

Photoelectron Spectroscopy of Benzene in the Liquid Phase and Dissolved in Liquid Ammonia

H. Christian Schewe^{*, 1, a)} Krystof Brezina,^{2, 1} Vojtech Kostal,¹ Philip E. Mason,¹ Tillmann Buttersack,³ Dominik M. Stemer,³ Robert Seidel,⁴ Wilson Quevedo,⁴ Florian Trinter,^{3, 5} Bernd Winter,³ and Pavel Jungwirth^{*1, b)}

¹⁾*Institute of Organic Chemistry and Biochemistry of the Czech Academy of Sciences, Flemingovo nám. 2, 166 10 Prague 6, Czech Republic*

²⁾*Charles University, Faculty of Mathematics and Physics, Ke Karlovu 3, 121 16 Prague 2, Czech Republic*

³⁾*Molecular Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany*

⁴⁾*Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, D-14109 Berlin, Germany*

⁵⁾*Institut für Kernphysik, Goethe-Universität Frankfurt, Max-von-Laue-Str. 1, D-60438 Frankfurt am Main, Germany*

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Abstract. We report valence band photoelectron spectroscopy measurements of gas-phase and liquid-phase benzene, as well as those of benzene dissolved in liquid ammonia, complemented by electronic structure calculations. Origins of the sizable gas-to-liquid-phase shifts in electron binding energies deduced from the benzene valence band spectral features are quantitatively characterized in terms of the Born–Haber solvation model. This model also allows for rationalizing the observation of almost identical shifts in liquid ammonia and benzene despite the fact that the former solvent is polar while the latter is not. For neutral solutes like benzene, it is the electronic polarization response determined by the high frequency dielectric constant of the solvent—which is practically the same in the two liquids—that primarily determines the observed gas-to-liquid shifts.

1. INTRODUCTION

The liquid microjet technique is a unique tool that enables measurement of the electronic structure of volatile solutions using X-ray photoelectron (PE) spectroscopy.^{1–3} Being well established for water and aqueous solutions,⁴ this approach has been also developed for cryogenic and room temperature non-polar liquids^{5,6} such as liquid nitrogen, liquid argon⁵ or most recently liquid ammonia and its solutions.^{7,8} Using photoelectron spectroscopy (PES) we are thus now in a unique position to investigate solvent effects on the electronic structure of a solute molecule in a wide variety of non-polar and polar liquids.

Benzene (C_6H_6) is the archetypal aromatic molecule. Its electronic structure has been thoroughly investigated in the gas phase using PES^{9–12} as well as quantum chemical computational methods.^{13–15} Despite theoretical studies,¹⁶ PE spectra of neither pure liquid benzene nor benzene in solutions have been recorded so far, with the closest study being a recent sophisticated PES measurement of gas and liquid trimethylbenzenes.⁶ In the liquid state, the detailed vibrational structure of the PE spectra of gaseous benzene¹² is supposed to be washed out similar analogous to liquid water, while other interesting features may arise that include changes and shifts of the characteristic line shapes due to the presence of

intermolecular interactions. As observed for other investigated dissolved species, interactions with the local solvent environment lead to measurable shifts of the peaks in the PE spectra compared to their positions in the gas phase.^{6,17} The size of these shifts depends both on the character of the solvent molecules and the charge of the solute.^{1,18–20}

Here, we investigate the electronic structure of solvated benzene using PE spectroscopy and quantum chemical calculations. Experimentally, we exploit a recent development in liquid-microjet PES which enables the measurement of accurate absolute electron binding energies (BEs).^{19,21,22} Using this technique, we determine the BEs of pure liquid ammonia and benzene, and also characterize the magnitude of solute-induced shifts on the solvent. In addition, we use quantum chemical calculations to guide the interpretation of the spectroscopic measurements. The principal result of the present study is that the shifts of the valence PE spectral features of benzene and ammonia from the gas to the liquid phase are sizable, however the BE shift of benzene upon solvation is almost the same in a liquid ammonia solution and in pure liquid benzene. This behavior can be rationalized by a simple thermodynamic cycle that approximates the solvent electronic polarization effects by the Born equation.

^{a)}Electronic mail: hannsch@uochb.cas.cz

^{b)}Electronic mail: pavel.jungwirth@uochb.cas.cz

2. METHODOLOGY

Experimental Methods

Experimental details and procedures. Liquid ammonia solutions were prepared in an evacuated borosilicate glass cylinder (hereafter referred to as the condensation unit) embedded in a bath of cooled ethanol at -60 °C. After condensing a known volume of gaseous ammonia (Westfalen, purity 5.0) defined amounts of NaI (Merck, purity 99.8 %) were dissolved to generate 50 mM concentrations to ensure conductivity of the liquid ammonia solution in order to prevent streaming potentials.

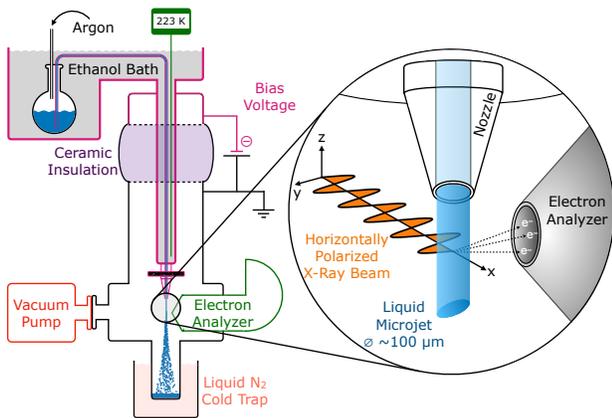


FIG. 1. The experimental set up illustrating how the cryogenic unit is mounted on top of the SOL³PES. Details are given in the main text.

