February 6, 2007

Prof. Gary E. Maciel
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Reference:
JP067353Q - Joseph A. DiVerdi, Takeshi Kobayashi, Gary E. Maciel
Molecular Dynamics of Pyridine Adsorbed on the Silica Surface"

Dear Prof. Maciel:

We have now received two reviews of your revised manuscript. Copies of the reviewer comments are included below. As you can see, Reviewer 65 raises significant issues and still does not recommend publication. Due to the difference in opinion between Reviewer 65 and Reviewer 66, who recommended publication of the original manuscript with minor modifications, we sent your manuscript, along with the reviews and your response, to an adjudicating reviewer (Reviewer 67). Based on the opinions of Reviewers 66 and 67, I have decided to accept your manuscript for publication in The Journal of Physical Chemistry. However, I would like to give you the opportunity to submit another revised manuscript that addresses the issues raised by Reviewer 65. We will accept this revised manuscript without further review.

After considering the comments, please submit your revised manuscript via the web as you did the original. Please submit a cover letter responding to all issues raised by the reviewers and describing the changes made to the manuscript in response to the comments. Your security key for the web revision is A17A2.

Sincerely,

Sharon Hammes-Schiffer
Senior Editor

REVIEWER 65

Manuscript Number: JP067353Q (REVISED)

I have read the authors reply to my report and I'm highly surprised to say the least. Apparently, they did not understand the points I raised and consequently did not follow my recommendation for complete rewriting, but just added a few lines. Therefore, I respond to their reply rather than to the few changes in the manuscript.

In their first statement the authors point out:

'The research result that yielded a new physical insight for us personally is the absence in the observed lineshapes of motional behavior characteristic of the 'intermediate-motion (exchange) regime'; that regime was present in all of our previous 2H NMR studies and in every 2H NMR study about which we had read in the literature before carrying out this work. Thus, in the sense of manifesting only the slow-motion (static) and fast-motion regimes, a behavior that has been reported only in a tiny fraction of the substantial 2H NMR literature to date, our variable-temperature observations are reminiscent of phase-change behavior.'

Contrary to the author's statement such lineshapes without the intermediate motional regime are well-known. Only at the end of their paper they cite a comprehensive paper on the subject with numerous references to earlier work, Ref. 41, E. Roessler et al. J. Chem. Phys. 92, 5847 (1990). In the abstract of that paper published more than 16 years ago the authors explicitly use the term ''two-phase'' spectra and point out that 'no spectra characteristic of intermediate mobility as found in crystal matrices are observed'. This paper describes in detail how to analyze such lineshapes in terms of distributions of motional rates and activation energies.

A recent paper describing these effects for molecules on zeolite surfaces is: P. Medick et al. J. Non-Crystal. Solids 307-310, 565 (2002).

In statement 5 of their letter the authors state:

'We did not analyze "motional rates" in terms of thermodynamic parameters. Figure 9 and Table 1 are concerned with fractional populations, not rates.'

This shows that the authors apparently did not understand ref. 41 and my comment:

It is the DISTRIBUTION OF MOTIONAL RATES, rather than fractional populations, that are reflected in the 2H NMR lineshape. Assuming a thermally activated process, ref. 41 describes how a temperature independent distribution of activation energies can then be determined from the 2H NMR spectra. Such an analysis has to be performed before further conclusions can be drawn.

Thus, I'm convinced that deduction of thermodynamic parameters in the present manuscript is NOT STATE OF THE ART and most likely incorrect.

To conclude, I'm sorry to say that the paper as it stands apparently reflects the limited knowledge of the authors of 2H NMR rather than giving new physical insight and is not suited for publication in a highly rated international journal.

REVIEWER 67

Manuscript Number: JP067353Q

I have read carefully the manuscript referenced above and the comments by reviewers 65 and 66. I find that many of the comments made by reviewer 65 are not valid. It is clear to me that the authors did indeed understand the comments of reviewer 65 and did a good job of responding to the reviewers concerns. The statement of reviewer number 65 that "the paper as it stands apparently reflects the limited knowledge of the authors of 2H NMR" is really ridiculous. Professor Maciel is a widely acknowledged international expert in the field of the structure and dynamics of materials on silica surfaces and he has played a major role in the development and applications of solid state NMR, including extensive deuterium NMR studies.

The paper provides some important new results of the structure and dynamics of a model organic molecule on a silica surface. Because of the ability to selectively deuterate the pyridine molecule an especially detailed experimental study can be carried out. It is especially nice to see that a variable temperature study has been done. The authors explain clearly why they have chosen to "present their results in a very strange way". I would agree completely with the authors comment that "the new knowledge regarding the nature of the motions on the surface is more significant from the point of view of chemical structure and dynamics."

In summary, I find many of the comments of review 65 indicate that he has made little effort to read the paper carefully and to understand the results. I find the revised paper to represent a significant contribution to structure and dynamics on silica surfaces and I recommend that the revised manuscript be published in The Journal of Physical Chemistry.

----end of comments-------

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February 21, 2007

Dr. Sharon Hammes-Schiffer
Journal of Physical Chemistry

Re: JP067353Q "Molecular Dynamics of Pyridine Adsorbed on the Silica Surface".

Dear Dr. Hammes-Schiffer:

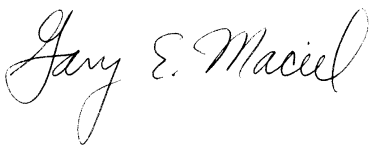
Attached is our manuscript, "Molecular Dynamics of Pyridine Adsorbed on the Silica Surface" (JP067353Q), by Joseph A. DiVerdi, Takeshi Kobayashi and Gary E. Maciel. We are, of course, pleased that the "adjudicating reviewer" (Reviewer 67) agrees that our paper should be published, in contrast to the opinion of Reviewer 65.

In response to the continuing concerns of Reviewer 65, we have added a new reference (45) and have added and/or modified some of the relevant wording to reflect this reviewer's opinion of the importance of the interpretation approach advanced by Rössler and co-workers. These rather minor modifications are found primarily in the Abstract and in the last two pages of text (last seven lines of p. 25 and first two lines of p. 26). It is clear that Reviewer 65 would very much like us to adopt the calculational approach of Rössler and co-workers. As stated in our additional wording, we agree *qualitatively* with the Rössler interpretation and now summarize it in a little more detail, but we don't believe that our current data set or any data that we anticipate obtaining in our future work (or most data sets in the literature) support a *quantitative* treatment of that approach.

In addition to the wording changes indicated above, we have also made numerous small wording changes throughout the paper, which don't change anything scientifically, but, we hope, enhance the readability of the paper.

Please let me know if you need anything more from us.

Sincerely,



Gary E. Maciel
Professor

GEM/eam