

Computer Analysis Tools for PDMS Spectra

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Computer analysis tools have been developed for evaluating PDMS-spectra consisting typically of 65,000 time bins. These include algorithms for efficient data reduction, algebra tools, a program for simulation of the fragmentation process in PDMS, and an algorithm which eventually will lead to prediction of cluster formation in PDMS.

PEAKS is a program [1] which extracts relevant mass line informations such as amplitude, area, width, asymmetry of relevant peaks in channel spectra by a new method, the *far moments*, in a very efficient way. The spectrum is just scanned once (with no fit of e.g. Gaussians) to extract the experimental lines. The new algorithm just calculates one set of sums (typically 3-1) per time bin of differently weighted channel contents over a region of about one line width, starting well to the left from an expected line. This procedure is extremely fast and works as well for noisy spectra and asymmetric line shapes. It can and has been automatized. The program package is available on request to the authors.

Results demonstrate the high sensitivity for extracting even small lines out of a large noise with no fit. It turned out to be especially useful for analyzing spectra of a Wadden Sea sediment PDMS spectrum [2].

The efficient algorithm allows the processing of huge amounts of data (typ. 220 kB / spectrum) on a 286-PC in competitive time. Further development and research is done to identify noise and matrix effects and to subtract these from the original spectrum automatically.

SIMILARY serves the usual algebra to condition and compare spectra. For comparison, differences or an euclidian scalar product is usually used. In both cases, the problem of possible negative terms occurs. To avoid this and to enhance resolution in the region of low similarity, **SIMILARY** provides (besides the usual algebra) a newly designed *linear scalar product* for two spectra Y_1, Y_2 , namely $P(Y_1, Y_2) = \sum_{\nu} \sqrt{Y_1(\nu)Y_2(\nu)}$. By using this method, the similarity P is a physical quantity which we call *comparison-length*. It can be associated with the length of the difference vector in a parameter space of the two spectra. Future development will be to integrate **SIMILARY** together with **PEAKS** into an intelligent package to identify substances more or less automatically.

CRUNCHER calculates the composition of a theoretical PDMS spectrum by assuming the chemical bond breaking probabilities for a molecule of known chemical structure to be independent of each other. This reflects the rather short (as compared to bond vibration times) deposition of a large amount of energy as thought of to occur in the PDMS-process (which we call *entropic*). The bond breaking probabilities are fitted to experimental spectra by using a linear scalar-product measure. The breaking algorithm has been given in ref. [1].

For a cobalt complex (bromo-bis(dimethylglyoximate)-pyridino-cobalt(III)-complex), the experimental PDMS spectrum of this complex has been taken as an example to test the strength of the method. Four parameter fits have been performed for the break-up probabilities of the Br-Co, Co-pyridine and Br-N bonds. As a powerful method for fits in a parameter space of many dimensions we used a Monte-Carlo start combined with a attached local minimum search. This proved optimal for the case of the here found many side-minima.

The aim is to get values for the breaking probabilities for certain bond types such as C-H, C-C etc. (which should be about the same for different substances) which we then try to explain by microscopic numerical calculations. In this way we hope to elucidate the mechanism which governs this fragmentation process and to enlarge the quality of the predictions made by **CRUNCHER**.

PIMC II is a computer code developed by us to investigate thermal properties of small clusters ($N < 100$) via the Path Integral Monte Carlo method. The thermal properties of clusters like pair correlation func-

The 40th ASMS Conference on Mass Spectrometry and Allied Topics

tion. specific heat and potential or kinetic energy are calculated for Fermi-, Bose- and Boltzmann quantum statistics as well as for classical Maxwell - statistics. The code is highly vectorized and uses very efficient algorithms. PIMC II runs a factor 20 to 120 faster than PIMC I [3, 4], which includes solely Boltzmann- and Maxwell-statistics.

Example: Denoting the binding energy of Neon clusters [5] for a temperature T with E_n , the second energy differences $\Delta^2 E_n = E_{n-1} + E_{n+1} - 2E_n$ have proved to be a good measure for cluster stability [6]. If $\Delta^2 E_n$ is positive, the process of fragmentation of a Ne_n - cluster into a Ne_{n-1} -cluster and a single Ne-atom is less favorable than the process of fragmentation of a Ne_{n+1} -cluster into a Ne_n -cluster and a single Ne - atom. i.e. positive values indicate high stability of Ne_n -clusters and thereby magic numbers. The result is that only with these quantum mechanical calculation the experimentally known magic numbers are reproduced thus emphasizing the importance of the quantum statistics for the stability of light mass atomic clusters.

The pair correlation function gives the distribution of distances between the atoms of a cluster. For Ne_{13} -clusters at 4.0 K the quantum kinetic energy increases the two-particle distances and broadens the distribution compared to the classical calculation. At 8.0 K the structure gets washed out and the clusters seems to become fluid-like.

First results for 3He -clusters will be presented on ISSPIC VI this year. Simulations for Li and molecular clusters are in progress.

References

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