VARIABLE TEMPERATURE LINE BROADENING AND SHIFTING AND INTERMOLECULAR FORCES: INTERPLAY BETWEEN THEORY AND EXPERIMENT

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In recent years our laboratory has made measurements of pressure broadening and center frequency shift cross sections for a variety of molecule-atom and molecule-molecule systems, including CO, H_2S, and CH_3F in collision with He and H_2. These measurements were carried out over the temperature range from 1 K to 600 K, which is broad enough to encompass the high energy semiclassical regime as well as the low energy regime where the cross sections are dominated by resonances due to the formation of quasibound states. These low energy cross sections are extremely sensitive to the form of the intermolecular potential, especially in the well region. Thus our line broadening and shifting data can be used as a test of both the accuracy of proposed model potential energy surfaces and the methodology which connects the potential surface to these observables.

At the present time, accurate model potential energy surfaces are available only for a limited number of simple collision systems; the CO-He system is one such example[a]. For most of the collision systems we have studied, however, there exist no model potential surfaces to compare with our data. Nevertheless, by examining our line broadening and shifting data as a whole and considering some basic physical principles, it is possible to draw a number of semi-quantitative conclusions about the nature of the relationship between intermolecular collisions and the forces which govern them.

[a] M. M. Beaky, T. M. Goyette and F. C. De Lucia, J. Chem. Phys. 105, 3994 (1996).