Good vibrations lead to molecular revelation

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(PhysOrg.com) -- A little luck and the wisdom to recognize what they were seeing helped Rice University researchers solve a molecular conundrum in a way that could be a boon to chemists.

Rice chemist Junrong Zheng and his colleagues in Houston and China have improved upon a long-standing theory for electrolytes through the discovery that vibrational energy transfer can be used to probe how ions cluster in such aqueous solutions.

The discovery opens a path for Zheng, an assistant professor of chemistry at Rice, to measure short-range intermolecular distances without fluorescent or other labeling devices that could skew results. The tool that makes it possible is an ultrafast, time-resolved infrared spectroscope he had custom-built to understand dynamic processes at the subnanoscale.

Zheng is planting a flag in a new field of research with the paper that appeared this week in the *Proceedings of the National Academy of Science*. The paper specifically shows how the vibrational energy common to all molecules can reveal the mechanics of ion clusters in a solution.

Very dilute solutions of electrolytes are well understood through Debye-Hueckel theory, which was developed in 1923, but as these solutions become slightly more concentrated the theory breaks down, as its authors predicted. A better understanding of electrolyte solutions is essential to scientists who study electochemistry, atmospheric aerosols

and biological systems. Zheng's work provides a new way to enlarge this understanding.

The Rice discovery is important for several reasons. First, the strength of an electrolyte -- think of the liquid in a car battery -- depends strongly on how well ions from salts or acids dissolve in the solution. More ions in a solution make it less ideal because of more opposite-charge attraction, according to Debye-Hueckel.

Zheng and his team found unexpected but clear evidence that a significant portion of ions of the same charge form clusters even in less-saturated solutions, in direct opposition to the equation.

Second, the Rice team's technique provides a window for scientists who want to view, for instance, concentrations of sodium and potassium ions in living cells, the ion-dependent movement of proteins or the properties of ion channels in cell membranes.

"Junrong's remarkable accomplishment is to devise a completely new way to learn much more about the structures present in concentrated ionic solutions," said Nobel laureate Robert Curl, Rice's University Professor Emeritus and the Kenneth S. Pitzer-Schlumberger Professor Emeritus of Natural Sciences, who advised Zheng on the paper. "This is exciting and it is important and should be expandable to other important situations."

"Our understanding of concentrated salt solutions is poor, yet these are highly relevant to practical applications, such as solar cells and batteries," said Gerald Meyer, the Bernard N. Baker Professor of Chemistry at Johns Hopkins University. "Junrong's approach is clever and provides some valuable insights from which new models can be developed. The use of isotopes for the demonstration of energy transfer within the clusters was particularly novel."

The path revealed itself to Zheng and Rice postdoctoral researcher Hongtao Bian last October. "This particular work was not intentionally designed," Zheng said. "It came from a small observation by Bian when I asked him to measure the rotation time constant of an anion in a concentrated solution.

"When he told me the rotation time was only 2.5 picoseconds, I knew something was wrong. I remembered the rotational time constant of this anion in a very dilute solution was around 3.7 picoseconds. We've measured this.

"In a dilute solution, the viscosity is very small," Zheng explained. "People move fast in an easy environment, but when it's crowded you cannot go so fast -- and the same applies here. When a solution is diluted, the molecules should move faster.

"But here in this very viscous solution, the molecules were moving too fast," he said. "Something was up. That's when I realized we weren't actually seeing the molecules rotate at all."

What the probe saw as a too-fast rotation was the vibrational energy as it transferred from one molecule to another with a different orientation. "I had thought that this, at some point, should happen, but I really couldn't experiment to demonstrate it," Zheng said. "The tools didn't exist. Then, just by this small accident, we're developing a whole methodology."

Zheng said his calculations may not apply to all electrolytes, but should cover a wide range of those of interest to researchers. "Only certain types of ions with active infrared modes and the vibrational lifetimes of the modes are comparable to the energy transfer time scales -- but that includes many important ions in biology or electrochemistry. Certainly this method is not limited to ions. It is, in principle, applicable to any molecules with active vibrational modes," he said.

Zheng, a native of China who came to Rice three years ago after completing his doctorate at Stanford, relied on the steady hands of Rice colleagues Anatoly Kolomeisky, an associate professor of chemistry, and Curl, who in fact carried his calculations one step beyond.

"It took us months to figure out a mathematical model to explain the data, and when Bob read it, he said, 'You know, I don't believe you're right,'" Zheng recalled. He said Curl objected to the fact that calculations were based on the average distribution of clusters in a given solution. "It was statistically right," Zheng said, "but it wasn't rigorous.

"Bob took our physical picture and counted the signal size from each cluster. He came up with a very rigorous model that accounts for the distribution of clusters. So his model is perfectly right. No assumptions."

Zheng said both his and Curl's models were in close agreement, since the averaged sample was so large. "But he really helped me to question every detail of the math, to make sure that this is really right.

"I had spent a month with a student who has a bachelor's degree in physics -- in math -- creating our model. It's hard to imagine that Bob could have figured all this out, by himself, in a week."

The paper's co-authors include graduate students Xiewen Wen, Jiebo Li and Hailong Chen, all of Rice; Suzee Han, a student at Clements High School in Sugar Land, Texas, who volunteered in Zheng's lab; and Xiuquan Sun, Jian Song and Wei Zhuang of the Chinese Academy of Sciences, Dalian, China.

More information: www.pnas.org/content/early/201 … /1019565108.abstract

Provided by Rice University