Valence and Core-Level X-ray Photoelectron Spectroscopy of a Liquid Ammonia Microjet

Tillmann Buttersack, Philip E. Mason, Ryan S. McMullen, Tomas Martinek, Krystof Brezina, Dennis Hein, Hebatallah Ali, Claudia Kolbeck, Christian Schewe, Sebastian Malerz, Bernd Winter, Robert Seidel, Ondrej Marsalek, Pavel Jungwirth, and Stephen E. Bradforth

ABSTRACT: Photoelectron spectroscopy of microjets expanded into vacuum allows access to orbital energies for solute or solvent molecules in the liquid phase. Microjets of water, acetonitrile and alcohols have previously been studied; however, it has been unclear whether jets of low temperature molecular solvents could be realized. Here we demonstrate a stable 20 μm jet of liquid ammonia (−60 °C) in a vacuum, which we use to record both valence and core-level band photoelectron spectra using soft X-ray synchrotron radiation. Significant shifts from isolated ammonia in the gas-phase are observed, as is the liquid-phase photoelectron angular anisotropy. Comparisons with spectra of ammonia in clusters and the solid phase, as well as spectra for water in various phases potentially reveal how hydrogen bonding is reflected in the condensed phase electronic structure.

Liquid ammonia is often used as a medium for organic chemistry due its ability to support long-lived highly reducing solvated electrons, first demonstrated by Birch in 1944.1 Solvated electrons can be generated simply by adding an alkali metal to anhydrous liquid ammonia; the solvated electrons have lifetimes on the order of months for solutions which are free from oxygen and moisture. It can be expected that photoelectron (PE) spectroscopy of these liquid solutions may reveal insights as to the binding energies of different electron motifs in ammonia.2,3 However, in a recent review of the spectroscopy of excess electrons in ammonia4 it is remarked that the electronic structure of neat liquid ammonia itself has not as yet been characterized through its photo-electron spectrum, although the PE spectrum of large ammonia clusters5 and ammonia ice6 on MoS2 has been reported. The liquid PE spectrum would be a crucial complement to the known ammonia orbital energies in both vapor7 and amorphous ice8; it is certainly a necessary prerequisite for an understanding of the band gap in liquid ammonia7 and to provide a more rounded understanding of excess electrons9 in liquid ammonia. A further interest in the liquid ammonia photoelectron spectrum is the comparison of the two simplest hydrogen bonded liquids: the question of how electronic structure evolves from isolated molecular H2O or NH3 through molecular clusters all the way to (bulk) liquid, and the effect of hydrogen bond strength on the orbital binding energies. Shifts from the gas phase in each band in the PE spectrum of liquid water are well-known not to be uniform reflecting different solvent-induced changes to individual molecular orbitals.10

A prerequisite to progress on the electronic structure of NH3(aq) is to demonstrate the generation of a stable liquid jet of ammonia to enable photoelectron studies in vacuum. This paper provides proof-of-principle photoelectron spectroscopy from a liquid jet of NH3. The technique of forcing a room temperature liquid jet into vacuum was first obtained using photoelectron spectra for liquid water, simple alcohols and nonane in 1997,11 with the first photoelectron spectrum of water using synchrotron extreme ultraviolet recorded in 2004.10

Liquid jets of cryogenic nitrogen and argon were achieved by Faubel in 2001 using a simple metal aperture,12 with a system cooled all the way to the outlet aperture. Liquid ammonia poses a different challenge to these liquids. It is a gas until cooled below −33 °C at atmospheric pressure; it was difficult for us to predict whether the liquid ammonia will immediately become a gas once a jet filament is introduced into vacuum due to ammonia’s high vapor pressure (10 kPa) even at −70 °C. Also, it was not clear that if a jet is formed, the length of the laminar flow region would be sufficient to collect high signal-to-noise photoelectron spectra.

