The paper by Vinklarek et al. describes the pickup of water and small alcohol molecules by benzene clusters and based on mass spectrometry and MD simulations. As pointed out in the introduction, this study is of potential interest for the formation of icy layers on dust particles in the interstellar medium as well as on hydration of PAH containing aerosols in the atmosphere of the Earth. The study is a nice extension of previous papers published by this group where argon clusters were used as the host clusters instead of benzene. However, at the present stage, I cannot recommend publication since several important issues are not considered in the current explanation of the pickup process.

The authors claim that the average cluster size of the initial benzene particles is around 300. The mass spectra of the resulting benzene cluster ions shows an exponentially decreasing series with the highest yield at the monomer. This is in stark contrast to the assumption of no or little loss of water or alcohol following the ionization process. Furthermore, only this average size is considered in the discussion which is more than questionable, since the benzene clusters are definitely not monodisperse but typically exhibit a broad lognormal distribution. In combination with the expected Poisson statistics for the pickup, the fits to the measured cluster size distributions in Figure 2 should actually be fitted by a lognormal distribution.

In the supporting information the authors provide the information how the experimental data were obtained and they apparently set for all three hydrogen bonded adducts a constant pressure in the pickup cell of 10^-4 mbar. The pressure was determined via an ion gauge and the values were corrected according to the different total ionization cross sections. In my opinion, the correction factor for ethanol should be 2.7 since the total cross sections for water, methanol and ethanol at 200eV are 1.9, 4 and 6 x10^-20m^2. Another question concerning the particle density of the dopants is the base pressure in this chamber without added sample but with the cluster beam on. Benzene (correction factor of 5.9) and Ar (correction factor of 1.29) are expected to form an appreciable base pressure onto which the dopant has to be added and all with the corresponding correction factors. Keeping this in mind, the uncertainty of the values obtained for the relative uptake values discussed in the paper may not be that relevant.

In addition, several suggestions on the English and comments and questions on the content are added to the pdf files of the manuscript and the supporting information that the authors should consider in a revised version they plan to submit.
Reviewer: 2

Comments to the Author

I started reading this manuscript with much excitement based on the title and abstract where the authors describe the uptake of hydrogen bonding molecules by benzene nanoparticles. However upon going through the body of the paper, i have come to the conclusion that this manuscript should be rewritten, and much of the SI should come into the main body and be resubmitted as a JPC article.

1. There are no surprises or novel insight here. Yes different molecules were picked up and their uptake quantified, however to understand what is happening mechanistically one has to keep going back and forth between the main text and SI at a very regular rate. This suggests that to explain the details one would like to read the full paper.

2. The simulations are to calculate the radial distribution functions of pure benzene clusters and there are no simulations to explain the dynamics of uptake of the various molecules into the benzene cluster. They use the simulation to essentially confirm that they have a cluster composed of 300 benzene molecules.

3. I am surprised that there are no experimental and theoretical details in the main manuscript. I started looking for whether the binding energies were calculated by the authors in table 2. They have this in the caption of the table - "The first column of each series compiles data from the literature, the second column (spelling mistake here) is the theoretical estimate obtained by the same procedure for all systems." I hazard that these are then all data from the literature, so then the subsequent discussion about uptake corresponding to binding energies is essentially a correlation analysis from literature to their experimental results.

4. Finally based on their experimental observations and simulation, i do not think they have adequately answered their own question - are benzene clusters liquid or solid?

My recommendation is that the authors rewrite the paper as a full one for JPC.

Author’s Response to Peer Review Comments:
Dear Professor Editor,

thank you for your examination of our manuscript and sending us the reviewers’ comments, and inviting us to resubmit the manuscript:

**Uptake of hydrogen bonding molecules by benzene nanoparticles**

*Ivo S. Vinklárek, Andriy Pysanenko, Eva Pluhařová and Michal Fárník*

Reviewer #1 suggested major revisions. We have answered all her/his questions below and revised the manuscript accordingly. We would like to thank this reviewer explicitly for providing very detailed language corrections, which we have all followed. We understand and appreciate that this goes far beyond the usual reviewers’ job.

