jz-2022-00587v.R1

Name: Peer Review Information for "The Role of Low Energy Resonances in the Stereodynamics of Cold He+D_2 Collisions"

First Round of Reviewer Comments

Reviewer: 1

Comments to the Author

The SARP technique is a powerful tool to investigate steric effects of collisional dynamics. The ro-vibrational state of the collision partners as well as the magnetic quantum numbers are well-defined in SARP experiments, so that the theory-experiment comparison can be very straightforward. The theoretical DCSs based on an accurate PES and convergent quantum dynamics calculations are in very good agreement with the experiment for some systems, such as HD+H2. But the agreement is poor for HD+He and D2+He, which shows the complexity of SARP studies. In this manuscript, the authors pointed out a possible origin for the poor theory-experiment comparison. In particular, by artificially removing the contributions of low-energy resonances, the agreement significantly improves. This is because the shape resonance is related to the L=1, which was found to be dominant at low collision energies. Further experimental studies are needed to measure the collision energy to prove if this is indeed the case.

1. What is the major advance reported in the paper? The major advance of this work is to provide a first principles simulation of the SARP experiment.

2. What is the immediate significance of this advance? The significance of this work is to point out the experimental results might not be accurate. A possible scenario is suggested for the experimental observation.

3. Technical suggestions

I have some questions and comments which should be addressed by the authors.

1) The shape resonances by L=1 and L=2 will produce different DCS shapes. However, it seems all the equations given by the authors show no connection to L. I believe that the cross section is obtained by summing over all the contributed L, so the authors should point out where this summation is done.

2) The authors stated in Page 14 that the DCSs were calculated by “excluding the averaging over Ecoll < 1 K” (so as for removing L=1 contribution). This literally leads to the absolute value of the averaged DCSs decrease by two or three orders of magnitude, because of the dominant peaks at Ecoll = 10-2 K. Then the authors stated that this “artificial DCS” can be in very consistent with the experiment. I am confused here about whether relative value or absolute value were compared. Since it is surely the key issue this manuscript is trying to discuss, I recommend the authors give more details about the treatment of “removing L=1 contribution”.

3). In Page 16, the authors provided some explanations that causes L=1 resonance difficult to observe in the experiment. As there are also an isotopic system HD+He suffers the theory-experiment discrepancy, can this explanation be applied to that system? And for the HD-H2 system, theoretical and experimental results converge very well, why does not this system meet such problem in the experiment?

Reviewer: 2

Comments to the Author

This paper reports very high-level quantum scattering calculations on stereodynamics in the He-D2 system at low collision energy. These are compared to experimental results reported by Mukherjee & Zare that are presented as a "molecular double slit" experiment recently published in Science. The results show a stark disagreement in that the theory predicts an l=1 resonance below 0.1K that dominates the scattering and gives completely different differential cross sections. Careful evaluation of the sensitivity of the theory to the PES and collision energy are performed and fail to account for the difference. The experimental results are recovered if the low energy collisions are excluded. These are very timely results on a system of wide interest, clearly presented, and I recommend publication as is.

Author's Response to Peer Review Comments:

See attached response to reviewers comments.

Reviewer: 1

Recommendation: This paper is publishable subject to minor revisions noted. Further review is not needed.

We thank the reviewer for his/her careful evaluation of the manuscript and the positive comments.

Comments:

The SARP technique is a powerful tool to investigate steric effects of collisional dynamics. The ro-vibrational state of the collision partners as well as the magnetic quantum numbers are well-defined in SARP experiments, so that the theory-experiment comparison can be very straightforward. The theoretical DCSs based on an accurate PES and convergent quantum dynamics calculations are in very good agreement with the experiment for some systems, such as HD+H2. But the agreement is poor for HD+He and D2+He, which shows the complexity of SARP studies.

We concur though agreement with experiment is still generally good for He+HD (Ref. [26]). Surely the reviewer means the complexity of the processes at low collision energies.

