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研究課題名(和文) Electronic structure characterization of non-aqueous solvents

研究課題名(英文) Electronic structure characterization of non-aqueous solvents

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研究成果の概要(和文)：液体の光電子分光を用いて主に非水溶液の電子構造を研究した。光電子分光法は生物学的プロセスでも重要な化学状態、電気化学的性質や反応生成物などを分子規模で観測できる方法である。それは溶媒の基準データと正確なイオン化エネルギーの決定がカギとなる。本研究は正確なイオン化エネルギーの新しい決定方法を開発し、液体の水とアルコールに適用した。そして初めて広いエネルギー範囲で液体のメタノールとエタノールの価電子構造を観測した。国際共同研究で液体アンモニアの測定が可能になり、初めて濃いアルカリ金属溶液中の金属絶縁体転移の観測に成功した。さらに、ナトリウムカリウム合金の小滴の表面上で水の金属転移も観測できた。

研究成果の学術的意義や社会的意義

Important steps for photoelectron spectroscopy on liquids were achieved: Development of a new energy-referencing method for obtaining more accurate chemical properties, and establishing much-needed reference data for non-aqueous solvents, starting with the characterization of methanol and ethanol.

研究成果の概要(英文)：Photoelectron spectroscopy was used to study the electronic structure of liquids, with focus on non-aqueous solvents. Photoelectron spectroscopy is able to directly reveal electrochemical properties, the chemical state and reaction products on a molecular scale, which is also crucial for understanding biological processes. However, the key is having robust reference data and the ability to measure accurate ionization energies. A new energy-referencing method for obtaining accurate ionization energies was developed and applied to liquid water and alcohols. Here, the full valence band of ethanol and methanol was characterized for the first time. Furthermore, measurements of liquid ammonia have been made possible in international collaboration, which enabled first direct study of an insulator-to-metal transition in an alkali metal-ammonia solution. The gained knowledge was applied to study metallic water-solutions by forming a liquid water layer on a sodium-potassium droplet.

研究分野：物理化学

キーワード：electron spectroscopy electronic structure ionization energy non-aqueous solvents

1 . 研究開始当初の背景

The application of photoelectron spectroscopy to water and aqueous solutions has become a staple technique thanks to the development of the liquid-microjet technique over 20 years ago, and can give direct access to binding energies, charge states and reorganization energies, but also electronic relaxation dynamics and the local solvation structure via secondary (Auger) electron emission. However, despite their importance, the study of liquids other than water, i.e., non-aqueous solvents, had been largely neglected. The gap in understanding of non-aqueous liquids had been recognized, but besides the initial low-resolution photoelectron spectra from the early days of the technique only a few scattered studies, mainly using X-ray emission spectroscopy, were reported in the last 20 years. No modern PE spectroscopic experiment had attempted to tackle this issue thoroughly and systematically.

While it was in principle possible to study highly-volatile liquids with available technology, practical obstacles persisted: The much larger vapor pressure of many non-aqueous solvents meant that on the one hand that experimental systems had to cope with much higher base pressures, increasing both electron scattering and pumping demands, and on the other hand spectra were often overwhelmed by gas signal contribution from the evaporated vapor. Overcoming both problems requires an optimized experimental setup, with the ability to cool the liquid prior to the injection into the vacuum system and application of a large enough bias voltage to energetically separate the liquid and gas contributions in the spectrum. While the latter had been shown to be effective in the early days of the technique, no subsequent study tried to apply this method since to reveal the liquid spectral contribution.

So far it has been impossible to study liquid ammonia, despite being an important hydrogen-bonded system and proposed as an alternative life-supporting solvent, since the cryogenic temperatures required for producing a vacuum-compatible liquid jet and the very high vapor pressures involved had been prohibitive. These problems have been overcome only last year, and enabled so far unprecedented studies on this important solvent.

2 . 研究の目的

The goal of this study was to solve the following problems, which presented an ongoing challenge in studying liquids with photoelectron spectroscopy at the time:

(1) Electronic structure information of non-aqueous solvents was seriously lacking, with basically no progress since the earlier days of liquid photoelectron spectroscopy over 20 years ago. The project aimed to establish methods to properly characterize solvents and to provide reference data of important liquids, starting with simple alcohols. This forms the basis for studying solutes which have a very low solubility in water (organic molecules, biomolecules) or which react with water (some alkali metals), and must be therefore studied in non-aqueous solvents. While proceeding with the project and tackling this problem, it was also recognized that established energy-referencing methods for inferring ionization energies from liquids have too many drawbacks, and thus a new way of calibrating ionization energies must be found.