Reviewer #2 suggested to include our extensive SI into the main article and rewrite the paper as a full one for JPC. We believe that our work provides a relatively short and simple – yet important – message about the uptake of different molecules on benzene nanoparticles, which is potentially interesting for the general community of physical chemists, namely in atmospheric chemistry and astrochemistry. Yet the experiment and its interpretation are relatively complex, requiring extensive explanation and discussion. We would like to provide the major message for the general community in a concise letter format accompanied by the extensive SI with all the details for interested specialists (see also our reply to Reviewer #2 below). Therefore, we have still revised our manuscript in the letter format.

We have revised it according to the reviewers’ comments and answered all their questions below. We hope that you will now find our revised manuscript suitable for publication in the Journal of Physical Chemistry Letters.

Sincerely yours,

Michal Fárník
The paper by Vinklarek et al. describes the pickup of water and small alcohol molecules by benzene clusters and based on mass spectrometry and MD simulations. As pointed out in the introduction, this study is of potential interest for the formation of icy layers on dust particles in the interstellar medium as well as on hydration of PAH containing aerosols in the atmosphere of the Earth. The study is a nice extension of previous papers published by this group where argon clusters were used as the host clusters instead of benzene. However, at the present stage, I cannot recommend publication since several important issues are not considered in the current explanation of the pickup process.

Answer: We thank the reviewer for her/his positive evaluation of our manuscript, and especially appreciate her/his careful reading of our manuscript and providing detailed language corrections. We consider all her/his corrections and comments and answer her/his questions below. We believe that this improves the scientific as well as presentation quality of our manuscript and the reviewer will recommend it for publication.

The authors claim that the average cluster size of the initial benzene particles is around 300. The mass spectra of the resulting benzene cluster ions shows an exponentially decreasing series with the highest yield at the monomer. This is in stark contrast to the assumption of no or little loss of water or alcohol following the ionization process.

Answer: We explain in the SI that our mass spectra are not a good representation of the actual neutral cluster size distribution for two reasons: (1) the clusters fragmentation upon electron ionization, and (2) more importantly, the mass discrimination due to the perpendicular arrangement of our TOF spectrometer.

(1) The Bz—Bz bond is much weaker compared to the M—M hydrogen bonding in water, methanol and ethanol clusters. The experimental value for Bz dimer binding energy is 6.7 kJ/mol [Krause et al. CPL 184, 411 (1991)] compared to the M-M binding energies around 20 kJ/mol in Table 2. Besides, the cooperative effects in the hydrogen bond network, strengthen the binding in Mk clusters significantly. Therefore, it is reasonable to assume that Bz evaporates from the clusters upon the ionization while the adsorbed molecular cluster can remain essentially unfragmented. Besides, our major argument for little loss of water or alcohol following the ionization is the agreement of the fitted Poisson distributions, which deliver consistently almost identical pickup cross sections, i.e., the same cluster size. In addition, if the molecular clusters on benzene fragmented upon the ionization, the actual neutral cluster size could be only larger than the one evaluated from the Poisson distribution.

(2) However, the mass discrimination due to the perpendicular TOF arrangement represents even more important factor. The mass range, which can be measured without a significant mass discrimination with our TOF corresponds roughly to m/z 600. Thus, the entire mass spectrum of our large benzene clusters cannot be measured without discrimination. By changing the deflection voltages, we can record different portions of the mass spectrum. This is illustrated in the figure below.
For these two reasons, the real neutral cluster size is rather reflected by the pickup process and the Poisson analysis. To make this clearer, we have added a brief note in the manuscript on p. 4 and extensive explanation with the figure in SI on p. S5:

Manuscript, page 4:
It ought to be mentioned that due to the cluster fragmentation and limited discrimination-free mass range of our TOF spectrometer, the mean cluster size has been derived from the Poisson distribution of the adsorbed molecular clusters rather than from the mass spectra, as is detailed in SI.