In a subsequent step and depending on the experimental details, defined amounts of liquid benzene (Merck, purity 99.8 %) were dissolved in a liquid ammonia solution as well. The solution was then transferred via a 6 mm diameter stainless steel tube from the condensation unit to the cryogenic unit (see Figure 1). The cryogenic unit itself consists of a double-walled stainless steel container which is evacuated to ensure thermal insulation. A ~ 50 mm diameter stainless steel tube mounted on top of the container feeds through a flange into the vacuum chamber. Liquid ethanol, cooled with liquid nitrogen, is recycled in the chamber using a commercial aquarium pump in order to keep the temperature of the ensemble constant at ~ 220 K. Liquid nitrogen was frequently poured on top of the ethanol bath to cool it, and to keep the temperature stable at ~ 220 K.

The liquid microjet was generated by applying pressure of up to 5 bar of argon at the top of the sample cylinder. The ammonia solution was then pressed through the 6 mm diameter stainless steel tube and through a commercially available polyethylene filter at the end. The solution was released into vacuum through a quartz-capillary (inner diameter of ~ 100 μm), which was glued into the outlet of the filter. In contrast to the liquid ammonia experiments, studies with liquid benzene

have been conducted at room temperature using the standard liquid jet setup described in Reference 23. Here, an HPLC pump (Watrex) was used to push the liquid benzene through a ~ 25 μm inner diameter nozzle into the vacuum chamber.

Two cooling traps and a 1500 l turbo-molecular pump maintained at least a pressure of $\sim 5 \times 10^{-4}$ mbar in the main vacuum chamber. Any liquid jet formed a laminar flow for at least 2 mm before disintegrating into droplets while falling into the catcher unit. There, any residual liquid was frozen out by placing a liquid nitrogen bath from outside the vacuum chamber. Both microjet assemblies were mounted on top of linear x - y - z -manipulators onto which additionally a ceramic flange was mounted. This ensured electric insulation of the whole cryostat unit and the liquid jet itself relative to the main instrument—the insulated part is framed in red in the top left part of Figure 1. In turn, this allowed the application of a DC bias voltage U using a power supply (Delta Elektronika). The polarity was chosen such that the main chamber and especially the electron analyzer are grounded while the cryostat unit and thus the liquid jet are on negative polarity. The resulting electric field accelerates the photoelectrons towards the electron analyzer. The right inset of Figure 1 depicts in schematic way the interaction of the microjet flowing down vertically from the top where it is illuminated by the synchrotron beam propagating along the x -direction, while the photons linear polarization axis lies in the x - y -plane. Photoelectrons were collected parallel to polarized electric field vector with the electron analyzer lying in the x - y -plane.

PE measurements were carried out at the SOL³PES setup²³ at the U49/2-PGM-1 beamline²⁴ at the BESSY II electron storage ring operated by the Helmholtz-Zentrum Berlin für Materialien und Energie. Valence PE spectra were recorded using a photon energy of $h\nu = 123.464 \pm 0.004$ eV, which was calibrated on a daily basis performing photoelectron yield measurement. We specifically obtained the so-called electron-yield X-ray absorption spectra generated by integration of the electron emission arising from the 2p3p3s Auger decay channel of an argon resonance at $h\nu = 246.928$ eV.²⁵ Note that at $h\nu = 123.464$ eV a 10% contribution from the respective 2nd harmonic light ($h\nu = 246.928$ eV) is present. The instrumental energy resolution for all measurements is ~ 0.25 eV (FWHM) determined by the settings of the electron analyzer (0.165 eV) and the beamline (0.125 eV). The X-ray spot size was defined by the beamline exit slit and had a rectangular shape of 40×60 μm (horizontal \times vertical).

Absolute binding energies. Upon application of a negative bias voltage U onto the electrically insulated microjet, the photoelectrons from the liquid are accelerated towards the grounded electron analyzer. As commonly done, we dissolved small amounts of ionic charge carriers (typically ~ 50 mM) of, *e.g.*, NaI or tetrabutylammonium iodide (TBAI) to ensure conductivity of the solutions. This enables to bias the whole liquid with the applied

offset potential U and to discharge local streaming potentials or the positive charging caused by the photoionization process.²⁶ Thus, the kinetic energies (KE) of the whole liquid-phase PE spectrum is shifted by the energy-offset eU , where e is the elementary charge. This allows to measure the kinetic energy (KE_{SF}) corresponding to a particular spectral feature, and at the same time to detect the electron distribution of the low kinetic energy curve resulting mostly from inelastically scattered electron processes.^{27,28} Most importantly, the onset of the low kinetic energy distribution defines the smallest electron KE by which a photoelectron can just be ionized and can escape the solution into vacuum, denoted here as KE_{cut} . Hence, we determine KE_{cut} by fitting the onset of the the low kinetic energy distribution—details are discussed in Reference 21 and the SI. Thus, the energy difference of $\text{KE}_{SF} - \text{KE}_{cut}$ at a given $h\nu$ allows to determine the absolute binding energy of a particular spectral feature BE_{SF} with respect to the vacuum ionization potential as

$$\text{BE}_{SF} = h\nu - (\text{KE}_{SF} - \text{KE}_{cut}). \quad (1)$$

This procedure is hereafter referred to as ‘absolute BE determination’. This BE calibration method is less prone to error—unlike calibration methods where gas-phase peaks are related to liquid-phase ones—because any kind of offset or contact potential induces an equal and simultaneous shift of the spectral features (KE_{SF}) and the KE_{cut} . Typical sources for these offset potentials are the streaming potential or charging induced by the photoionization.²¹ As long as the offset potentials remain constant as a function of time, also the value of the applied bias voltage U can be chosen conveniently. Figure 3 shows an example of this method—the left and right parts of the upper panel respectively show the low kinetic energy curve and the valence band (VB) PE features of a 50 mM NaI liquid ammonia solution as a function of the measured KE illustrated by the top horizontal axis. Note that the steep slope of the low kinetic energy curve is located at $\text{KE} \sim 50$ eV resulting from the applied bias voltage of $U = 50$ V. The BE axis illustrated at the bottom horizontal axis has been determined using the calibrated photon energy of $h\nu = 123.464 \pm 0.004$ eV.