(2) The project further aimed at understanding the effects of hydrogen bonding on the electronic structure and the dynamics of electronic relaxation in hydrogen-bonded liquids, which can give a new perspective on the nature of hydrogen bonds in liquid water. Ethanol was proposed as a first test case for non-aqueous hydrogen-bonding effects.

(3) The project aimed to provide new insights into binding energy shifts and bonding behavior of solutes with the focus on non-aqueous solutions. This task was given a new direction thanks to the development of the novel energy-referencing method, which revealed that even solute binding energies in aqueous solutions are prone to calibration errors. While initially only proposed as a

far goal, the study of liquid ammonia and its solutions has been made possible thanks to international collaboration, which enabled the study of alkali-halide solutions in this cryogenic solvent.

3 . 研究の方法

Liquid alcohols were measured using a high-resolution liquid-microjet PE spectroscopy setup utilizing a He emission lamp in the laboratory at Kyoto university. Using a He plasma discharge lamp is optimal to study the valence band structure: The continuous high-flux operation ensures good signal with preventing spectral distortion from space-charge often encountered with pulsed light sources. Also, the photon energy of He II radiation is sufficient to reveal the full valence structure including lower lying orbitals, while being available in the lab, unlike limited time at synchrotron radiation sources.

To mitigate the high vapor pressure of these liquids, an in-vacu cooling system was developed, consisting of a recirculating chiller and a custom-designed vacuum rod operating on a closed-cycle, for cooling the liquid before being injected into the vacuum system. With this system a given liquid can be cooled to -10 °C and lower, reducing the vapor pressure of alcohols by a factor 5 or more. This not only increased the overall signal from reduced electron scattering, but at the same time reduced the background signal from the gas itself.

Furthermore, a method for applying a highly stable bias voltage between the liquid sample and the detection system was installed to energetically separate the liquid and gas signal contributions. This led to the development of a novel accurate energy-referencing method for liquids and solutions in general, which was first applied to liquid water. The demonstration of the applicability of this novel energy-referencing method to higher photon energies (synchrotrons) was achieved in international collaboration.

The measurement of liquid ammonia solutions as well as metallic water was enabled in international collaboration as well, by working with groups in Germany and the Czech Republic. Due to interference of the Corona pandemic, the study of these topics was done in remote operation, where the setup and execution of experiments were done in Europe, while data analysis, interpretation of the results and discussion of the next steps was done in Japan while communicating online.

4 . 研究成果

(1) The full valence band of liquid ethanol and methanol have been measured by utilizing sample biasing of up to -70 V, which revealed the detailed band structure of these alcohols for the first time (Fig. 1). The energy has been referenced to the gas phase, which was also measured in great detail. The assigned ionization energies and band shape will serve as important reference data for studies of solutions with these solvents. Analysis revealed that, unlike water, the molecular character is largely preserved even in the liquid state for these alcohols and mainly a spectral shift occurs from the screening of the surrounding molecules, which is however somewhat smaller than in water due to the larger size of the alcohol molecules. However, an indication of split band features was found, which may originate from hydrogen bonding. This result is a first milestone in investigating the effects of hydrogen-bonding on the electronic structure in liquids other than water. Furthermore, a comparison with X-ray emission spectra revealed that there is a good agreement if nuclear dynamics is omitted from the spectral composition, which confirmed involvement of nuclear dynamics in the X-ray emission process within its lifetime of the ionized state. The established measurement protocol can be readily expanded to other non-aqueous liquids in the future and should lead to an increased interest in studying these and other solvents. The results were published in the Journal of Physical Chemistry A.