SI, page S5
In addition, the size information about the large cluster ion fragments is limited in our experiment due to the perpendicular TOF arrangement, which limits its size range. All the clusters generated in supersonic expansions attain essentially the same velocity with a very narrow distribution. When the ionized clusters are extracted in the TOF region perpendicularly to the beam velocity, they keep the component of velocity parallel to the beam, and thus the heavier ones, which spend longer time in the TOF region, can escape the detection. We can partially compensate for that effect by applying a deflection voltage in the beam direction, however, that can lead to a loss of the smaller cluster ions. The effect of the deflection voltage is illustrated in Figure S2.

Figure S2: Dependence of the measured mass spectra on the deflection voltage dX.

A different method to determine the neutral cluster size based on the pickup of molecules will be introduced below. It assumes the Poisson statistics for the pickup process, which has been well established for clusters in the literature. It suggests that the actual mean neutral cluster size is rather N ≈ 300, which is much larger than the observed maximum cluster fragment ion size, however, due to the above mentioned TOF perpendicular arrangement, we cannot observe such large clusters. The estimated size N ≈ 300 is quite realistic based on comparison with, e.g., water or argon clusters generated in our experiments, where also strongly fragmented spectra were observed for the large clusters.

Furthermore, only this average size is considered in the discussion which is more than questionable, since the benzene clusters are definitely not monodisperse but typically exhibit a broad lognormal distribution. In combination with the expected Poisson statistics for the pickup, the fits to the measured cluster size distributions in Figure 2 should actually be fitted by a lognormal distribution.

**Answer:** The reviewer is correct. The neutral cluster size distribution corresponds to a lognormal distribution, and the pickup process for each cluster size within this distribution follows the Poisson
statistics. Thus, in principle, one should convolute the lognormal cluster size distribution with the Poisson distributions with different cross sections for different sizes. However, this convolution will not result in a simple lognormal distribution. Thus, fitting the measured cluster size distributions in Figure 2 by a lognormal distribution is not correct. The convolution of lognormal and Poisson distributions might be too complex. We could find one attempt in the available literature to provide more accurate model [Vongehr et al. Chinese Phys. B 19 023602 (2010)] and a special case which did not follow the Poisson distribution [Vongehr and Kresin J. Chem Phys 119, 11124 (2003)]. However, for all practical purposes just the Poisson distribution has been used assuming that the host clusters can be represented by a mean cluster size, as broadly documented in the literature, e.g., [J. Chem. Phys. 102, 8191 (1995); J. Phys. Chem. A 101, 145 (1997); Int. Rev. Phys. Chem. 16, 215 (1997); J. Chem. Phys. 111, 2436 (1999); J. Phys. Chem. A 109, 9494 (2005); J. Phys. B: At. Mol. Opt. Phys. 39, R127 (2006), J. Chem. Phys. 135, 104305 (2011); J. Phys. Chem. A 125, 4750 (2021)]. Therefore, we find the Poisson distribution well justified in our present case upon the assumptions discussed in the manuscript in details. We have added the corresponding explanation and some of the references on p. 9:

It should be noted that the above approach assumes that all the clusters can be represented by the mean pickup cross section corresponding to the mean size $N$. Large clusters have log-normal size distributions and thus, in principle, a convolution of the log-normal and Poisson distributions should be used in the analysis. Nevertheless, for practical purposes the Poisson distribution has been mostly considered in the literature. Therefore, we find the use of the Poisson fits in the present case justified.

In the supporting information the authors provide the information how the experimental data were obtained and they apparently set for all three hydrogen bonded adducts a constant pressure in the pickup cell of $10^{-4}$ mbar. The pressure was determined via an ion gauge and the values were corrected according to the different total ionization cross sections. In my opinion, the correction factor for ethanol should be 2.7 since the total cross sections for water, methanol and ethanol at 200eV are 1.9, 4 and 6 x10^{-20} m^2.