A liquid ammonia sampling system, submerged in a cold ethanol bath held at −60 °C, was employed. A 50 mM KBr solution was used to diminish the streaming potential, in analogy with water liquid jets.13 High-purity argon was...
introduced into the head space of the sample cylinder to force the liquid ammonia through 6 mm diameter steel tubing to a 20 μm diameter nozzle by pressurization (5 bar), keeping the line at the same temperature until reaching the beginning of the glass jet nozzle.

PE experiments were carried out with the SOL3PES experimental setup14 at the variable polarization UE52-SGM-1 beamline at the synchrotron radiation facility BESSY II.15 Valence PE spectra were recorded using a photon energy of 310 eV and core PE spectra were recorded with a photon energy of 640 eV; polarization with respect to the lab frame was varied relative to the facility floor. The energy resolution of the UE52-SGM1 beamline was better than 90 meV for 310 eV photon energy and 260 meV for 640 eV, respectively. The electron analyzer offered a resolution of 125 meV at the pass energy of 100 eV used in our experiments. The rectangular X-ray spot size was 60 μm × 100 μm (exit slit) with the liquid ammonia microjet ~20 cm behind the focus, such that the spot size at the liquid jet was roughly 400 μm.

A liquid jet of ammonia is formed with an argon backing pressure of 5 bar. After priming, a laminar flow region is formed 1–5 cm long; a stable liquid jet can be maintained for hours with a base chamber pressure of ∼4 × 10⁻³ mbar until the exhaustion of the reservoir (flow rate of about 0.5 mL/min; jet velocity ~30 m/s). Unlike with water, evaporative cooling does not lead to ice formation as part of the flow.

The recorded photoelectron spectra are shown in Figure 1. Calibration of the absolute binding energies in the photoelectron spectrum of liquid ammonia was carried out by measuring the lowest binding energy 3a₁ PE band at consecutively lowered photon fluxes until both gas and liquid phase peaks no longer shifted due to the charging of the jet caused by ionized ammonia molecules (see Figure S1). Then the valence spectrum is calibrated against the literature gas-phase lowest vertical ionization potential of 10.93 eV.7 We find a gas–liquid shift of 1.84 eV, giving the liquid 3a₁ peak at 9.1 ± 0.1 eV. The calibrated valence photoelectron (Figure 1, top) spectrum shows, as expected, three bands for the gas and three bands that can be assigned to the liquid. The large gas-phase contribution is due to the high vapor pressure around the liquid ammonia jet as well as the large X-ray illuminated volume.

By subtracting the appropriately normalized gas phase spectrum, the PE peaks due to the liquid can be obtained (Figure 1 middle, Figure S2) and fit by three Gaussians (Figure S2, red line). A discernible shift to lower binding energies for all features arising from the liquid-phase is evident (see Table 1). A similar lowering of binding energies of the valence orbitals is also seen for the valence peaks in liquid water, but the shifts here are greater than for water.10 Furthermore, as for water, the shifts for the different bands are not the same. In ammonia, the shift is smallest for the lone pair 3a₁, which is the orbital affected most by H-bond donation. A subtlety here is that the 1e band is split already in the gas phase due to degeneracy breaking in the resultant ²E cation state (see Supporting Information). The binding energies for the 2s dominated orbitals (labeled 2a₁ in both water and ammonia) are shifted the most in both liquids.

The liquid PE spectrum resembles that observed for large ammonia clusters.5 Compared to amorphous ammonia ice, the PE features are shifted to a greater extent from the gas phase. The solid phase 3a₁ band peak at 9.5 eV is almost 2 eV wide and is distinctly asymmetric unlike the liquid phase peak, which is shifted to 9.1 eV and more or less Gaussian. The 1e band in ammonia ice peaks at 15.1 eV (and is also ~2 eV broad shading to the low BE side), whereas in liquid we see a further decrease in BE to 14.3 eV for the band peak.

The angular anisotropy of the valence PE spectrum has been recorded but for a different photon energy, 265 eV (Figure S3). For the 3a₁ and 1e bands, which are well separated from their vapor counterparts, the electron angular distributions are characterized by β(3a₁) = 1.5/1.0 (gas/liquid) and β(1e) = 1.3/0.9 (gas/liquid), respectively.