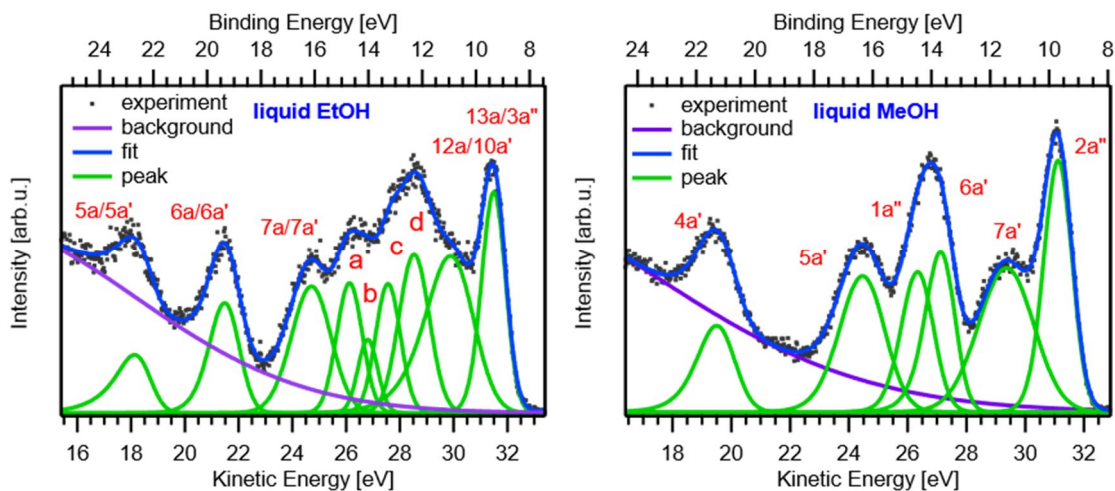


Figure 1: Calibrated liquid methanol (left) and ethanol (right) photoelectron spectra with a spectral deconvolution into individual molecular bands (green peaks).

(2) In parallel, a novel energy-referencing method for measuring absolute ionization energies was developed. It became clear that referencing ionization energies via the vapor phase of the respective liquid is subject to influences of many experimental parameters (sample charge-up, the so-called streaming potential and work function differences). An accurate energy-scale determination via gas-phase reference spectra is very time consuming and needs to be repeated for every solution under study. Measuring accurate ionization energies is a prerequisite to study the electronic structure and chemistry of solutions. Instead, a much more promising method is to calibrate ionization energies via the local vacuum level of the liquid itself. For this, a large bias is applied to reveal the lowest-energy electrons in the spectrum. This has also the aforementioned benefit of energetically separating the liquid from the gas spectral contribution.

The new method was applied to liquid water over a wide range of photon energies from UV up to X-ray energies (measurements at synchrotron facilities were carried out in international collaboration). This revealed that inelastic electron scattering in liquids becomes severe at lower energies below about a kinetic energy of 10-15 eV, and spectral features quickly deteriorate below this threshold (Fig. 2). This phenomenon could not be explained with current knowledge of electron scattering cross-sections, and hints at a so far unexplored new type to scattering process in water at low energies. These results were published in *Physical Chemistry Chemical Physics*. A second publication describing the novel energy-referencing method over the full energy range is currently submitted to *Chemical Science*. The new energy-referencing method and the reference data gained for liquid water is promising to become a new standard for liquid photoelectron spectroscopy.

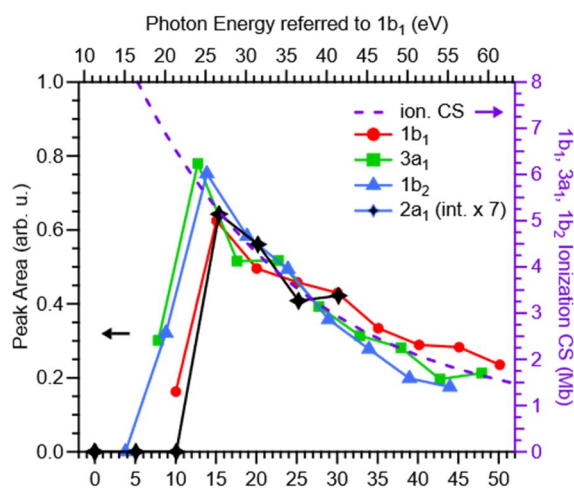


Figure 2: In the liquid, a sudden decrease of peak intensity for the four water valence orbitals ($1b_1$, $3a_1$, $1b_2$ and $2a_1$) is observed below a critical electron kinetic energy of 10-15 eV.