Gas-to-liquid-phase binding energy shifts. In order to obtain a physically motivated estimate of the gas-to-liquid BE shifts of solutes, including benzene in liquid ammonia as well as in pure liquid benzene, we use the relevant Born–Haber thermodynamic cycle²⁹ in combination with the Born equation for solvation free energies in a dielectric continuum. This cycle is illustrated in Figure 2. By summing the cycle up, we find that the gas-to-liquid BE shift $\Delta^{\text{BH}}\text{BE}$ can be expressed as

$$\Delta^{\text{BH}}\text{BE} = \text{BE}^{\text{liq}} - \text{BE}^{\text{gas}} = -(E^{\text{vap}} + E^{\text{solv}}), \quad (2)$$

where BE^{liq} is the vertical BE in the liquid environment, BE^{gas} is the vertical BE in the gas phase, E^{vap} is the vaporization free energy and, finally, E^{solv} represents the solvation free energy.

Clearly, the respective values of the vaporization and solvation free energies of oxidation states of species X prior to (X_{solv}^Z) and after (X_{solv}^{Z+1}) the photoionization have to be known in order to apply the Born–Haber cycle in Figure 2. Within the dielectric continuum description of the solvent, these quantities, generally denoted as changes in Gibbs free energy ΔG , are approximated by the well-known Born equation³⁰

$$\Delta G = \frac{Z^2 e^2}{8\pi\epsilon_0 R} \left(1 - \frac{1}{\epsilon_r}\right), \quad (3)$$

where Z is the oxidation number of the solute, ϵ_0 is the vacuum permittivity, ϵ_r is the relative dielectric constant of the environment and R is the effective radius of the sphere that approximates the shape of the solute. In contrast to the fully relaxed solvation processes described by the Born equation, PES probes vertical BEs of the final ionized state X_{solv}^{Z+1} , which corresponds to ionization processes happening on much faster time scales than needed for solvent reorganization. Therefore, the photoionization of the initial state X_{solv}^Z induces only electronic relaxation of the solvent without a rearrangement of the molecular geometry.²⁹

In order to be able to close the Born–Haber cycle, the solvation free energy E^{solv} must thus describe only the electronic part of the solvent relaxation during solute solvation. This is accounted for by replacing the full static dielectric constant ϵ_r by its high frequency limit, which is equal to the square of the refractive index n^2 . This yields the relevant modified form of the Born equation for E^{solv}

$$E^{\text{solv}} = \frac{Z^2 e^2}{8\pi\epsilon_0 R} \left(1 - \frac{1}{n^2}\right). \quad (4)$$

Importantly, the corresponding vaporization free energy E^{vap} is zero for neutral species with $Z = 0$ within

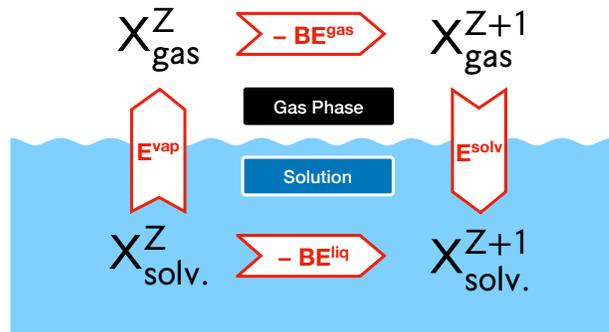


FIG. 2. Schematic illustration of the Born–Haber cycle: when probing the neutral solute ($Z=0$) of e.g. X being benzene via photoionization in a given solvent, the solute changes its oxidation number and becomes in the present case the benzene radical cation ($Z+1=1$).

the continuum electrostatic description as follows from Equation 3. For realistic systems, the (non-zero) vaporization enthalpy and entropy data are tabulated for common compounds³¹ and the corresponding free energies are calculated in the SI. However, even in realistic systems, this quantity can be neglected in comparison to the solvation energy E^{solv} of the nascent radical cations (Figure 2) since it is typically on the order of the error bar (as shown below). It follows that the gas-to-liquid shift depends only on the value of E^{solv} and, consequently, only on the refractive index n of the surrounding solvent. Since its typical values lie in the range from 1.3 to 2.0 for most solvents, in spite of the fact the corresponding static dielectric constants may vary by an order of magnitude, the Born–Haber model predicts that gas-to-liquid shifts will be similar for neutral solutes among a multitude of solvents. Note that if the initial state ($X_{\text{solv}}^{Z \neq 0}$) was charged, the situation would be quite different as one could not exclude the solvent nuclear reorganization and the corresponding dependence on ϵ_r from the picture. The effect of the specific choice of solvent on gas-to-liquid shifts of charged solutes is discussed in References 1 and 20.

Last to discuss is the estimation of the solute effective radius R to be used in Equation 4. In this work we use the first maximum of the relevant radial distribution function (RDF) while the deviation of the molecular structure from a perfect sphere is estimated using the width of the corresponding RDF peak. Note that the more the molecular geometries deviate from the assumed spherical shape, the less accurate the Born equation and the following gas-to-liquid BE shift estimates become.

Computational Methods

Gas-phase calculations. The gas-phase thermal structures of benzene were sampled using *ab initio* molecular dynamics (AIMD) performed in CP2K 7.1 software equipped with the Quickstep module.³² The energies and forces were obtained on the fly using the revPBE0-D3^{33–36} hybrid density functional to describe the valence electronic structure, while the carbon core electrons were modeled by the Gödecker-Tetter-Hütter (GTH) pseudopotentials.³⁷ The Kohn–Sham orbitals were expanded into the TZV2P-MOLOPT-GTH primary basis set³⁸ and the electron density was represented in a plane wave basis capped at the energy of 600 Ry. To accelerate the calculation, we additionally employed the Auxiliary density matrix method with the cpFIT3 fitting basis set.³⁹ To comply with the employed Poisson electrostatics solver, the simulated molecule was placed into a 11 Å wide cubic box and kept in its center throughout the course of the simulation, however, the boundary conditions were kept open. With these settings, the nuclei were numerically propagated using the Verlet integrator with a 0.5 fs integration time step. Canonical sampling was ensured by a local stochastic velocity thermostat⁴⁰ with a 50 fs

time constant keeping the temperature fixed at 300 K and the total simulated time was 20 ps. The G_0W_0 calculations^{41,42} were performed consistently in the CP2K 7.1 software package on top of AIMD geometries separated by 20 fs. The same DFT method and primary basis were employed to calculate the initial Kohn–Sham wavefunction and the RI-TZ resolution-of-identity auxiliary basis set was used to decompose the Hartree–Fock integrals. The self energy was continued analytically on the real frequency axis using the Padé approximation and the Newton-Raphson fixed point iteration was used for the numerical solutions.

