its constituent components [34]. Another instance where new possibilities could be unlocked arises when considering the merger between 2D NMR and nuclear hyperpolarization methods. The latter include a number of specialized spin physics methodologies [35-37] capable of building up nuclear magnetizations that exceed their thermal equilibrium counterparts by several orders of magnitude. While the relatively long pre-polarizing periods and less-than-perfect reproducibility characterizing these methods do not make them suitable starting points for conventional 2D NMR experiments, they could constitute ideal counterparts to the single-scan acquisitions introduced in the preceding Paragraph. Figure 7 shows a preliminary step in that direction, with a single-scan 2D TOCSY spectrum acquired following a brief period of CIDNP polarization enhancement [38]. The sub-mM concentration then required for implementing such study serves to exemplify the promises held by this new kind of NMR applications.

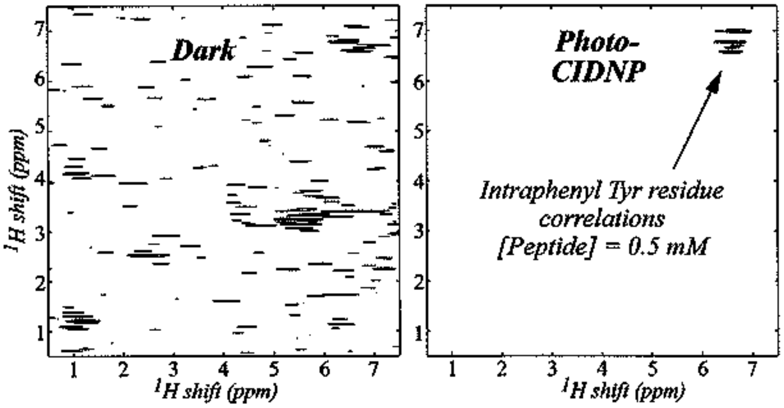

Figure 7: Example of the potential benefits resulting from the combination of pre-polarization and ultrafast 2D NMR methods. Both traces correspond to single-scan 2D TOCSY ^{1}H NMR spectra recorded on a Tyrosine-containing cyclic octapeptide dissolved in D_2O at a 0.5 mM concentration. Shown on the left are the results observed under standard conditions; shown on the right are the results observed after pre-irradiating the sample for 0.5 sec using a 480 nm light sources (2W) capable of inducing a CIDNP enhancement [38].

Spatial Encoding as a New Approach to Ultrafast 2D MRI

The encoding principles described in the preceding Paragraph could also find applications in more MRI-oriented investigations. Here the goals sought usually go beyond a purely chemical or structural characterization, and include finding information about the spatial placing of the spins. There are at least two immediate ways by which ultrafast 2D NMR could help retrieve this information. One of these involves adapting the spatial encoding principle so as to transform it from a 2D spectroscopy protocol into a 2D imaging one. A simple route to achieving this is by spoiling the gradient echoing procedure deliberately inserted along ultrafast's indirect domain, imparting an evolution that instead of being purely spectroscopic encodes a position-related information [39]. Fig. 8 illustrates such a transition from a spectroscopic into an imaging scenario, where as usual in imaging instances we are assuming that the spin evolution is solely dictated by the offsets introduced by gradients (and local interactions are negligible). By doing this modification one consequently ends up with an alternative that although based on different physical principles than EPI, also enables the acquisition of multidimensional MR images within a single scan. An intriguing issue is whether this new protocol offers any competitive advantage over any of the existing ultrafast 2D MRI scanning options; at this point, this remains to be seen.

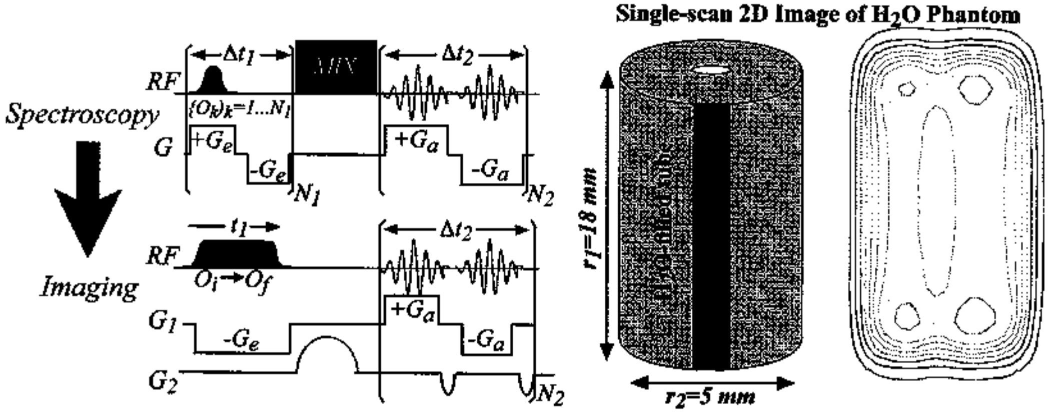

Figure 8: (Left) Translating the spatial encoding idea from a purely spectroscopic setting, to one where single-scan 2D imaging of positions is the goal [39]. In the illustrated imaging sequence only G_1 is assumed to be spatially encoded by the application of a frequency sweep; gradient evolution along the second dimension is conventional. (Right) Application of the sequence shown on the bottom left to a single-scan imaging experiment carried out on a water phantom at 11.7 T.