Applying above method to alcohols (ethanol and methanol) revealed a distinct energy shift in ethanol, which hints at the presence of surface dipoles from orientated molecules at the liquid's surface. This may pave the way for novel ways to study the surface structure of liquids. A study comparing the so-far established and the newly developed energy-referencing methods with the example of both liquid water and alcohols is in preparation for publication.

(3) A few breakthroughs in studying extreme conditions and exotic states in liquids have been made possible thanks to international collaboration, mainly with groups in Germany and the Czech Republic.

Measurements of liquid ammonia with an unprecedented cryogenic liquid-jet allowed for the first direct observation of an insulator-to-metal transition in an alkali metal-ammonia solution. Alkali metals release solvated electrons, which can boost the conductivity of a solution by orders of magnitude and lead to metallic behavior. However, because of their high reactivity, aqueous solutions of alkali metals are extremely unstable and explosive. Liquid ammonia instead can solve alkali ions up to a very high concentration without issues. Alkali-halide solutions exhibit a blue color at lower concentration, which shows the formation of stable solvated electrons, and then turn to a reflective golden color after the transition to metallic behavior at high concentration. For the first time, such an insulator-to-metal transition, and its impact on the electronic structure, could be directly observed using liquid-jet photoelectron spectroscopy (Fig. 3). At low concentration, a peak indicative of the solvated electron appeared for the blue solution, which increase in intensity proportional to the alkali concentration. Then, above a concentration where the previously isolated solvated electrons (electron pairs) start interacting, a metallic band with a characteristic Fermi-edge formed in the spectrum, indicating the onset of metallic behavior. At the same concentration also a plasmon-peak appeared, which matches well with the expected electron density in the solution. This result will pave the way to study the conditions for metallic behavior in general, with freely tunable electron density by adjusting the alkali metal concentration. This result was published in Science.

The gained knowledge was applied to study metallic water-solutions by forming a liquid water layer on a sodium-potassium droplet. Here, pure sodium-potassium was slowly introduced into the vacuum chamber to form a growing droplet. At the same time, water vapor was introduced, which successively adsorbed onto the droplet and formed a thin liquid layer while solving sodium and potassium ions in large amounts. This enable the transient formation of a highly-concentrated alkali-metal aqueous solution without the explosive behavior. The formation of a metallic band and a plasmon feature have been confirmed with this approach, showing the creation of a metallic water solution. So far, metallic water has only been proposed to be able to exist under extreme pressures and has not been observed experimentally. This novel approach not only opens up a possibility to study such metallic solutions but also confirmed a similar behavior to the liquid ammonia solutions studied before (see above). This result has been accepted to Nature.

Overall, the project has expanded the scope and applicability of photoelectron spectroscopy to both aqueous and non-aqueous solutions for studying novel phenomena and chemically relevant parameters.

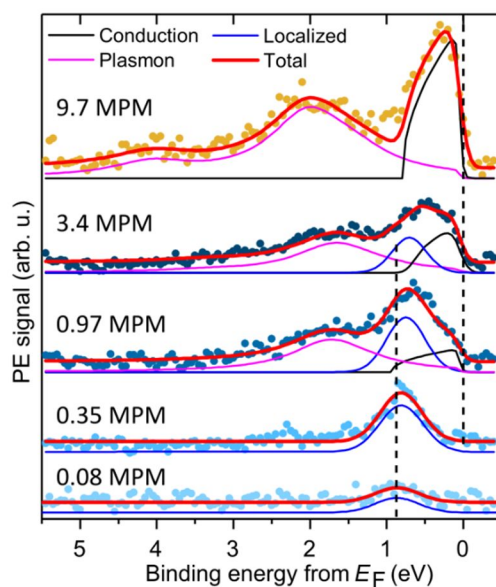


Figure 3: Evolution of the photoelectron spectra of alkali-halide solution in liquid ammonia from low (bottom) to high (top) concentration. The signal changes from a single peak (solvated electron) to a metallic band including the sharp Fermi-edge cutoff at high energies and several plasmon-loss features indicating metallic behavior.

5. 主な発表論文等

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〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

	氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関			
ドイツ	Fritz Haber Institute	Helmholtz Zentrum Berlin	Humboldt-Universitaet zu Berlin	
チェコ	Czech Academy of Sciences			