Calculations in liquid ammonia The solution of benzene in liquid ammonia was simulated with a similar computational methodology to the one described above used for the gas phase. The liquid ammonia environment surrounding the benzene molecule was represented using 64 explicit solvent molecules under periodic boundary conditions—this corresponds to a simulated concentration of 0.65 mol l⁻¹. In this case, the temperature was set to 223 K to keep the solvent liquid and the total simulated time was 100 ps. The G_0W_0 calculations were consistently performed on top of the simulated ensemble of explicitly solvated structures. A detailed description of the performed condensed-phase simulations can be found in References 16 and 43.

3. RESULTS AND DISCUSSION

Gas-Liquid-Phase Shift in Ammonia

The upper panel of Figure 3 shows in its left and right part the measured PE spectrum of the low kinetic energy curve and the VB, respectively, as a function of the kinetic energy (on the top horizontal axis), with the binding energy axis (plotted as the horizontal axis at the bottom) being absolute BE determined using equation 1. The liquid highest occupied molecular orbital (HOMO) corresponding to the $3a_1$ molecular orbital of the gas phase ammonia molecule is determined at $BE_{3a_1}^{\text{liq}} = -8.96 \pm 0.02$ eV. This value is in good agreement with the value $BE_{3a_1} = -9.09 \pm 0.05$ eV stated in Reference 17. There, the binding energy calibration was performed by referencing the gas-phase peak to a previously determined value of $BE_{3a_1}^{\text{gas}} = -10.93$ eV.⁴⁴ Using $BE_{3a_1}^{\text{gas}}$ we now determine the gas-to-liquid shift in ammonia to be $\Delta BE_{\text{NH}_3} = -1.97$ eV, which differs only by 13 meV compared to the value stated in Reference 17—small systematic errors may have led to cancellation of errors in the assignment done in the previous paper as pointed out in the SI.

The experimental liquid ammonia spectrum is in excellent agreement with the theoretical prediction of the electronic density of states¹⁷ (EDOS) calculated by a combination of condensed-phase AIMD and G_0W_0 calculations⁴¹ performed on the obtained thermal structures, which are shown as red curve in the lower panel of Fig-

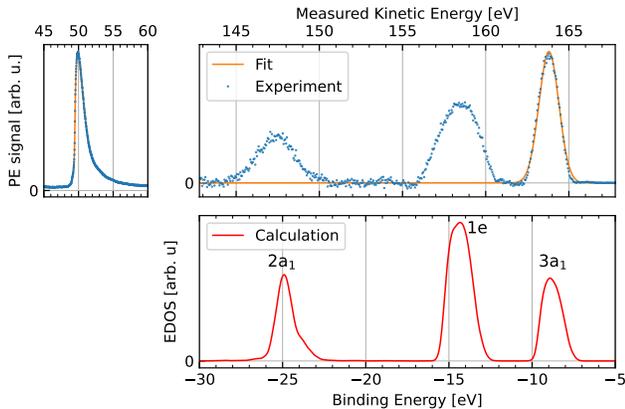


FIG. 3. The top left and right parts depict the low kinetic energy curve and the valence band PE spectrum (blue dotted line) of a 50 mM NaI liquid NH_3 solution - both shifted by ~ 50 eV upon application of a bias voltage of $U = 50$ V. The indicated fits (red curves) to the low kinetic energy curve and the liquid HOMO ($3a_1$) enable to determine the liquid-phase binding energy axis - depicted in the lower panel - being determined on an absolute scale using the well calibrated photon energy of $h\nu = 123.464 \pm 0.004$ eV. Bottom: comparison with the calculated electronic density of states (red line) using the G_0W_0 method clearly shows that the experimental spectral features are broadened.

ure 3. Note that while the relative peak positions between the experiment and the calculation are reproduced extremely well, the predicted peak widths are systematically smaller in the theoretical data. This effect is common to all calculations of this type and is caused by a combination of several factors. Notably, the calculation relies on classical AIMD and, therefore, samples, unlike the experiment, a classical ensemble of configurations. Moreover, the experiment captures non-elastic scattering processes which lead to slightly asymmetric line shapes towards higher BEs in the experimental spectra—the description of this goes beyond the level of theory used here.

We calculated the gas-to-liquid shift of ammonia in liquid ammonia to be $\Delta^{\text{BH}}\text{BE}_{\text{NH}_3}^{\text{NH}_3(1)} = -2.01$ eV using Equation 4. For this, we estimate the radius R using half of distance estimated for the maximum of the first peak of the RDF in ammonia. The average nitrogen-nitrogen distance is 3.45 \AA ⁴⁵. These estimates from the Born-Haber approximation thus recover the measured gas-to-liquid shift in ammonia of $\Delta\text{BE}_{\text{NH}_3} = -1.97$ eV extremely well.

There are a number of other effects that are not captured within the Born model such as the dipole-dipole interactions between the ammonia molecules or various effects at the liquid surface. There is a contribution to the gas-to-liquid shift from a net surface dipole resulting from the orientation of dipolar molecules at the surface. For example this has been calculated to be ~ 0.14 eV for water.^{46,47} Since we can only speculate about the orien-

tation of ammonia at the liquid surface, we assume the value of the surface potential to be smaller for ammonia. The surface dipole effect of benzene should be zero, since benzene does not possess a permanent electric dipole moment. Other sources for potential differences can result from surface active in contrast to bulk active species.⁴⁸ In conclusion, all these effects only have minor influences to the gas-to-liquid phase BE shift in terms of their order of magnitude compared to the major contribution conceived within the Born-Haber model.