In addition to the approach just described ultrafast 2D NMR offers an alternative, somewhat less evident route to the retrieval of spatial information. As explained earlier 2D NMR spectra arise from these experiments by taking 2D data sets acquired as a function of k and t2, and subjecting them to FT solely along t_2 - peaks along the indirect domain appearing simply as a result of echo phenomena upon the continued application of G_a. A question that then arises is: what would happen if one were to subject the resulting data to a second FT along the yet unprocessed domain? Since the corresponding peaks stem from an acquisition that took place while under the action of a gradient, one could assume that they will contain some imaging information. And indeed under ideal conditions, the point spread function characterizing each diagonal and/or cross peak along the indirect dimension of ultrafast spectra contains the signature of the spatial distribution originating a particular 2D NMR peak. All that is needed to retrieve such distribution is to extract this complex signal and subject it to a Fourier analysis along the k/v_1 domain: no additional imaging ingredient is necessary, beyond what had already been included in the original ultrafast 2D NMR pulse sequence. This in turn opens a very attractive route to spatial localization, as it means that the same protocol originating the 2D NMR spectrum within a single scan can also be exploited to retrieve the spatial origin of the spins at no additional expense in either acquisition time or sequence complexity.

Fig. 9 presents an example of this procedure [40], which demonstrates the possibility of collecting spatially-resolved information from 2D NMR spectra while remaining in a sub-second timescale. Retrieving such spatially-localized information may be quite valuable, particularly when dealing with in vivo systems where the anatomical distribution associated to a particular NMR peak is of essence.

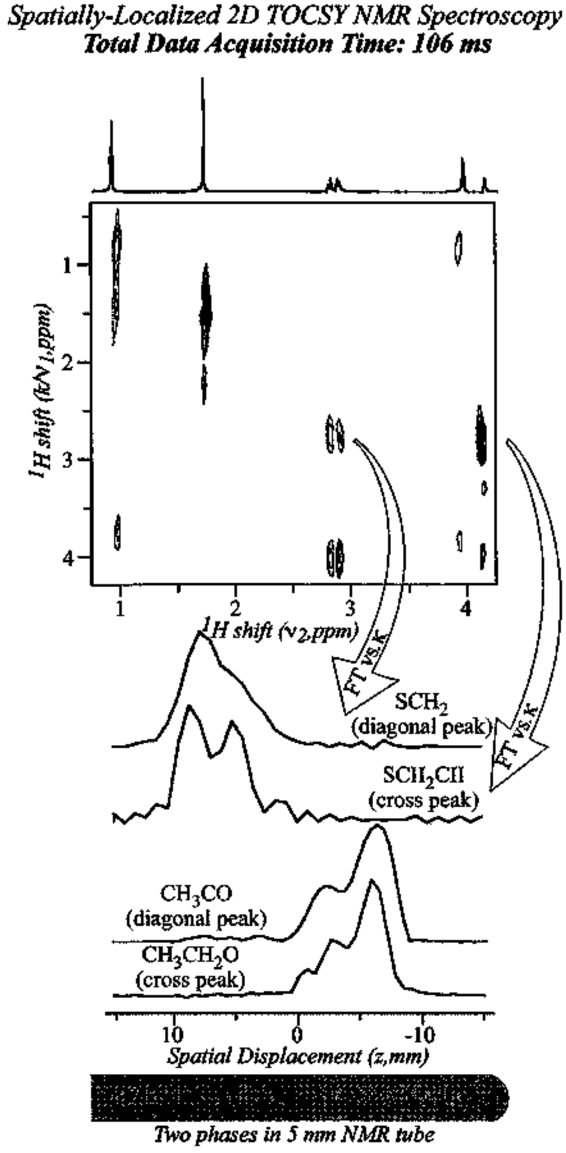

Figure 9: Illustration of how the post-processing of ultrafast 2D NMR spectroscopic data can afford additional information on spatial positions [40]. A single-scan 2D TOCSY ^{1}H NMR spectrum was recorded on the indicated analytes, which were dissolved in separate organic (CCl_4, pink) and aqueous (D_2O, purple). The spatial profiles indicated on the bottom resulted from extracting ca. 20 points in the neighborhood of the indicated 2D NMR peaks, and subjecting the resulting data to FT against their k/ν_1 variable.

3. Perspectives

Few scientists need nowadays be reminded of the importance played by multidimensional magnetic resonance. Whether because of the need to characterize a new material, to elucidate a protein structure, to synthesize a new drug or to evaluate the possibility of disease, scientists involved in a wide variety of endeavors have already had the chance (or perhaps the forced duty) to become acquainted with those peculiar map-like plots first conceived by J. Jeener. The possibilities that could open by speeding up the acquisition of such multidimensional NMR data - speeding up in some instances by several orders of magnitude - are definitely alluring. Yet instead of summarizing the various opportunities that could thus be opened it is perhaps more adequate to conclude the present account with a word of caution. Indeed it should be kept in mind that in spite of all the exciting potential that ultrafast nD NMR acquisition schemes may bring, they will not perform "magic". Accelerated acquisition schemes may be capable of affording nD NMR spectra within a single scan, but will only do so if sufficient S/N is available to monitor the desired features within that single scan. This in turn highlights the importance of sensitivity as another major goal to focus upon - even if all these efforts are invested and then used up within a fraction of a second [41].

Acknowledgments

My thanks go to all the talented coworkers I had the luck to collaborate with over the course of

this project, and in particular to past and present members of my group: A. Lupulescu, B. Shapira, Y. Shrot, N. Sela, E. Morris, M. Mishkovsky, A. Tal, M Gal and F. Kramer. Financial support from the Ilse Katz Magnetic Resonance Center (Weizmann Institute), the Israel Science Foundation (grant 296/01), the Minerva Foundation (Munich), and the U. S. National Institute of Health (GM72565), is also gratefully acknowledged.

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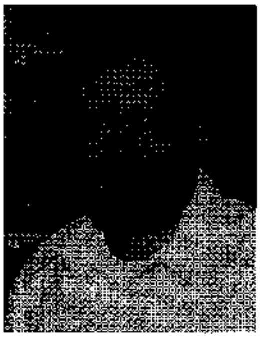


Prof. Lucio Frydman was born in Argentina in 1965, and received both B.Sc. (1986) and Ph.D. degrees (1990) from the University of Buenos Aires. After undertaking postdoctoral studies at the Lawrence Berkeley Laboratory with Prof. A Pines he joined the Faculty of the University of Illinois in Chicago, serving in its Department of Chemistry as an Assistant (1992-1996), Associate (1996-1999) and later as Full Professor (1999-2001). Since 2001 he has been serving as a Professor in the Weizmann Institute's Department of Chemical Physics. Over the years Prof. Frydman has been the recipient of numerous recognitions including the Dreyfus New Faculty and Dreyfus Scholar Awards; the Sloan, Beckman and U. S. National Science Foundation Career Fellowships; the Laukien Award for achievements in NMR and the ICS Prize for Young Chemists 2004. Prof. Frydman has also served as Chairman and co-organizer of numerous scientific conferences, and is currently Associate Editor of the Journal of Magnetic Resonance.