We have modeled the valence photoelectron bands using hybrid density functional calculations employing the G_0W_0 approach. Calculations for the gas phase spectrum originate from a set of 5000 single point G_0W_0 calculations for geometries sampled every 10 fs from a 50 ps long ab initio molecular dynamics (AIMD) trajectory of a single ammonia molecule. For liquid phase spectra, we simulated 64 ammonia molecules in a box employing periodic boundary conditions; for 100 configurational snapshots separated by 2 ps from a 200 ps run, the 256 highest G_0W_0 energies (i.e., four energies per NH₃ molecule) were used for obtaining the quasi-particle energy distribution to model the spectra. Full details of the computational methodology are given in the Supporting Information.

The results of our calculations are summarized in the bottom part of Figure 1. First, we reproduced well the gas
Due to the use of periodic boundary conditions, values of electronic orbital energies are not directly accessible primarily due to approximations used in describing the terms of absolute peak positions. Small residual deviations are high photon flux resulting in Figure 2. As before, a substantial gas-liquid was recorded with a photon energy of 640 eV, and the valence 3a1 liquid peak and not against the N 1s gas phase orbital shown.

The isolated molecule spectrum is calibrated using the position of the valence 3a1 liquid peak, because we have not yet excluded charging effects in the di 1a1 (N 1s) 2a1 1e 3a1 orbital. 25.07 14.63 9.09

Table 1. Binding Energies and Full Width at Half Maxima (FWHM) of All Molecular Orbitals

| orbital        | 1a1 (N 1s) | 2a1 | 1e     | 3a1 |
|----------------|------------|------|--------|-----|
| BE liquid (eV) | 403.49 ± 0.05 | 25.36 ± 0.02 | 14.31 ± 0.03 | 9.09 ± 0.05 |
| fwhm liquid (eV) | 1.3 ± 0.1 | 3.35 ± 0.04 | 2.38 ± 0.08 | 1.54 ± 0.04 |
| lit. BE gas (eV) | 405.5(2)b | 27.7f | 16.6f | 10.93f |
| calc. BE liquid (eV)c | - | 25.07 | 14.63 | 9.09 |
| calc. BE gas (eV)c | - | 26.64 | 16.47 | 10.67 |

°Error bars reflect fitting uncertainty. Ref 5. Ref 7. Ref 16. Aligned with experiment for the 3a1 orbital.

Ammonia molecules suggesting that charging is not a significant problem. Using a literature value for the gas, the gas—liquid shift for this band is 2.0 eV, compared to a smaller shift of 1.77 eV on the O 1s for water. The difference in the gas—liquid shifts between water and ammonia for the N 1s and O 1s may in part reflect the different optical dielectric response of the two liquids via the Born stabilization of the final state.

Finally, varying the X-ray polarization over six angles with respect to the detection direction for N 1s PE band at 640 eV (Figures S4 and S5) gives β(gas/liquid) = 1.9/1.7 showing only a small diminution of the photoelectron anisotropy due to elastic scattering of the outgoing electron through the liquid.

In conclusion, we have presented the first measurements from a liquid ammonia microjet and demonstrated significant shifts in the photoelectron binding energies for both the valence and core orbitals of ammonia on condensation. The decrease in binding energies is more significant than those seen for amorphous ammonia ice deposited on MoS2. However, as for PE spectra from large clusters, we can clearly identify bands that match those from the isolated molecule. The basic shifts observed in experiment are recovered by calculations based on ab initio molecular dynamics and G0W0 with a hybrid functional. Evidence for the degree of delocalization of the valence orbitals can be analyzed from the PE band anisotropy and peak splitting. Experiments that probe liquid ammonia increasingly doped with excess electrons are currently underway; the issue of delocalization and anisotropy will be particularly topical in this context and will be further explored in a future publication.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b10942.