Gas-Phase Benzene

The top panel of Figure 4 depicts the gas-phase PE spectrum of benzene which has been recorded by moving the liquid jet out of the synchrotron light beam such that only benzene molecules that evaporated from the liquid surface are ionized. The binding energy of the spectrum has been calibrated like the spectrum shown in the top panel of Figure 5—details are discussed in the section on ‘Liquid Benzene’.

Following Reference 12, the spectral features as a function of decreasing binding energy can be assigned with the molecular orbitals $1e_{1g}$, $3e_{2g}$, $1a_{2u}$, $3e_{1u}$, $1b_{2u}$, $2b_{1u}$, $3a_{1g}$, $2e_{2g}$, $2e_{1u}$ and $2a_{1g}$, which represents the electronic configuration of the neutral single-determinant ground state. The orbitals $1e_{1g}$, $3e_{2g}$ and $3a_{1g}$ show a vibrational progression very similar to the spectra shown in Reference 12, which contains the most recent benzene gas-phase investigation containing the best resolved spectra.

The binding energy of the gas-phase HOMO $1e_{1g}$ has been determined from the peak maximum of the convoluted experimental data as $\text{BE}_{1e_{1g}}^{\text{gas,exp}} = -8.92 \pm 0.08$ eV, which is in excellent agreement with the mean of the calculated HOMO of $\text{BE}_{1e_{1g}}^{\text{gas,calc}} = -8.90$ eV, as shown in the lower panel of Figure 4.

Consistent with the previously published theoretical data focusing on liquid ammonia¹⁷ (Figure 3, bottom panel), the gas-phase benzene experimental peak positions are closely reproduced by the G_0W_0 calculations. The individual peaks in the calculated EDOS were furnished with the corresponding orbital irreducible representation labels and the assignment was confirmed by comparison of the calculated degeneracies with those predicted by the symmetry labels (see Section S7 of the SI) as well as by comparison of the labels with the symmetries of the spatial orbitals themselves. These are shown in the bottom part of Figure 4. However, it appears that the calculation at the chosen level of theory systematically tends to underestimate energy differences between close-to-degenerate levels (in particular the $1a_{2u}$ and $3e_{2g}$ peaks) and, as a result, the resolution in several experimental peaks is suppressed in the computational counterpart. In section S6 of the SI, we discuss that the simple iterative version of G_0W_0 , the evGW method,⁴² allows to recover some of these missing features, but also

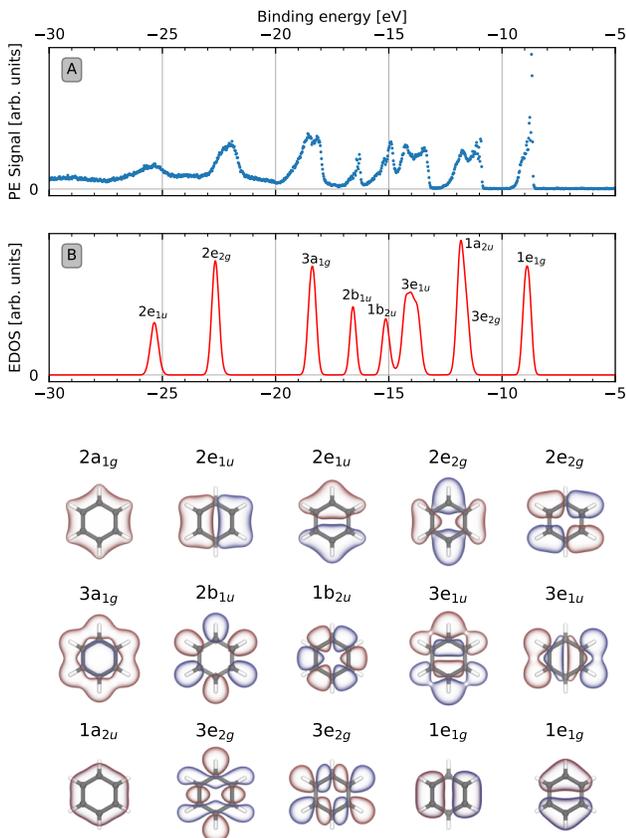


FIG. 4. Electron binding energies of gas-phase benzene. Panel A: PES spectrum of the gas phase. Panel B: calculated electronic density of states using the G_0W_0 method. Grid: Kohn-Sham canonical molecular orbitals of minimum-geometry benzene calculated by the revPBE0-D3/TZV2P-MOLOPT-GTH method. The red surface shows a contour of the orbitals at $0.025 a_0^{-3/2}$, the blue surface then a contour at the same magnitude with a negative sign.

causes an overall worsening of the EDOS quality. Moreover, note that the gas-phase experiment captures the fine vibrational structure clearly in several peaks; this effect is not reproduced by the calculations that build on classical thermal structures with a continuous energy distribution. In this direction, far more advanced calculation methods are available for gas-phase systems,¹² however, the present computational results are sufficient for the investigations we undertake here, since we are primarily interested in the BE shift of the gas-to-liquid-phase peak upon solvation. These gas-phase calculations are methodologically complementary to the ones used for the liquid system and, therefore, represent a reasonably consistent foundation to compare the theoretical results to the experimentally determined ones. In general, our findings are in good agreement with values stated in Reference 12, where the gas-phase HOMO is experimentally determined to -9.24 eV and computationally to -9.12 eV without additional error bars.