דיווחים מן הנעשה בארץ

One-day Symposium in Honor of The 2005 Chemistry Wolf Prize Laureate

Prof. Richard N. Zare

May 24, 2005
Department of Chemistry, Technion, Haifa

Y. Apeloig, S. Speiser, E. Keinan Opening and congratulations
R.D. Levine, I. Schechter About Prof. Zare's scientific achievements
I. Willner Harnessing nanotechnology for biological systems
E. Grushka The use of dynamically coated stationary phases in HPLC.
A. Lewis Second harmonic generation: A sensitive method for optically measuring membrane potential in complex living systems
F. Stoddart Nano meccano in action
I. Oref Collisional energy transfer between polyatomic molecules
M. Shapiro Quantum control - new perspectives
S. Cheskis Laser absorption spectroscopy for combustion diagnostics
R. Naaman Angular momentum and surprising electronic properties of organized organic monolayers
R. N. Zare Adventures in chemical analysis

Organizing committee: **E. Kolodney, R.D. Levine, I. Schechter**

Acknowledgment: This symposium has been generously supported by the Israel Chemical Society

Special Kolthoff Prize Colloquium

Professor Reshef Tenne

2005 Kolthoff Prize Recipient

Weizmann Institute of Science, Rehovot
March 28 and 31, 2005, Department of Chemistry, Technion, Haifa

"Inorganic Fullerene-like Nanotubes: Synthetic Aspects".
"Inorganic Nanotubes and Fullerene-like Materials: State of the art".

Symposium Honoring

Christoph Dellago, Christopher Jarzynski and David R. Reichman,
recipients of the **Sackler Prize** in the Physical Sciences and
Richard N. Zare, recipient of the **Wolf Prize in Chemistry**

Was held on May 23, 2005, in Tel-Aviv University

The Lectures were given by:
Harvey Scher, Weizmann Institute, Anomalous transport and scales of disorder: submicron to kilometers
Anne Bernheim, Technion, Transitions from lamellipodia to filopodia in membrane free systems
Noam Agmon, Hebrew University, Proton pathways in green fluorescence protein
Richard N. Zare, Stanford University, All that glitters
Christoph Dellago, University of Vienna, Exploring complex dynamics with computer simulations
Christopher Jarzynski, Los Alamos National Laboratory, Nonequlibrium thermodynamics at the nanoscale
David R. Reichman, Columbia University, Glassy state of matter: recent answers and questions
Eran Rabani, Tel-Aviv University, Structural quantum glasses
Robert J. Silbey, MIT, Single molecule spectroscopy: from small molecules to light harvesting complexes

The Dan David Prize In the Material Sciences

Was awarded in a ceremony held at the Tel-Aviv University, on May 23, 2005, to

Professors Robert Langer, George Whitesides and C.N.R. Rao.

Their outstanding achievements were described in the following citations:

Prof. Robert Langer
Robert Langer is the Kenneth L. Germeshausen Professor of Chemical and Biomedical Engineering at the Massachusetts Institute of Technology, USA.

Prof. Langer has pioneered the field of biomaterials and tissue engineering. He has contributed to the development of biocompatible polymers for drug delivery and synthetic polymers to form specific tissue structures creating the field of tissue engineering. His work has allowed the controlled release of macromolecules using biocompatible polymers.

Prof. Langer is also responsible for the creation of numerous novel biomaterials, such as shape memory polymers and materials with switchable surfaces, aerosols and microchips. His work has led to the development of synthetic polymers to deliver cells to form specific tissue structures.

Prof. George Whitesides
George Whitesides is Woodford L. and Ann A. Flowers Professor at the Department of Chemistry and Chemical Biology, Harvard University, USA.

Prof. Whitesides has been a prolific contributor to the field of materials science. He was the first to explore the intersection of molecular-scale synthesis and surface science, which led to his work on self-assembly monolayers (SAMs). The development of SAMs has led to the transformation of surface science into a much broader discipline of microfabrication and biological interactions.

Particularly significant was Prof. Whitesides pioneering development of soft lithography, which is now widely used for patterning non-traditional substrates. This work has also led to the development of the field of microfluidics and the fabrication of microanalytical systems.

Prof. Whitesides' work has also opened up new domains of research in nanoscience and technology. He is one of the world's most widely cited authors in materials science. Whitesides has bridged the fields of chemistry, chemical engineering and biology to new heights through the development of novel functional materials and systems.

Prof. C.N.R. Rao
C.N.R. Rao is the Linus Pauling Research Professor at the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India.

Prof. Rao is one of the world's foremost solid state and materials chemists. He has made prolific and sustained contributions to the development of the field over five decades. His work on transition metal oxides has led to basic understanding of novel phenomena and the relationship between materials properties and the structural chemistry of these materials.

Prof. Rao was one of the earliest to synthesize two-dimensional oxide materials such as La2CuO4. His work has led to a systematic study of compositionally controlled metal-insulator transitions. Such studies have had a profound impact in application fields such as colossal magneto resistance and high temperature superconductivity. Oxide semiconductors have unusual promise.

