THE IMPACT OF LONG RANGE INTERACTIONS ON LOW TEMPERATURE PRESSURE BROADENING: THE CASE OF HE–OCS

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We address a persistent and troubling discrepancy between low temperature pressure broadening measurements and the predictions of high quality, experimentally-confirmed potential surfaces. In particular we focus on recent low temperature (4-30 K) pressure broadening measurements of OCS broadened by He[a] and the corresponding predictions of a recent He-OCS potential[b] surface which gives excellent agreement with observed rotational transitions of the bound complex, yet predicts cross sections which diverge sharply from experiment at temperatures below 10 K. By modifying the long range, asymptotic portion of the potential, forcing the potential to approach zero more rapidly, we are able to significantly improve agreement with the low temperature data. The modifications are made well out from the global minimum and thus should have a minimal impact on the calculated energies of the bound complex. Two modifications were tried, an isotropic version and an anisotropic version. While both versions gave improved agreement with the pressure broadening results, the isotropic modification was more successful at reproducing the experimental measurements.

[a] K. A. Ross & D. R. Willey, J. Chem. Phys. 122, 204308 (2005)
[b] J. M. M. Howson & J. M. Hutson, J. Chem. Phys 115, 5059 (2001)