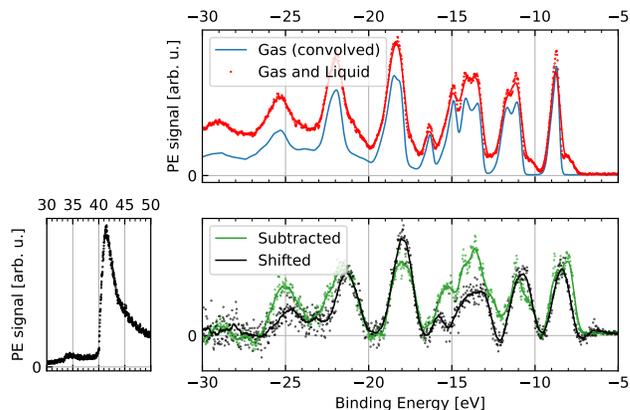


FIG. 5. Top panel: measured gas-and-liquid-phase spectrum (red line) and gas-phase spectrum (blue line) from a pure liquid benzene microjet (without any salt). Bottom panel: liquid-phase PE spectrum of benzene derived via the two different procedures as described in the main text: the difference spectrum resulting from the subtraction of the spectra in the upper panel is plotted in green. The spectra of the low kinetic energy curve and the VB of the 50 mM TBAI solution mixture—consisting of 90% benzene and 10% 2-propanol—are shown in black in the left and right panel, respectively. Note: the low kinetic energy curve is plotted as a function of the measured kinetic energy upon application of a bias of -40 V while the VB has been absolute BE determined and plotted as a function of BE to give a better comparison with the difference spectrum shown in green.

Liquid Benzene

The liquid phase VB spectrum of benzene has been measured using two different procedures in the experiment, with details on the analysis given in the SI. Only the two procedures combined allowed to unambiguously determine the valence band peak structure and its absolute calibrated BEs. This is a consequence of the fact that we have not managed to dissolve considerable amounts of ionic species in pure liquid benzene to ensure sufficient conductivity, therefore, we needed to admix a small amount of a second solvent in addition to the salt. Firstly, the gas-and-liquid-phase spectrum of pure liquid benzene (without any salts dissolved) has been measured and is plotted as a red line in the upper part of Figure 5. It is shown together with the pure gas-phase spectrum (blue line). The respective liquid-only PE spectrum is obtained from the difference between the two spectra which is plotted as green dots in the lower part of Figure 5 (the green line corresponds to a convolution of the experimental data by a box kernel 20 datapoints wide). The pure gas-phase spectrum (blue line) has been convoluted using a Gaussian function with a full-width-at-half-maximum of 0.11 eV to match the broadened gas-phase peaks of the gas-and-liquid-phase spectrum in order to avoid artificial peaks in the subtraction process.

In our second approach, we used a 50 mM tetrabutyl-

lammonium iodide (TBAI) solution mixture consisting of 90% benzene and 10% 2-propanol. In this way, we could dissolve ions at a sufficient amount in the benzene and 2-propanol mixture to ensure conductivity, which was impossible in pure benzene. This allowed us to apply a bias voltage onto the liquid jet enabling the same procedure as for ammonia to determine absolute BEs of the liquid-phase spectral features by additionally determining KE_{cut} . The left part of the lower panel of Figure 5 depicts the spectrum of the low kinetic energy curve as a function of the kinetic energy, while the right part shows the VB spectrum as a function of the binding energy (absolute BE determined). The black straight line again corresponds to a convolution of the data points with a box kernel as above. Qualitatively, the two different experimental procedures yield almost the same BEs of the individual spectral features of the VB of the liquid-phase of benzene which can clearly be distinguished. The solid green and black line indicate intensity fluctuations of the same peak. Comparing the scatter plots of the individual data points shows that the spectral features coincide also quantitatively well within the experimental uncertainty. We find that the liquid phase spectrum can essentially be considered as a shifted and slightly broadened gas-phase spectrum and the same gas-phase orbital assignment can directly be applied.

Using the analysis described in the SI, the absolute BE determination procedure has been performed using the photon energy of $h\nu = 123.464$ eV. The BE of the liquid-phase HOMO corresponding to the gas-phase $1e_{1g}$ orbital has been determined in the experiment as $BE_{1e_{1g}}^{liq} = -8.42 \pm 0.05$ eV. Using the absolute BE method together with known benzene gas-phase energies $BE_{1e_{1g}}^{gas} = -9.24$ eV¹² we determine the gas-to-liquid-energy shift to be $\Delta BE_{C_6H_6}^{C_6H_6(1)} = -0.82 \pm 0.05$ eV. This value is only slightly larger than the value $\Delta BE_{C_6H_6}^{C_6H_6(1)} = 0.50 \pm 0.18$ eV obtained when we apply the gas-phase reference method using the spectra of gas-phase and gas-and-liquid-phase benzene shown in Figure 5. Comparing this to the estimate of the Gibbs free energy of solvation using the Born equation where we approximated $\Delta^{BH}BE_{C_6H_6}^{C_6H_6(1)} = -1.36$ eV using $R = 2.95$ Å.⁴⁹ We find that the Born–Haber model overestimates the gas-to-liquid-shift compared to the experimentally determined one of $\Delta BE_{C_6H_6}^{C_6H_6(1)} = -0.82 \pm 0.05$ eV by ~ 0.5 eV. We attribute this discrepancy to the fact that the benzene molecular geometry is planar and thus deviates to a large extent from a sphere which is assumed in the derivation of the Born equation.