PINCUS, DJERASSI AND ORAL CONTRACEPTIVES

Bob Weintraub, Director of the Libraries, Sami Shamoon College of Engineering, Beersheva and Ashdod

"More than 100 years ago, W. E. H. Lecky, in his book, made the following observation: 'The causes which most disturbed or accelerated the normal progress of society in antiquity were the appearance of great men; in modern times they have been appearance of great inventions. 'The discovery of the Pill was a great invention. And I hope that I have made it clear that it was the result of a major effort by hundreds of men and women driven by a variety of motives, among which, however, the urge of scientific inquiry was always predominant, and so was indeed the role played by Gregory Pincus. As he puts it with modesty with a minimum of rhetoric: 'The era of oral contraception by ovulation inhibitors appears to have been ushered into existence by the clinical application of our animal studies with progesterone and the gestagenic 19-norsteroids.'" (E. Diczfalusy: J. Steroid Biochemistry, 1979)

When Carl Djerassi was asked as to what he considered to be his most important contribution to science, he answered in part as follows: "From a societal point of view, the first synthesis of an oral contraceptive is without doubt the most important. This was almost 45 years ago, October 15, 1951. It's a very specific date recorded in our lab notebook when we synthesized the steroid that was the active ingredient of oral contraceptives eventually taken by hundreds of millions of people. There are very few synthetic drugs that have been around for forty-some years. I don't really know if there has been any more important discovery from a societal standpoint during the postwar period." (in Candid Science, I. Hargittai). Carl Djerassi was the first recipient in 1978 of the Wolf Prize in Chemistry for his work in bioorganic chemistry, application of new spectroscopic techniques, and his support of international cooperation. He has been at Stanford University since 1959. I am grateful to Prof. Djerassi for clarifying for me several points.

In 1919 Ludwig Haberlandt, professor of physiology at the University of Innsbruck, implanted the ovaries of a pregnant rabbit under the skin of a non-pregnant one, making it infertile for several months despite frequent coitus. Haberlandt appreciated the significance of his experiment - that a hormone secreted by the corpus luteum inhibited ovulation - and he suggested that a substance with similar biological properties could be the basis for a human oral contraceptive. According to Djerassi, "if there ever was a grandfather of the Pill, Ludwig Haberlandt above all others deserves that honor.

Carl Djerassi:

Carl Djerassi was born in 1923 in Vienna to Jewish parents, his father Bulgarian and his mother Viennese. The routine of his family life ended abruptly in 1938 with the Anschluss: "Our second-floor apartment had a long balcony overlooking the Donau Kanal, a branch of the Danube separating the fashionable first *Bezirk* from the largely Jewish second one. The day after the Anschluss, I crouched behind the balcony's balustrade to watch the Brown Shirts with the swastika armbands pour across the bridge. In retrospect, it seems strange that I had no foreboding of Hitler's takeover of Austria..." In 1939 at age 16 Djerassi fled Europe via Bulgaria for the United States, where he was aided by the Hebrew Immigrant Aid Society, known as HIAS. During the Nazi period protests from the Bulgarian people saved the Bulgarian Jews from deportation to death camps.

In 1945 Djerassi earned his Ph.D. in Chemistry from the University of Wisconsin with a thesis on the transformation of testosterone into estradiol and related syntheses. In 1949, after working at the Swiss company Ciba in New Jersey, he accepted a position to head a research team at Syntex in Mexico City. Djerassi was to attempt a practical synthesis of cortisone.

Syntex was using Mexican Yams as the source of diosgenin as the starting material to synthesize the hormones testosterone and progesterone, needed for therapeutic uses. During the war cortisone was important to the military as it was thought to reduce stress levels in fighter pilots and after the war cortisone was found to have anti-arthritic properties. There was an immense international effort to find a cheaper synthesis, the number of researchers working on cortisone being greater than that of any other medical project since the development of penicillin. In 1951 Djerassi's group achieved the first chemical synthesis of cortisone from a plant source, diosgenin, but about the same time the Upjohn Company of Kalamazoo patented an easier to achieve synthesis of cortisone starting from progesterone by a fermentation process. The impact of the massive research effort on cortisone and consequently on that of steroids in general laid the foundation for advances in contraceptive steroid work that was soon to follow.

Djerassi and his colleagues worked on novel steroid compounds. "Initially, we were not focusing on contraception when we developed an oral progestational compound. Our research was undertaken because at that time progesterone was used clinically for treatment of menstrual disorders, for certain conditions of infertility, and at a research level, for the treatment of cervical cancer in women by local administration of a high dose of the hormone. Such administration was extremely painful because it involved injecting a fairly concentrated oil solution of large amounts of progesterone into the cervix. What drove us was the desire to create a more powerful progestational compound that would be active orally. "

In 1951 Syntex filed a patent based on the work of Djerassi's group for the compound 19-nor-17α-ethynyltestosterone, known as *norethisterone* or *norethindrone*. *Nor* indicates a missing CH_3 group. In 1953 a patent was filed by G. D. Searle Laboratories of Skokie, Illinois, for the synthesis and uses of *norethynodrel*, prepared by Dr. Frank B. Colton. These two compounds were several times as potent as the natural hormone progesterone and could be administered orally. Both compounds were chemically similar and both Djerassi and Colton did not see their potential for contraceptive purposes. Djerassi's compound was stable in the stomach, while Colton's compound is largely converted into Djerassi's by the action of stomach acids.

Gregory Pincus (1903-1967):

Gregory Goodwin Pincus was born in Woodbine, New Jersey, to Russian Jewish immigrants. Woodbine was organized in 1891 and was one of the agricultural settlements founded in the United States by Baron de Hirsch as a haven for Jews from Eastern Europe. Pincus' father was at one time the editor of the *The Jewish Farmer*. Pincus earned his doctorate in biology at Harvard in 1927 and joined the faculty in 1930.