Photon flux, angular distribution experimental data, as well as computational methodology and benchmarking (PDF)

AUTHOR INFORMATION

Corresponding Authors
*ondrej.marsalek@mff.cuni.cz
*winter@fhi-berlin.mpg.de
*pavel.jungwirth@uochb.cas.cz
*stephen.bradforth@usc.edu

ORCID

Bernd Winter: 0000-0002-5597-8888
Ondrej Marsalek: 0000-0002-8624-8837
Pavel Jungwirth: 0000-0002-6892-3288
Stephen E. Bradforth: 0000-0002-6164-3347

Author Contributions
*These authors contributed equally.
Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the HZB staff prior to and during the beamtime for their assistance at BESSY II. P.E.M. acknowledges support from the viewers of his YouTube science channel. S.E.B. and R.S.M. are supported by the U.S. National Science Foundation (CHE-1665532). R.S.M. received additional funds from the States of Jersey Postgraduate Bursary. R.S. and B.W. gratefully acknowledge financial support from the German Research Foundation (DFG) within the Collaborative Research Center (SFB) 1109. R.S. also acknowledges an Emmy Noether Young Investigator stipend through the DFG (project SE 2253/3-1). O.M. was supported by the project Primus16/SCI/27/247019. T.B. was supported by the Czech Ministry of Education and the EU (Grant CZ.02.2.69/0.0/0.0/16_027/0008477). P.J. acknowledges support from the Czech Ministry of Education and the EU (Grant CZ.02.2.69/0.0/0.0/16_027/0008477). P.J. acknowledges support from the viewers of his YouTube science channel. S.E.B. and R.S.M. are supported by the U.S. National Science Foundation (CHE-1665532). R.S.M. received additional funds from the States of Jersey Postgraduate Bursary. R.S. and B.W. gratefully acknowledge financial support from the German Research Foundation (DFG) within the Collaborative Research Center (SFB) 1109. R.S. also acknowledges an Emmy Noether Young Investigator stipend through the DFG (project SE 2253/3-1). O.M. was supported by the project Primus16/SCI/27/247019. T.B. was supported by the Czech Ministry of Education and the EU (Grant CZ.02.2.69/0.0/0.0/16_027/0008477). P.J. acknowledges support from the viewers of his YouTube science channel. S.E.B. and R.S.M. are supported by the U.S. National Science Foundation (CHE-1665532). R.S.M. received additional funds from the States of Jersey Postgraduate Bursary. R.S. and B.W. gratefully acknowledge financial support from the German Research Foundation (DFG) within the Collaborative Research Center (SFB) 1109. R.S. also acknowledges an Emmy Noether Young Investigator stipend through the DFG (project SE 2253/3-1). O.M. was supported by the project Primus16/SCI/27/247019. T.B. was supported by the Czech Ministry of Education and the EU (Grant CZ.02.2.69/0.0/0.0/16_027/0008477).