Benzene in Liquid Ammonia

The top panel of Figure 6 shows the measured VB PE spectrum of a solution of a 0.05 M NaI + 0.25 M benzene in liquid ammonia (blue data points). The binding energy axis has been absolute BE determined using a bias

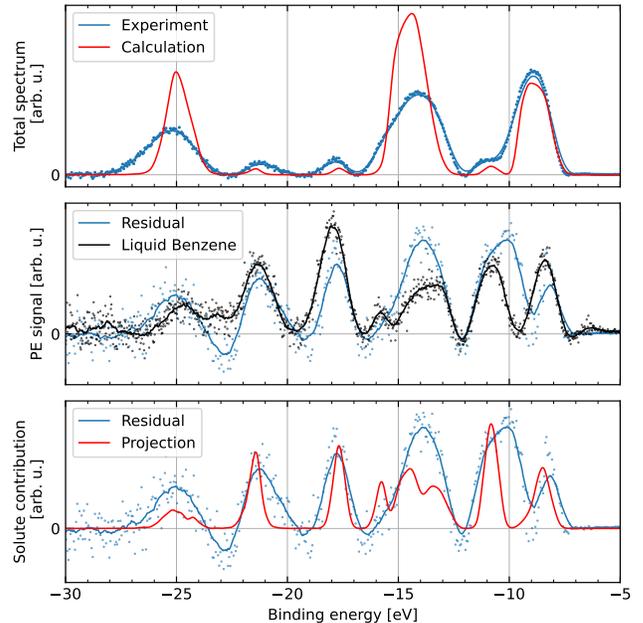


FIG. 6. Experimental results and theoretical prediction of the XPS of the liquid ammonia solution of benzene. Top panel: The total PE spectrum of 0.05 M NaI and 0.25 M benzene in liquid ammonia (blue data points) and the computational prediction of the EDOS corresponding model (red curve). Central panel: Difference spectrum (Residuals, blue curve) of the 0.05 M NaI and 0.25 M benzene in liquid ammonia spectrum minus the pure ammonia spectrum shown in the top panel of Figure 3 is plotted together with the benzene and 2-propanol spectra (black curve)—both spectra are absolute BE determined. Bottom panel: The same difference spectrum (Residuals, blue curve) corresponding to the solute contribution is compared to the theoretical benzene PDOS.

voltage of $U = -50$ V, together with a calibrated photon energy of $h\nu = 123.464$ eV. The computational prediction of the EDOS (red curve) well reproduces not only the overall VB spectral shape but also the individual BE peak positions. All experimentally recorded spectral features show a peak broadening relative to the computed ones, as discussed previously.

The central panel of Figure 6 shows a difference spectrum (residuals) where the pure ammonia spectrum shown in the top panel of Figure 3 has been subtracted from the experimentally recorded 0.05 M NaI and 0.25 M benzene in liquid ammonia spectral intensity distribution shown in the top panel of Figure 6. It has been calculated by first scaling the peak maximum of the liquid HOMO of each spectrum to unity, while the BE axis both spectra has been absolute BE determined before the subtraction has been performed. The residual spectral intensity is plotted as blue dots in the central and bottom panel of Figure 6 together with the experimentally determined liquid phase VB spectrum of the benzene and 2-propanol solution (black curve) which is also shown in Figure 5. The VB peaks of both spectra coincides very well com-

paring the centroid BE positions as well as their spectral shapes. The only part of the VB where discrepancies appear in the residuals relative to the pure benzene spectrum are between the peaks corresponding to the molecular orbitals of $1e_{1g}$ and $3e_{2g}$. The liquid HOMO peak seems squeezed at higher binding energies while the $3e_{2g}$ peak seems broadened towards lower BE: we attribute this discrepancy as an artefact resulting from the subtraction procedure.

The agreement between the two independently constructed spectra provides strong experimental evidence that a solution of solvated benzene in ammonia may be understood as a simple sum of its constituent parts (i.e., the pure liquid-phase spectra of benzene and ammonia). The bottom panel of Figure 6 depicts again the experimental residuals resulting from the subtraction and the calculated projected density of states (PDOS) of benzene in liquid ammonia which has been projected onto the appropriate atomic basis functions localized on benzene and thus showing only the solute contribution.^{16,50}

Using Equation 4, the solvation free energy of the benzene radical cation in liquid ammonia has been calculated as $\Delta^{\text{BH}}\text{BE}_{\text{C}_6\text{H}_6}^{\text{NH}_3(1)} = -1.18$ eV—we use the same radius $R = 2.95$ Å⁴⁹ as in the case of benzene in liquid benzene – details are given in the SI. Similar to the case of benzene in liquid benzene we attribute the discrepancy between $\Delta\text{BE}_{\text{C}_6\text{H}_6}^{\text{NH}_3(1)} = -0.82$ eV and $\Delta^{\text{BH}}\text{BE}_{\text{C}_6\text{H}_6}^{\text{NH}_3(1)} = -1.18$ eV to the large deviation of the planar molecular geometry of benzene relative to a sphere. However, when comparing the values of $\Delta^{\text{BH}}\text{BE}_{\text{C}_6\text{H}_6}^{\text{NH}_3(1)} = -1.36$ eV and $\Delta^{\text{BH}}\text{BE}_{\text{C}_6\text{H}_6}^{\text{C}_6\text{H}_6(1)} = -1.18$ eV, they only differ by 0.18 eV. Despite the fact that the approximated absolute values differ from the experimental ones by ~ 0.5 eV, the modified Born model given in Equation 4 estimates almost the same solvation free energy. Replacing the static dielectric polarizability by the fast component of the dielectric response essentially captures the observed phenomenon: while we have observed large BE shifts of the VB peaks for benzene and ammonia upon solvation from the gas-phase, the solvation of benzene in ammonia induces practically no measurable BE shifts compared to the situation in pure liquid benzene.

Surface activity of Benzene in liquid Ammonia

Upon using a photon energy of ~ 123 eV we are probing approximately 1–3 nm into the liquid phase.⁴ This corresponds on average to 3–10 monolayers when assuming the average inter-particle distance of ammonia to be ~ 0.345 nm (details are given in the SI). As shown in the previous section, the spectra of benzene dissolved in liquid ammonia can be decomposed using a simple addition of the pure benzene and pure ammonia spectra, therefore, we do not anticipate BE shifts of individual spectral features when going from the bulk to the surface. At the same time, benzene is expected to be surface active in