J. Segal (Pincus' friend and colleague): "When he took up Margaret Sanger's challenge in 1950 to develop an oral contraceptive, he had already achieved in vitro fertilization of rabbit eggs, foreshadowing later successes in assisted human reproduction that have enabled tens of thousands of couples to overcome infertility. The controversy generated by this pioneering work probably cost him tenure at Harvard, prompting his move to Clark University in Worcester, Mass. Screaming headlines about "test-tube babies" and "fatherless rabbits" had elicited anti-science and anti-Semitic attacks. This notoriety may have made Harvard too uncomfortable to keep Pincus on the faculty, but it did not prevent the University from citing his work as one of Harvard's outstanding scientific achievements in its 300-year history. At Clark, Pincus teamed up with Hudson Hoagland, another scientific pioneer-explorer, to create the Worcester Foundation for Experimental Biology in 1944. Pincus attracted Cambridge-trained physiologist M.C. Chang to the foundation." (Popul Today, 2000)

Pincus: "In 1937, Makepeace, Weinstein, and Friedman noted the effectiveness of progesterone as an ovulation inhibitor in the rabbit, but the logical extension of this observation into a more intensive study of the nature of the progesterone derivatives and the putative metabolites were not reported by us until 1953. Why this "logical extension" occurred after a latent period of approximately 16 years is a question concerning which we have raised some speculation. ....In our case, the special demands of "war" research accounted for a shift of interest to studies of adrenocortical function, particularly in relation to physical and mental stress, and this interest has continued to a greater or lesser degree. Indeed, World War II probably accounts for the lapse observed generally. In our case, the increase of activity as indicated by publications from 1950 on has been due to two overtly ascertainable factors: (a) a visit from Mrs. Margaret Sanger in 1951 and (b) the emergence of the appreciation of the importance of the 'population explosion'.

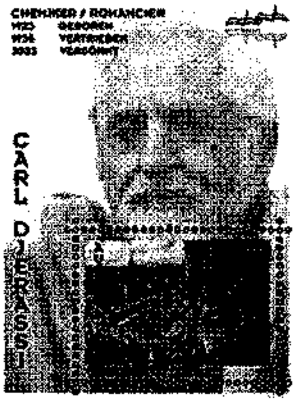
At the time of her visit, Mrs Sanger's interest in the world-wide dissemination of information on birth control was at a high tide. Her experience as President of the International Planned Parenthood Federation had made her aware of the deficiencies of conventional contraceptive methods, particularly in underdeveloped areas of the world. Her hope, expressed to us, was that a relatively simple and fool-proof method might be developed through laboratory research. Drs. Chang and Pirie and I had already had some experience with hyaluronidase inhibitors in the rabbit, but we had found that such potent inhibitors could act only on direct contact with sperm and that there was no possibility of an effect by parenteral administration. Although some preliminary experiments by the late Dr. Abraham Stone had indicated that at least one of these inhibitors might be quite active as the component of an intravaginal preparation in the human, the limitations to its use still appeared to be rather formidable. Accordingly, Dr. Chang and I drew up a modest project proposal that received support under a grant from the Planned Parenthood Federation of America. Work under this grant resulted in a paper on the rabbits mentioned above and in the finding that the compounds that we found to be potent as ovulation inhibitors in the rabbit were also quite active as antifertility agents in the rat. "The rabbit ovulates within ten hours of mating. The rat ovulates periodically making the monitoring of experiments more difficult but give the findings added relevance to the reaction in the human female".

Pincus: "... the definition of progestational activities is essential to the understanding of their roles in the regulation of reproductive processes. A true progestin may be defined as a compound which acts upon the uterus to induce endometrial proliferation and myometrial activity characteristic of pregnancy and which maintains pregnancy in ovariectomized animals carrying fertilized ova or fetuses; both of these functions may be enhanced by the committan use of small amounts of estrogen, but the progestin alone should be sufficient at adequate dose."

Gregory Pincus teamed up with Dr. John Rock, Professor of Gynecology at Harvard, to collaborate on human testing and clinical trials. Rock was interested in progestins as a cure for certain types of infertility and Pincus was interested in progestins as a means to prevent pregnancy. Pincus' group screened over 200 synthetic compounds for oral progestin activity. At about this time two synthetic steroids became available for testing, each of which was claimed to be orally effective for menstrual cycle regulation. One was norethindrone from Syntex prepared by Carl Djerasi and the other norethynodrel from G.D. Searle, prepared by Dr. Frank Colton. Pincus recognized their value for use as oral contraceptives. In 1955 Pincus reported their preliminary results on the possibility of using progestational compounds for human oral contraception.

Following clinical trials, in 1957, the U.S. Food and Drug Administration (FDA) approved the use of Syntex's *norethindrone* and of Searle's *norethynodrel* for oral treatment of menstrual disorders and for certain conditions of infertility. In 1960, the FDA approved the use for oral contraception, Searle's norethynodrel (under the trade name *Enovid*) and two years later, Syntex's norethinodrone (under the trade name *Ortho-Novum*).

Pincus (1965): Birth control and the allied areas of sexual physiology and sexual behavior have long been battlegrounds of opinion-voicers. They have suffered from clashes among differing culture patterns, theologies, moralities, even politics. These struggles still continue, but they are being more and more delimited by the findings of science. Objective appraisal is surely but slowly replacing heated partisanship...The mystery and wonder of conception becomes describable in terms of gamates and their movements, in terms of fertilization reactions and the operation of replication mechanisms, in terms of oviduct chemistry and hormonal regulation. In each of these is also mystery and wonder, for there is still more to discover than we now know. But in the blazing or flickering light of what we do know a priori judgements and willful prejudices fade. And our considered and tested knowledge offers a firm basis for what we can and should do.



Stamp issued by the Austrian Post Office, in honor of Carl Djerassi on his 80th birthday. For more information on the stamp see:
Autobiography of a Stamp by Carl Djerassi, Philatelia Chimica et Physica 27, 68, 2005. http://www.cpossu.org/Djerassistamp.pdf

לזכרם

פרופ' שלמה אפרימה 2005 - 1948

הדרת כבוד, הערצה, רגשי תודה ובקשת סליחה הינם ארבעת המרכיבים של הספד זה לשלמה: עמית, מורה, מרצה, חוקר ו"מנטש", שעזב אותנו טרם עת (בן 57 במותו) בעקבות מחלה כה קשה, עמה נלחם בדרך האופיינית לו: מלחמה שאותה ניצח כל יום, כל שעה וכל דקה. שלמה אמר לי בשיחתי עמו בחג החנוכה האחרון, ואני מצטט: "החסרתי רק 1/2 יום מהעבודה עד כה, והיה זה כשאשתי לא הרגישה טוב". הוא המשיך לתפקד ללא הפסקה תוך כדי ובמשך הטיפולים שעבר מבלי שנתן לאף אחד מעקרונותיו להתעקם, ולו במעט.

