Dear Editor,

This paper discusses an interesting approach to the efficient calculation of Franck-Condon integrals (FCI’s) for large systems. I think the problem is presented well and the basic algorithm is clearly presented. I have a number of suggestions though, which I think should be addressed in a revision of the manuscript. The incorporation of some of the remarks below would require some more calculations / implementations.

1. There is an error in the formulas published by Doctor et al, which however do not influence the calculation of FCI’s involving the ground state of the initial state. Nonetheless it would be helpful if this error was mentioned in papers reporting on the calculation of FCI’s. It is discussed in reference 11, and their result was confirmed independently in a derivation by K. K. Lehmann in unpublished work.

2. On page 5 the initial overlap integral is denoted $\langle 0|0 \rangle$ rather than $\langle 0'|0 \rangle$.

3. I am not familiar with eqn. 4. Is there a reference or derivation of this result? It could be that this is a well known result in mathematics.

4. It took me a little while to pick up on the ‘initial and final state labels’ on page 7. I think the representation might be improved if the final state labels would carry a prime, or a totally different index. It is only a suggestion.

5. I think a potential drawback of the algorithm is that the blocking of normal modes may not yield a reduction. For example if I would apply this technique to a “Hückel” triangular matrix, I would not achieve any subblocks (I assume this is correct). Hence there is an assumption that Duschinsky matrices in real molecules do not have such a “pathological” structure. I think the authors should point this out. Their algorithm may break down.

6. On page 7 in step 6, I think it would be helpful if the projection were discussed a bit more extensively, and that it is pointed out that the projection leads precisely to the block structure in the modified Duschinsky matrix. At this point the interested reader has to do the work him-/herself. It would take little space and improves understanding.

7. There is another possibility to achieve the block-diagonal form in step 6. Instead of adjusting the modes $L'$ the same type of procedure could be used to modify the initial modes $L$ instead. This may be a preferred strategy as all integrals are transformed perhaps more equally, as only the initial ground state is used explicitly in the FCI’s. This
will be slightly wrong, but I would think this is less essential. Importantly, only $J$ is affected but not $K$. This procedure might be very close to simply setting the off-diagonal $J$-elements to zero. It also avoids the problem that no identification is needed between the model normal modes and exact normal modes in the final state. It just appears far more logical to me to proceed in this way.

8. The fact that very different variants are possible raises the question: how would one gauge the two approaches. It actually points to an emission in the manuscript. I think it would be a very suitable test of the model to compare the model integrals with the final integrals. One could simply calculate maximum/mean absolute deviations but in particular develop a gauge in errors of integrals that are close to the threshold. I think this would be very instructive. It could be used as an indicator if the model is good enough.

9. In all of the FC calculations employed here the user has to specify an energy range. This is a great distinction (disadvantage?) from the algorithm of Hazra and Nooijen in which integrals are calculated just referring to their size. This energy range is not something a user wishes to specify. The calculation time will depend on the energy range, and it very much depends on the spectrum of interest. Maybe I am pessimistic. It would be useful if the authors could provide an automatic adjustment of the energy range (for example based on the total summed intensity, once convergence is reached for a given energy range).

10. It would be most instructive if there was an indication of how many integrals are actually calculated exactly in the final recursion procedure. This could be compared to the exact FC approach, and it would give a good indication of the effectiveness of the screening (in combination with the estimate of the accuracy of the model integrals).

11. It would also be interesting to have an idea about the relative cost of the model calculation compared to the final exact calculation. This information could easily be provided.

12. The authors do not give an in depth discussion of Table 1. Sometimes the BDA speedup is spectacular (e.g. systems 11 and 12), sometimes the algorithm is significantly slower than the exact algorithm (systems 14, 15). I assume in the latter case that the overhead of the model is significant, while it leads to only minor improvements. It is absolutely vital to provide some insight to the reader on these aspects.

13. In the conclusion the authors reduce 97 hours to several hours instead of several days. I think for most readers that pay attention this leaves a poor impression. I am personally convinced that the algorithm by Hazra and Nooijen would be far more effective for this problem, as the spectrum does not look complicated at all. The authors are absolutely correct that the H&N algorithm can make errors. These are likely to be very small, but I fully agree that exact results are preferred, if the algorithms are of comparable efficiency. It is clear that the approaches presented here and the approach by Hazra and Nooijen can be combined, using the H&N approach for the model system to screen the FCI’s. This might be most effective, without presumably any loss in accuracy.
After raising the above concerns, I think a substantial revision of the manuscript is required. I would prefer to have another look at the manuscript when it is resubmitted.

Yours Sincerely,

Marcel Nooijen