**Answer:** Our value of 3.6 of the correction factor for ethanol has been taken directly from our ion gauge manual as recommended by producer. We can find slightly different values for different ion gauges and in the literature. The reviewer suggests the value of 2.7 based on the ionization cross section in the literature. Indeed, her/his value might be correct, however, that would not change anything on our results. Figure S6 in the SI shows that the measured relative uptake values are quite independent of the pressure in the given region and thus the shift due to a different correction factor would not change the relative uptake value at the actual pressure of $\approx 1.1 \times 10^{-4}$ mbar. We have added this explanation in SI on p S2:

Different correction factors could be found, e.g., 2.7 for EtOH. We show below (Figure S7) that the measured relative uptake ratios $R_{up}$ are independent of the pickup pressure in the investigated range $0.8-2.0 \times 10^{-4}$ mbar. Therefore, use of the different correction factor would not influence our results.

Another question concerning the particle density of the dopants is the base pressure in this chamber without added sample but with the cluster beam on. Benzene (correction factor of 5.9) and Ar (correction factor of 1.29) are expected to form an appreciable base pressure onto which the dopant has to be added and all with the corresponding correction factors. Keeping this in mind, the uncertainty of the values obtained for the relative uptake values discussed in the paper may not be that relevant.
Answer: The pressure in the pickup chamber with the cluster beam on is of the order of $10^{-6}$ mbar, i.e., two orders of magnitude lower that the corresponding pickup pressure of $\approx 1.1 \times 10^{-4}$ mbar. Therefore, any correction of this background pressure is negligible in the view of the error bars on the values obtained for the relative uptake values. We have added a note in this respect in SI on p. S2: The background pressure in the pickup chamber with the cluster beam on is of the order of $10^{-6}$ mbar.

In addition, several suggestions on the English and comments and questions on the content are added to the pdf files of the manuscript and the supporting information that the authors should consider in a revised version they plan to submit.

Answer: Once again, we thank the reviewer for the careful reading our manuscript including the accompanied SI, and we really appreciate the detailed language corrections, which we have all incorporated in the manuscript.

Reviewer: #2

I started reading this manuscript with much excitement based on the title and abstract where the authors describe the uptake of hydrogen bonding molecules by benzene nanoparticles. However upon going through the body of the paper, I have come to the conclusion that this manuscript should be rewritten, and much of the SI should come into the main body and be resubmitted as a JPC article.

1. There are no surprises or novel insight here. Yes different molecules were picked up and their uptake quantified, however to understand what is happening mechanistically one has to keep going back and forth between the main text and SI at a very regular rate. This suggests that to explain the details one would like to read the full paper.

Answer: We thank the reviewer for reading our manuscript and providing her/his comments and provide our answers below. Concerning the first comment above, we understand the reviewers’ point. Our experiment is relatively complex and many different factors have to be considered in the careful analysis of our data. It is difficult to discuss all the details and provide all supporting measurements within a concise letter format. On the other hand, the major message is relatively short and clear: we quantify experimentally an uptake of different hydrogen bonding molecules by nanometer-size benzene clusters; water is picked up less efficiently than methanol and ethanol. This conclusion is not interesting only for scientists specialized in clusters, but it can be important in many processes in atmospheric chemistry and astrochemistry. This makes our findings potentially relevant for the general community of chemical physicists, namely to atmospheric scientists and astro-chemists. Therefore, we chose the letter format where the main story is concisely told for the major part of the community, and provide comprehensive SI where the interested specialists can find all the details of the experiment and its analysis.

We value the reviewers’ suggestion to rewrite the manuscript with the SI as a comprehensive JPC article. However, in such case the actual interesting major message of our work could be lost in many technical details of a long and difficult to read article. Therefore, we extend the revised manuscript with some details based on the suggestions of both reviewers, yet, we keep the JPC Letter format.
2. The simulations are to calculate the radial distribution functions of pure benzene clusters and there are no simulations to explain the dynamics of uptake of the various molecules into the benzene cluster. They use the simulation to essentially confirm that they have a cluster composed of 300 benzene molecules.