שלמה נולד בארצות־הברית והגיע ארצה כילד בן שש. את לימודי הכימיה שלו סיים בהצטיינות באוניברסיטת תל־אביב. לאחר השתלמות בארצות הברית עם Prof. Metiu Horia מאוניברסיטת קליפורניה בסנטה ברברה בנושאי כימיה תאורטית, חזר ארצה והצטרף לסגל המחלקה לכימיה באוניברסיטת בן-גוריון בשנת 1979.

הדרת הכבוד שכולנו חשנו כלפיו נבעה מכך שהתמודדותו עם המחלה אך חידדה את תכונות אישיותו המיוחדות של כבוד עצמי, אי הטרדת הסביבה, הימנעות מקבלת עזרה, התמדה בלתי מתפשרת בעשייה המדעית היום יומית על כל הכרוך בכך:

- הדרכת סטודנטים לתארים גבוהים.
- פרסום מאמרים בכתבי־עת מדעיים החשובים ביותר.
- השתתפות בכנסים בין לאומיים.
- יזום, ארגון, קיום וטפול במסלול הננוטכנולוגיה שהביא לנו את טובי הסטודנטים, ומאידך הכוונתם להמשך לימודים לא אצלו, מתוך אחריות אישית מקצועית.
- בניית מערכת מדידה ייחודית לו, מערכת הראמאן על כל מורכבותה.
- הדרך שבה בחר "מה כן להמשיך לעשות וממה להתנתק" בשל הזמן הקצר שעמד לרשותו.
- הערצה על היכולת הוירטואוזית הארגונית שלו, אשר בשיקול ובשלווה כה אופייניים לו, עבר מכימיה תיאורטית לכימיה ניסיונית, הקים יש מאין מערכות שלמות ייחודיות לו ללימודי כימית השטח. הפעיל את המערכת המינימלית שקיימת באוניברסיטה דרך שרותי בית המלאכה, אלקטרוניקה, אופטיקה וכו' על מנת להקים מערכות ניסיוניות מתפקדות.
- הערצה על הדרך שבה חיבר, פשטות בהסבר עם מורכבות ומסובכות של בעיה.

וכל אלה עשה בדרך היחודית לו, בה תמיד תמיד, דרש מעצמו הרבה יותר משמסביבותו !

פרופ' אפרימה הינו מושא להערצה על עבודתו המדעית הרצופה והתרומה הגדולה שלו בשטח ה־ Surface Enhanced Raman אשר כבר בתחילת דרכו המדעית הציע מנגנון ופיתח מודל תיאורטי שמסביר את התופעה - מודל שעד היום הינו אחד מהמקובלים ע"י אנשי המדע. בהמשך דרכו בדק ניסיונית מודל זה במעבדתו. בשנים האחרונות התמקד בתחום הננוטכנולוגיה של מוליכים למחצה.

אנו כולנו מרגישים חובה להביע את תודתנו על תרומתו האדירה למחלקה, לפקולטה, לאוניברסיטה, למדע הישראלי והעולמי.

תודה על הקשר ההדוק עם הסטודנטים.

תודה על ההקדשה, משך שנים, לחשיפת הכימיה לתלמידי תיכון, ארגון הכימיאדה.

תודה בשם כל אותם תלמידים וחוקרים, לכשנתקלו בבעיה מדעית וחיפשו מענה נכון, מדויק, פשוט ומובן, באו לשלמה, ומצאו בו את האדם המתאים לכך.

שלמה השאיר אחריו אשה, חנה, ארבעה ילדים ושני נכדים.

יהיה זכרו ברוך.

פרופ' אברהם פרולה, אוניברסיטת בן־גוריון בנגב

Prof. Bilha Segev 1963 - 2005

Professor Bilha Segev was born and grew up in Haifa. She received her B.Sc. in 1988, Suma cum Laude, her M.Sc. in 1992, and her Ph.D. in 1996 from the Technion. She won a Rothchild Fellowship and a Fulbright Fellowship, and from 1996 to 1998 she was a Research Associate at the Institute for Theoretical Atomic and Molecular Physics (ITAMP) at Harvard University; she also won a prestigious ITAMP Fellowship. At ITAMP she worked on varied topics such as electron-positron pair production in heavy ion collisions, evanescent-wave atomic mirrors, energy transfer processes between Born-Oppenheimer surfaces in molecules, and superluminal light propagation and quantum noise. She joined the faculty of Ben-Gurion University in 1998, after receiving the prestigious Alon Fellowship for outstanding young faculty. In 2002, she received the Toronto Prize for excellence in research. Her main research interests were in theoretical and mathematical physics and chemistry. In particular she worked on the following topics: quantum and QED effects in atomic and molecular optics, time dependence in quantum scattering processes, formulation of the principle of causality in the quantum regime, tunneling phenomena, phase-space dynamics in the Wigner representation, applications of the above to quantum gates of cold atoms in optical lattices, non-perturbative effects in quantum electrodynamics, and radiationless transitions in polyatomic molecules.

Bilha was a gifted teacher and lecturer, and was awarded several Ben-Gurion University awards for teaching excellence. Her ability to anticipate potential sources of confusion, and explain these away to her students and colleagues, was phenomenal. Her lectures at scientific meetings were universally lauded. Her students venerated her.

Prof. Bilha Segev was "noach labriot" and was universally loved by her students and colleagues. Her smile was contagious, and her wisdom, inspirational. We lost a very dear colleague; a colleague who shared her enthusiasm for science and for life with us. She will be sorely missed.

