Collision Broadening of Rotational Spectrum

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Abstract:

The problem studied is the rotational absorption spectrum of linear molecules of moment inertia I in a simple nonpolar buffer gas. The focus is on the behavior of the spectrum as the buffer gas pressure and the associated collision frequency v is increased. Four regions are distinguished. (1) v $\ll \hbar/I$, there are sharp lines with a van Vleck-Weisskopf line shape; (2) v $\simeq \hbar/I$, the contributions from overlapping lines are summed analytically. The ratio of minimum to maximum absorption in the weakly oscillatory spectrum is computed. (3) $\hbar/I < v < (2kT/I)1/2$, This is the classical inertial region where there is a single maximum in the absorption per cycle. We compute its position as it moves from an angular frequency (2kT/I)1/2 to lower frequencies with increasing collision frequency. (4) v>(2kT/I)1/2, this is the region where the Debye frequency profile is valid, with the peak of absorption at an angular frequency (1/v) (2kT/I). The calculations are based on a kinetic equation for the density matrix with a single relaxation time, no position change, collision model. We also compute the time dependent correlation functions needed in the theory of the rotational Raman effect of linear molecules