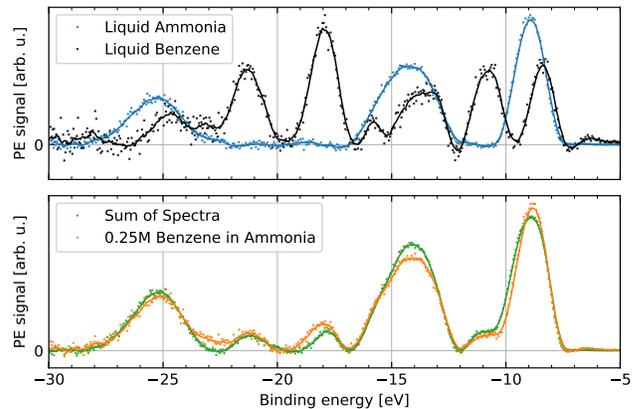


FIG. 7. Top panel: normalized VB PE signal intensities $I_{\text{C}_6\text{H}_6}$ of pure benzene (blue curve) and I_{NH_3} of ammonia (red curve) plotted as a function of the BE using the absolute BE determination. Lower panel: a weighted sum of both normalized pure spectra (green line).

liquid ammonia, which should result in an observable effect when comparing the ratio of the integrated spectral intensity of benzene relative to that of ammonia.

The top panel of Figure 7 shows the normalized VB PE signal intensities $I_{\text{C}_6\text{H}_6}$ of pure liquid benzene (blue curve) and I_{NH_3} of pure liquid ammonia (red curve) plotted as a function of the BE using the absolute BE determination. For the normalization process the area under all spectral features of the entire VB have been summed up such that all VB ionization features are captured. The lower panel of Figure 7 shows a weighted sum of both normalized pure spectra (green line) where $I_{\text{C}_6\text{H}_6}$ has been scaled by a factor α before it was added up to I_{NH_3} . An optimizing procedure has been implemented where the factor α is manipulated until the area of the weighted sum spectrum equals the area of the measured spectrum of 0.25 M benzene in liquid ammonia (yellow line in Figure 7 and further details on the procedure in the SI). The sum spectrum (green line) corresponds well with the measured spectrum of 0.25 M benzene in liquid ammonia (yellow line) which gives us confidence in our conclusions of the additivity of the spectra of the individual species.

Thus, a ratio of spectral intensities $I_{\text{C}_6\text{H}_6} / I_{\text{NH}_3} = 0.2$ has been determined, meaning that the normalized spectral intensity of benzene observed in the PE studies is ~ 5 times smaller than the one of ammonia. At the same time, in the solution prepared for the experiment, the concentration was 0.25 mol l^{-1} . By taking the number of valence electrons and the atomic abundances of the two different molecules into account, we get a ratio that reflects the density of populated states (DoS) of the VB: $\text{DoS}_{\text{C}_6\text{H}_6} / \text{DoS}_{\text{NH}_3} \sim 1/44$. This ratio reproduces quantitatively the ratio of $\sim 1/43$ of the EDOS determined from the theoretical calculations (red curve shown in the top panel of Figure 6).

In order to compare the ratio of the DoSs with the

ratio of the signal intensities of the measured spectrum, properties of the ionization process during the photoemission process need to be accounted for, namely the different ionization cross sections as well as anisotropies related to experimental geometries (details of this calculation are given in the SI). Thus, the ammonia peak areas should be about ~ 147 times larger than the benzene ones. The discrepancy between the ratio of ~ 5 observed in the measured PE spectra and the above deduced ratio of ~ 147 can be explained by assuming that benzene is surface active. Following this reasoning we can deduce that the concentration of benzene at the surface is on average about an order of magnitude higher than in the bulk. This implies the possibility of aggregation alongside with an increased benzene-benzene interaction or even phase separation of the solute on the liquid microjet surface, which would provide an alternative explanation of the observed spectral additivity. There is no practical way to judge the state of the jet surface experimentally with the current set-up in order to completely exclude the possibility of a phase separation. However, there are several arguments favoring that our result are not a product of phase segregation. When estimating an error of the above approximation (details are given in the SI) we conclude that the uncertainty by which the concentration of benzene is enriched at the surface is $>20\%$. The liquid jet is in a non-equilibrated state when it is released into vacuum; there is significant evaporation going on from its surface into the vacuum which in turn induces rearrangement of the particles at the surface. Additionally, by comparison with the theoretical calculations of the benzene-ammonia solution where the solute is fully solvated at all times and where the spectral additivity is preserved, we conclude that the experimentally observed additivity must be possible without phase separation and corresponds simply to what is anticipated for a surface-active species like benzene in liquid ammonia.

4. CONCLUSION

The major finding of this study is the observation of large solvent-induced shifts in valence electron binding energies of benzene, as observed via X-ray PE spectroscopy. Notably, these gas-to-liquid shifts are almost the same for liquid ammonia as a polar solvent and pure benzene as a non-polar one. This observation can be rationalized in terms of the Born-Haber solvation model. When interpreting shifts in electron binding energies extracted from PE spectra this model accounts for solvent response to charged solutes only. In case of solutes that are neutral before photoionization, such as benzene in the present case, the solvent shift within the Born-Haber model is solely due to the high frequency dielectric response of the solvent to the nascent benzene radical cation. The vertical photoionization process does not involve any nuclear solvent relaxation around the newly formed cationic solute. This explains why the solvent-

induced shifts are practically the same in liquid ammonia and in benzene—while these two liquids have very different static dielectric constants (reflecting different nuclear relaxation in polar vs non-polar solvents), their high frequency dielectric constants (due to electronic relaxation) are almost the same.⁵¹

SUPPORTING INFORMATION

Supporting information on the experimental measurement of the solubility of benzene in ammonia including additional graphics (Figure S1). Supporting information on the calibration procedure of absolute binding energies including additional graphics (Figure S2). Detailed discussion of the estimation of the solvation energy using the Born equation. Supporting information on the spectral intensity estimation for the benzene-ammonia solution including additional graphics (Figure S3). Supporting information on the gas-to-liquid shift in pure ammonia including additional graphics (Figure S4). Comparison of G_0W_0 and $evGW$ calculation for gas-phase benzene including additional graphics (Figure S5). Supporting information on gas-phase benzene orbital assignment including additional graphics (Figure S6).

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