Prof. Yehuda Band, Ben-Gurion University.

פרופ' שמעונה גרש 1948-2004

פרופ' שמעונה גרש, ראש המחלקה להנדסת ביוטכנולוגיה והיחידה להנדסה סביבתית באוניברסיטת בן־גוריון בנגב, הלכה לעולמה לאחר מחלה קשה.

שמעונה עמדה בגבורה בתלאות המחלה והטפולים הממושכים, חודשים ארוכים, אך לא נכנעה לקשיים ולמצוקות, והתמידה להגיע לעבודה, למלא חובותיה כחוקרת, כמורה וכחברה בוועדות ופעילויות שונות. לא התלוננה, לא בקשה הקלות ולא היתה מוכנה לוותר על תפקידים ומחויבויות, למרות הקושי הרב והסבל בשנות המחלה.

שמעונה גרש סיימה את למודי התואר הראשון בכימיה בטכניון בשנת 1970, ואת למודיה לתאר שני בכימיה באוניברסיטת בן־גוריון, בהנחית פרופ' ארנון שני, בנושא מתחום הפוטוכימיה האורגנית ב־ 1973. את למודי התואר השלישי, בהנחית פרופ' רוברט גלזר, סיימה במחלקה לכימיה, בשנת 1978 ואז יצאה לארה"ב, שם עשתה את מחקר הבתר־דוקטורט בקבוצתו של George Whitesides.

בשנת 1981 חזרה לאוניברסיטת בן־גוריון והצטרפה לקבוצת המחקר של פרופ' ארנון שני וד"ר יעקב קלוג מהמכון לכימיה וטכנולוגיה, במכונים למחקר שמושי. בתחילת דרכה עסקה בסינתיזה של פרומונים ולאחר מכן, כחוקרת עצמאית, התמקדה בתחום האנזימולוגיה השמושית.

לפני כשנה מונתה לעמוד בראש מרכז הידע לסוכרים ופוליסוכרים, והיתה חברה בוועדת ההגוי של המכון הלאומי לביוטכנולוגיה בנגב, וזאת בשל התמחותה והידע הרב שצברה בתחום זה. במשך מספר רב של שנים חקרה את תכונות הרב־סוכרים הייחודיים של אצות. תחומי מחקר נוספים אשר עסקה בהם כללו קטליזה הומוגנית והטרוגנית, ובשנים האחרונות התמסרה לחקר ופתוח ממסים יוניים לסינתזות אורגניות, תחום חדש ומבטיח, הן במעבדה ובעיקר בתעשיה הכימית.

לצד מחקריה האקדמיים, אשר בכולם הצטיינה והגיעה לחזית המחקר, התמסרה שמעונה להוראה והקדישה הרבה מזמנה לקידומם של תלמידיה אשר אהבו והעריכו אותה מאד.

שמעונה הלכה מאתנו בטרם עת. במלוא מובן המלה. מבחינה מקצועית - כמדענית וכחוקרת, במעלה הדרך, אל הפסגה, וכמורה מצטיינת האהובה על כל תלמידיה. ומבחינה חברתית - אשת חברה, אבדה לכל ידידיה, חבריה, מוקיריה ומכריה- לכולם חסר היום משהו בעולמם.

מתוך כל התכונות המיוחדות והייחודיות של שמעונה רוצה אני לציין תכונה אחת בולטת ומרשימה: ההסתגלות המהירה של שמעונה, היכולת להתאים עצמה למצבים חדשים. הדבר בא לידי ביטוי הן בהוראה והן במחקר. אם היה נדרש, באפן מידי, ללמד קורס מסוים, הפנייה לשמעונה היתה כמעט מובנת מאליה - שמעונה היתה נקראת לדגל, ותוך זמן קצר העמידה קורס מרשים. ובמחקר, כבר ניתן היה להבחין בזאת בעבודה המחקר לתאר שני, כאשר נדרשו שיטות בדיקה השונות מהמקובל בכימיה אורגנית. שמחה על האפשרות ללמוד משהו חדש, ותוך זמן קצר למדה, הבינה והשתלטה על השיטה והעבודה. או כאשר במכונים למחקר שמושי היה מתקבל פרויקט מחקר, שלא התאים לאף אחד מחוקרי המכון לכימיה, שמעונה היתה מקבלת על עצמה את המשימה ותוך מספר שבועות היתה חוזרת עם תכנית עבודה ומחקר, שולטת בחומר, מבינה ויודעת לשאול את השאלות הנכונות.

שמעונה נלחמה במחלה הקשה, התנהגה באצילות האופינית לה והותירה חותם עמוק שאינו ניתן למחיקה. היא הניחה אחריה בעל, בן, נכדה, כלה ואחות.

שמעונה גרש היתה מיוחדת והיא חסרה לכולנו.

ינון זכרה בלבנו

מתוך דברים שנאמרו לזכרה ע"י פרופ' ארנון שני, המחלקה לכימיה, אוניברסיטת בן-גוריון בנגב.

Single-Scan 2D NMR

Lucio Frydman
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Multidimensional spectroscopy plays a number of essential roles in contemporary magnetic resonance. It brings a resolution enhancement without which numerous NMR applications in organic and inorganic chemistry would be unattainable, it serves as a basic tool in the assignment and structural elucidation of complex biological structures, and it is an integral part of the image formation protocol in MRI. The present review describes a recent scheme which we have developed, enabling the acquisition of complete 2D NMR data sets within a single continuous acquisition. Provided that an analyte's signal is sufficiently strong, the acquisition time of multidimensional NMR experiments can thus be shortened by several orders of magnitude. The new methodology is compatible with existing multidimensional pulse sequences (COSY, TOCSY, HSQC, MRI) and can be implemented using conventional hardware. The spatial encoding of the NMR interactions - which is the new principle underlying this ultrafast NMR protocol - is discussed, and the protocol's performance is exemplified with a variety of homonuclear and heteronuclear 2D NMR and MRI acquisitions.

