

Laser Cooling of Molecules: A Theory of Purity Increasing Transformations

*David J. Tannor and Alon Bartana
Department of Chemical Physics
Weizmann Institute, Rehovot, Israel*

*Ronnie Kosloff
Department of Chemistry and the Fritz Haber Institute for Molecular Dynamics
The Hebrew University, Jerusalem, Israel*

The powerful techniques of Optimal Control Theory (OCT), used in recent years to design laser pulse sequences to control chemical bond breaking, are applied to the problem of laser cooling in a non-closed system. The result is a striking new mechanism in which spontaneous emission builds coherences between all the populated levels creating a pure state, only at the end of the process transferring the amplitude to the the lowest energy state. This novel mechanism accelerates the cooling process by exploiting the cooling induced by spontaneous emission to *all* the ground electronic state levels, not just the lowest level. The mechanism suggests the calibration of cooling in terms of increasing purity of the system as measured by the quantity $Tr(\rho^2)$. An analytical theory of the cooling mechanism is developed in terms of a two-stage interplay between the control fields and the spontaneous emission. One of the main results of the analytical theory is a differential equation for the optimal cooling rate. The key components of the theory — the definition of cooling as purity increase; the invariance of purity to control fields; and the maximum rate of approach to absolute zero — are fully general, and correspond to the zeroth, second and third law of thermodynamics, filling a longstanding need for a thermodynamic formulation of laser cooling. The formulation of cooling in terms of the coherence measure $Tr(\rho^2)$ has an additional, profound implication: that our results carry over immediately to the problem of control of quantum decoherence, suggesting both a new mechanism and fundamental limitations on the control of that process.