In this manuscript, the authors pointed out a possible origin for the poor theory-experiment comparison. In particular, by artificially removing the contributions of low-energy resonances, the agreement significantly improves. This is because the shape resonance is related to the L=1, which was found to be dominant at low collision energies. Further experimental studies are needed to measure the collision energy to prove if this is indeed the case.

We agree.

1. What is the major advance reported in the paper? The major advance of this work is to provide a first principles simulation of the SARP experiment.

We agree.

2. What is the immediate significance of this advance? The significance of this work is to point out the experimental results might not be accurate. A possible scenario is suggested for the experimental observation.

As we concluded in the manuscript, further experiments and new theoretical calculations seems to be in order. The possible missing of products at low energies in the experiment cannot be ruled out completely.

3. Technical suggestions

I have some questions and comments which should be addressed by the authors.

1) The shape resonances by L=1 and L=2 will produce different DCS shapes. However, it seems all the equations given by the authors show no connection to L. I believe that the cross section is obtained by summing over all the contributed L, so the authors should point out where this summation is done.

We thank the Reviewer for pointing this out. Due to limited space in the main manuscript, we have revised the Supplementary Materials (SM) to include expressions for scattering amplitude and differential cross sections in the orbital angular momentum representation. These quantities are defined in eq. (S1)-S(5) in pages 2 & 3 of the revised SM.

The L-resolved integral cross sections along with the total cross section presented in the left panel of Fig.2 clearly illustrate contributions from L=1 and L=2 (also L=3). The energy-averaged DCS presented in Fig. 4 is dominated by L=1 as can be inferred by comparison with the results shown in Fig. S1 at 2×10^{-2} K (corresponding to the L=1 resonance). The contribution from L=2 is well portrayed in Fig. 5, where the contribution from L=1 is suppressed and hence the resulting DCS is to a large extent due L=2. For this reason we deem the plot of DCSs resolved in L unnecessary.

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As in most cross-beam (or merged beam) experiments, the DCSs measured by Zhou et al. (refs. 13 and 18) are determined on a relative scale. Thus, the comparison is on a relative scale. The theoretical DCS resulting from the suppression of contributions below 1 K in the energy averaging is compared in their relative shape with the measured result. The procedure of "removing L=1 contribution" cannot be simpler: the averaging is done with the results only from collision energies above 1 K. As Fig. 2 illustrates, below 1 K, most of the cross section is due to L=1, above 1K only a residual (non-resonant part) from L=1 is kept. Of course, if the dominant L=1 resonant contribution is removed, the absolute value of the calculated energy averaged DCS decreases by two or more orders of magnitude.

3). In Page 16, the authors provided some explanations that causes L=1 resonance difficult to observe in the experiment. As there are also an isotopic system HD+He suffers the theory-experiment discrepancy, can this explanation be applied to that system? And for the HD-H2 system, theoretical and experimental results converge very well, why does not this system meet such problem in the experiment?

As shown in Fig. S4 the collision flux distribution (collision energy multiplied by the relative velocity) largely favors the DCS at energies above 0.3 K. Therefore, had the contribution from L=1 been comparable to that from L=2 (or larger L values), the signal due L=1 would have been hardly detectable. However, in the present case, the contribution from L=1 is so dominant (10^3 times that of L=2) that it more than compensates the lower value of the collision flux and the resulting energy averaged DCS is to a large extent due to L=1.

In the case of the HD+H_2 no resonance was found for L=1, and therefore the contributions from L=2 and L=3 (enhanced by the maximum of the flux distribution) were predominant leading to a better agreement with the experiment. For He+HD, an L=1 resonance was observed near 0.3 K and reasonable agreement with experiment was obtained without excluding contributions from L=1 as discussed in Ref.[26] and its supplementary material. For this case, the L=1 resonance is less intense than for the present system and it occurs at a higher energy.

Reviewer 2

We thank Reviewer to for the careful evaluation of the manuscript and recommending its publication without further changes.