ABSTRACTS

Excursions in cluster science; from dynamics of large finite systems to ultracold clouds

Joshua Jortner and Isidore Last
School of Chemistry, Tel Aviv University, Tel Aviv, Israel

We report on the exploration of new scientific territories of energetics, response, dynamics and function of large, finite atomic and molecular systems. Studies of ultrafast (attosecond 10^{-18}s to femtosecond 10^{-15}s) electron and nuclear dynamics of clusters in ultraintense laser fields (peak intensity 10^{15}–10^{20}Wcm^{-2}) led to the advent of table-top nuclear fusion driven by cluster Coulomb explosion. The eighty years' quest for nuclear fusion driven by chemical reactions was achieved by "hot–cold" fusion in the chemical physics laboratory. Moving from femtosecond nuclear dynamics in the energy domain of nuclear physics (1keV–1MeV) towards ultralow energies and ultraslow millisecond dynamics in ultracold ($T = 100\mu K$–1nK) finite systems, we address the bridging between nuclear dynamics of clusters and of finite, ultracold atomic clouds.

Some topics in quantum chemistry

Ruben Pauncz, Dept. of chemistry, Technion, Haifa, Israel

The article deals with three topics: (a) the alternant molecular orbital method, (b) the construction of spin eigenfunctions, and (c) the use of the symmetric and the unitary group in quantum chemistry. In the final part it presents my experience in the teaching of quantum chemistry

The Fascinating World of Low-Coordination Silicon Compounds. Theory and Experiment in Synergy

Miriam Karni and Yitzhak Apeloig, Dept. of Chemistry, Technion, Haifa, Israel

Silicon is the closest element to carbon in the Periodic Table, but, the structural rules, chemical behavior and physical properties of their compounds are very different. In this paper we will discuss mainly the structural properties of doubly- and triply-bonded silicon compounds, in particular, disilenes ($R_2Si{=}SiR_2$), trisilaallenes ($R_2Si{=}Si{=}SiR_2$), disilynes ($RSi{\equiv}SiR$) and silynes ($RSi{\equiv}CR$). Because until recently many of these compounds did not exist, theory played a major role in predicting and understanding their structures and in directing experiments in this field. These fruitful interplay and synergism between theory and experiment is demonstrated in this article.

Unlike ethylene which is planar, the silicon atoms in the analogous disilene are pyramidal. In contrast to allene and acetylene which are linear, trisilaallene has a strongly bent skeleton, and disilynes and silynes, the silicon analogs of acetylene are trans-bent. The unique structural behavior of multiply-bonded silicon compounds (and of the higher congeners of group 14) can be attributed to a large extent to the mismatch between the radii of the 3p and 3s orbitals of Si, reducing the degree of hybridization and dictating different structural rules for its compounds compared with analogous carbon compounds.

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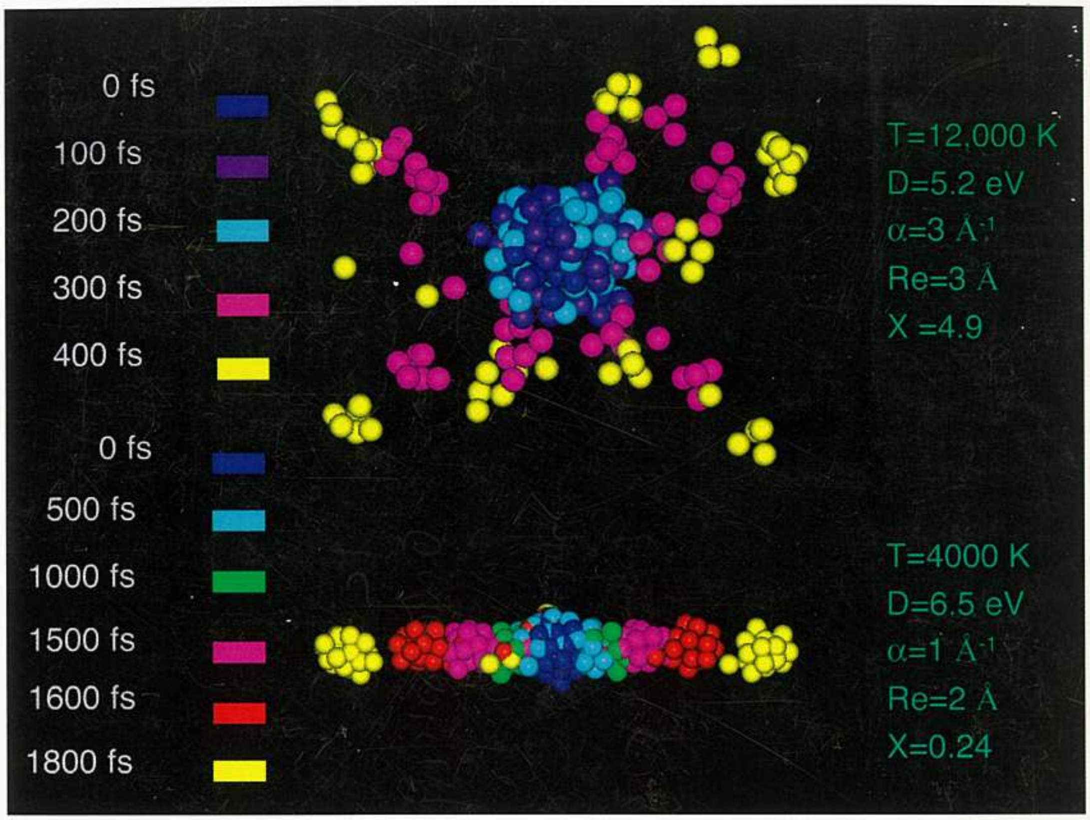

Time resolved nuclear dynamics of the fragmentation of highly charged $(A^{+})_{55}$ Morse clusters (see article by Jortner and Last)

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