■ REFERENCES

(1) Birch, A. J. 117. Reduction by Dissolving Metals. Part I. J. Chem. Soc. 1944, 430−437.
(2) Aulich, H.; Baron, B.; Delahay, P.; Lugo, R. Photoelectron Emission by Solvated Electrons in Liquid-Ammonia. J. Chem. Phys. 1973, 58 (10), 4439−4443.
(3) Hartweg, S.; West, A. H. C.; Yoder, B. L.; Signorell, R. Metal Transition in Sodium-Ammonia Nanodroplets. Angew. Chem. 2016, 128 (40), 12535−12538.
(4) Vöhringer, P. Ultrafast Dynamics of Electrons in Ammonia. Annu. Rev. Phys. Chem. 2015, 66 (1), 97−118.
(5) Lindblad, A.; Bergersen, H.; Pokapanich, W.; Tchaplyguine, M.; Ohrvall, G.; Bjorneholm, O. Charge Delocalization Dynamics of Ammonia in Different Hydrogen Bonding Environments: Free Clusters and in Liquid Water Solution. Phys. Chem. Chem. Phys. 2009, 11 (11), 1758−7.
(6) Yu, K.-Y.; McMenamin, J. C.; Spicer, W. E. UPS Measurements of Molecular Energy Level of Condensed Gases. Surf. Sci. 1975, 50 (1), 149−156.
(7) Edvardsson, D.; Baltzer, P.; Karlsson, L.; Wannberg, B.; Holland, D. M. P.; Shaw, D. A.; Rennie, E. E. A Photoabsorption, Photodissociation and Photoelectron Spectroscopy Study of NH3 and ND3. J. Phys. B: At., Mol. Opt. Phys. 1999, 32 (11), 2583−2609.
(8) Vogler, T.; Vöhringer, P. Probing the Band Gap of Liquid Ammonia with Femtosecond Multiphoton Ionization Spectroscopy. Phys. Chem. Chem. Phys. 2018, 20 (40), 25657−25665.
(9) Zurek, E.; Edwards, P. P.; Hoffmann, R. A Molecular Perspective on Lithium-Ammonia Solutions. Angew. Chem., Int. Ed. 2009, 48 (44), 8198−8232.
(10) Winter, B.; Weber, R.; Widdra, W.; Dittmar, M.; Faubel, M.; Hertel, I. V. Full Valence Band Photoemission from Liquid Water Using EUV Synchrotron Radiation. J. Phys. Chem. A 2004, 108 (14), 2625−2632.
(11) Faubel, M.; Steiner, B.; Toennies, J. P. Photoelectron Spectroscopy of Liquid Water, Some Alcohols, and Pure Nonane in Free Micro Jets. J. Chem. Phys. 1997, 106 (22), 9013−9031.
(12) Wieland, M.; Wilhein, T.; Faubel, M.; Ellert, C.; Schmidt, M.; Sublemontier, O. EUV and Fast Ion Emission from Cryogenic Liquid Jet Target. Appl. Phys. B: Lasers Opt. 2001, 72 (5), 591−597.
(13) Kurahashi, N.; Karashima, S.; Tang, Y.; Horio, T.; Abulimiti, B.; Suzuki, Y.; Ogi, Y.; Oura, M.; Suzuki, T. Photoelectron Spectroscopy of Aqueous Solutions: Streaming Potentials of NaX (X = Cl, Br, and I) Solutions and Electron Binding Energies of Liquid Water and X−. J. Chem. Phys. 2014, 140 (17), 174506.
(14) Seidel, R.; Pohl, M. N.; Ali, H.; Winter, B.; Aaziz, E. F. Advances in Liquid Phase Soft-X-Ray Photoemission Spectroscopy: a New Experimental Setup at BESSY II. Rev. Sci. Instrum. 2017, 88 (7), 073107.
(15) Helmholtz Zentrum Berlin für Materialien und Energie, The Variable Polarization Undulator Beamline UES2 SGM at BESSY II. J. Large-Scale Res. Facilities 2016, 2, A70.
(16) Banna, M. S.; Shirley, D. A. Molecular Photoelectron Spectroscopy at 132.3 eV: the Second-Row Hydrides. J. Chem. Phys. 1975, 63 (11), 4759−4766.
(17) Chen, W.; Ambrosio, F.; Miceli, G.; Pasquarrello, A. Ab Initio Electronic Structure of Liquid Water. Phys. Rev. Lett. 2016, 117 (18), 186401.
(18) Ambrosio, F.; Guo, Z.; Pasquarrello, A. Absolute Energy Levels of Liquid Water. J. Phys. Chem. Lett. 2018, 9 (12), 3212−3216.
(19) Gaiduk, A. P.; Pham, T. A.; Govoni, M.; Paesani, F.; Galli, G. Electron Affinity of Liquid Water. Nat. Commun. 2018, 9 (1), 247.
(20) Luckhaus, D.; Yamamoto, Y.-I.; Suzuki, T.; Signorell, R. Genuine Binding Energy of the Hydrated Electron. Sci. Adv. 2017, 3 (4), e1603224.
(21) Thürmer, S.; Seidel, R.; Faubel, M.; Eberhardt, W.; Hemminger, J. C.; Bradford, S. E.; Winter, B. Photoelectron Angular Distributions from Liquid Water: Effects of Electron Scattering. Phys. Rev. Lett. 2013, 111 (17), 173005.