ANGULAR MOMENTUM TRANSFER IN ROTATIONAL ENERGY TRANSFER: TESTS OF GENERALIZED SCALING LAWS APPLIED TO O_2

STEPHEN L. COY, K. RYBAK, J. I. STEINFELD, *MIT Department of Chemistry, Cambridge, MA 02139.*

In inverting experimental data to relaxation matrix elements and to basis rates with predictive power, only Boyd, Ho and Rabitz [a] have tried to avoid restrictive and arbitrary limitations to angular momentum scaling models. The commonly applied scaling models (such as ECS-EP) enforce a few-parameter smooth basis rate variation which is quite different from calculated results, especially at low values of angular momentum transfer. The Rabitz approach has met with very limited success, but the more restricted forms do not extract all the information available in current data sets. We have used the extensive linewidth dataset available for $A_¡$-X O_2 transitions to develop and test a new method of determining angular momentum transfer basis rates via global optimization with non-negative constraints. This makes use of the experimental results that we have recently reported. [b] We will describe these results, relate them to other scaling schemes, and show how these differences can be experimentally tested.

[a] Boyd R, Ho TS, Rabitz H, J Chem Phys 108,1780(1998)

[b] Yang SF, Canagaratna M, Witonsky S, Coy SL, Steinfeld JI, and Kachanov A, submitted to J. Molec. Spectrosc.