**Answer:** Our work was mainly experimental and theory was implemented to calculate the large benzene clusters and also to calculate some of the pairwise interactions (M—Bz, M—M) so that we can provide consistent numbers at the same level of theory, see point 3. below. Simulating the collisions of the benzene clusters with the molecules, and subsequent dynamics of the molecules on/in the clusters would shed more light into the observed processes. However, this goes far beyond the possibilities of our experimental group supported by one colleague from a theory department. Nevertheless, our paper can stimulate such theoretical work in the future.

3. I am surprised that there are no experimental and theoretical details in the main manuscript. I started looking for whether the binding energies were calculated by the authors in table 2. They have this in the caption of the table - "The first column of each series compiles data from the literature, the second column (spelling mistake here) is the theoretical estimate obtained by the same procedure for all systems." I hazard that these are then all data from the literature, so then the subsequent discussion about uptake corresponding to binding energies is essentially a correlation analysis from literature to their experimental results.

**Answer:** There are no experimental and theoretical details in the main manuscript, since we opted for the letter format (see our answer to point 1.). Nevertheless, all the details can be found in the accompanying SI. Actually, our theoretical contribution was more extensive than suggested by the reviewer. As outlined above, we had to calculate all the M—Bz pairwise interactions, so that we could provide consistent numbers at the same level of theory for them. Surprisingly, not all data could be found in the literature. This has been mentioned explicitly in the footnote in Table 2: "In this work, the same procedure as in ". Since the footnote might escape the readers’ attention, now we mention this also in the text on p. 13 in the revised manuscript:

Therefore, we have calculated all the (M···Bz) binding strengths in the third column of Table 2 by the same method as used in Ref. 49.

4. Finally based on their experimental observations and simulation, I do not think they have adequately answered their own question - are benzene clusters liquid or solid?

**Answer:** Our experiments and calculations cannot answer this question unambiguously. We can only summarize all the evidence from our experiments and calculations, as well as the results of previous works. Based on this, we have arrived to the conclusions: “In this respect, the present experiments suggest that the molecules behave similarly on benzene cluster, i.e., the benzene clusters are liquid like or poses a QLL, and the embedded molecules are highly mobile and coagulate to the hydrogen bonded molecular clusters.” We are sorry that the reviewer is not satisfied with this answer, yet we refrain from any further speculations on this question. Besides, our major question was not the state of the benzene clusters, rather the uptake and behavior of other molecules by benzene clusters. We believe that our work has clarified this question unambiguously.
My recommendation is that the authors rewrite the paper as a full one for JPC.

Answer: Although we value and understand the reviewers’ recommendation, we argue in our answer to point 1. above, why we resubmit our revised manuscript in JPC Letter format.
Name: Peer Review Information for "Uptake of Hydrogen Bonding Molecules by Benzene Nanoparticles"

Second Round of Reviewer Comments

Reviewer: 1

Comments to the Author

The authors substantially improved the manuscript and answered my questions in great detail. I particularly like the explanation of the mass discrimination due to the orthogonal extraction and the different kinetic energy of large and small ions formed from a supersonic jet. This is now an exciting topic of relevance for a chemists, physicists, geo physicists and astronomers. I recommend publication of this paper as is.

Author's Response to Peer Review Comments:

Dear Professor Editor,

thank you very much for willing to accept our manuscript provided that we make the requested non-scientific changes. We have carefully checked the references in both the main article and SI and corrected the issues mentioned in your letter and several other minor errors which we have spotted. We apologize for these mistakes.

We are very pleased with the positive comment of Reviewer 1, and very grateful for her/his careful job and for helping us improving our manuscript.

Thank you very much again for accepting our manuscript for publication in JPCL.

With sincere regards,
Michal Farnik