Reprinted from the JOURNAL OF CHEMICAL PHYSICS, Vol. 32, No. 2, 617–618, February, 1960
Printed in U. S. A.

Radiant Energy Emission from Excited Harmonic Oscillators*

S. S. PENNER

Daniel and Florence Guggenheim Jet Propulsion Center,
California Institute of Technology,
Pasadena, California

(Received October 14, 1959)

THE total radiant energy emitted by spontaneous transitions[1] is independent, to the harmonic oscillator approximation, of the initially excited vibrational level(s) for a fixed total energy input. The preceding statement may be verified readily by the following considerations.

Let $x_n(t)$ denote the number of vibrationally excited emitters in the nth quantum state at time t. Let n^* denote the vibrational quantum number of the energy level which is excited initially. Then

$$dx_{n^*}/dt = -A_{n^*,n^*-1}x_{n^*} = -A_{1,0}n^*x_{n^*} \qquad (1)$$

where we use the relation $A_{n,n-1}=nA_{1,0}$ between the Einstein coefficients for spontaneous emission, which is applicable to the harmonic oscillator approximation. It is apparent from Eq. (1) that $x_{n^*}=N\exp(-A_{1,0}n^*t)$ if $x_{n^*}(0)=N$. Similarly,

$$dx_{n^*-1}/dt=[n^*N\exp(-A_{1,0}n^*t)-(n^*-1)x_{n^*-1}]A_{1,0}$$

or

$$x_{n^*-1}(t)=n^*N\exp[-A_{1,0}(n^*-1)t][1-\exp(-A_{1,0}t)];$$

$$x_{n^*-m}(t)=(1/m!)[n^*!/(n^*-m)!]N \cdot\exp[-A_{1,0}(n^*-m)t][1-\exp(-A_{1,0}t)]^m,$$

$$m=0, 1, \cdots, n^*-1, n^*. \qquad (2)$$

The set of relations represented by Eq. (2) constitutes a general solution for the number of emitters in any energy level between the ground level ($m=n^*$, $n^*-m=0$) and the most highly excited level ($m=0$, $n^*-m=n^*$).

The total radiant energy transfer equals the product of the number of transitions per second and the energy per transition. To the order of approximation used in the present analysis, $\nu_{n,n-1}=\nu=$constant. Hence the total radiant energy emitted in unit time is

$$d\epsilon/dt=A_{1,0}h\nu\sum_{m=n^*-1}^{0}(n^*-m)x_{n^*-m}(t)$$

or, using Eq. (2),

$$d\epsilon/dt=A_{1,0}h\nu n^*N\exp(-A_{1,0}t). \qquad (3)$$

Reference to Eq. (3) shows immediately that the rate of radiant energy emission is independent of the value of n^* for the fixed energy input $n^*Nh\nu$.

The preceding result permits ready generalization to an arbitrary initial distribution in which $x_n(0)=N_n$. These distributions relax independently in such a way that the total rate of energy output becomes

$$d\epsilon_T/dt=A_{1,0}h\nu\left(\sum_{n=1}^{\infty}nN_n\right)\exp(-A_{1,0}t)$$

$$=A_{1,0}h\nu N_T\exp(-A_{1,0}t) \qquad (4)$$

where

$$N_T=\sum_{n=1}^{\infty}nN_n$$

represents the total number of quanta of energy $h\nu$ distributed among the various vibrational energy states.

* Supported by the Office of Scientific Research, U.S. Air Force, under Contract AF 18(603)-2.

[1] For a general discussion of de-excitation of harmonic oscillators, see K. E. Shuler *et al.*, J. Chem. Phys. **26,** 454 (1957); J. Phys. Chem. **61,** 849 (1957); J. Chem. Phys. **28,** 4 (1958); **29,** 366 (1958).