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The Effects of Saturation with Microwaves on Thermal Properties

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It is assumed that saturation with microwave is observed because the two states, J and $J+1$, are statistically filled. Under these conditions the change in the rotational partition function is temperature dependent so that thermal properties of the system could be changed. The changes in the rotational specific heat are calculated for a linear molecule. This effect would produce a change in the specific heat of HCN of about 2 parts in 10,000 if the $J=0 \rightarrow 1$ transition is saturated.

IN recent studies^{1,2} of the absorption of microwaves by molecules, "saturation effects" have been observed which cause a decrease in the absorption coefficient and a broadening of the absorption line. Townes¹ has observed that "saturation effects" just become noticeable when radiation of 1.8 millivolts is transmitted through an absorption tube of 10.7 mm \times 4.3 mm cross section at a pressure of 4×10^{-2} mm. This indicates that saturation effects only become significant when the rate of absorption of the microwave is comparable with the rate of collision between the molecules.

As was first suggested by Townes,¹ Karplus and Schwinger³ have theoretically explained both the decrease in the absorption coefficient and the broadening of the absorption line in terms of the disturbance of the thermal distribution of the molecules between the ground and excited states. The disturbance of thermal equilibrium will also result in a change in the partition function of a system saturated with microwaves. This is particularly significant for the rotational partition function, since the energy differences between states belonging to successive rotational quantum numbers are different; thus a characteristic frequency will excite only the molecules in one particular state J to the state $J+1$. If one assumes that at saturation the states J and $J+1$ are statistically filled, these two states would not be able to partake in the distribution of additional thermal energy. Thus the change in the rotational partition function is temperature dependent and would consequently result in a modification of the thermodynamic properties of the gas. It is the purpose of this paper to calculate the effects of saturation on some of the properties of a gas whose molecules can be considered as rigid rotators.

For a gas consisting of linear dipole molecules in thermal equilibrium, the rotation partition function is usually written thus

$$Q = \sum_{J=0}^{\infty} (2J+1) \exp\left[-\frac{J(J+1)\sigma}{kT}\right], \quad (1)$$

where J is the rotational quantum number, k is Boltzmann's constant, T , the absolute temperature and

$\sigma = h^2/(8\pi^2 I)$ where I is the moment of inertia of the molecule and h is Planck's constant. Now consider the gas saturated with microwaves having the frequency of the $J=0 \rightarrow 1$ transition; this means that the number of particles in the $J=0$ level are not in thermal equilibrium with those in the $J=1$ and do not determine the relative number of particles in states $J \geq 1$. However, we assume that there is thermal equilibrium between successive J -states higher than 1. The "saturated" partition function thus becomes

$$Q' = 1 + 3 + \sum_{J \geq 2} (2J+1) \exp\left[-\frac{J(J+1)\sigma}{kT}\right], \quad (2)$$

$$Q' = q(Q + \delta) \quad (3)$$

where $q = e^{2\sigma/kT}$ and $\delta = (e^{-2\sigma/kT} - 1)$.

Equation (3) is valid when thermal transitions are allowed between neighboring states only, i.e., $\Delta J = \pm 1$. This is true in the following cases: (a) if the transitions are mainly due to blackbody radiation in dipole molecules, i.e., if the pressure is very small; (b) if collisions are involved but the interaction energy between colliding particles is such that it contains only the first power of θ , where θ is the angle of rotation. In that case the matrix element for the collision is similar to the one for dipole radiation.

In the general collision case, however, when ΔJ may be anything, the relative number of particles in any state is influenced by the number of particles in both states $J=0$ and $J=1$ and, therefore, is affected by the fact that these two states are not in thermal equilibrium. The principle of detailed balancing is then violated and one must write the following infinite set of linear equations. $N_0 = N_1$

$$\sum_{i=0}^{\infty} K_{i \rightarrow J} N_i = (\sum K_{J \rightarrow i}) N_J, \quad J = 2, 3, \dots, \quad (4)$$

$$K_{J \rightarrow i} = K_{i \rightarrow J} \frac{g_i}{g_J} \exp\left(-\frac{\epsilon_i - \epsilon_J}{kT}\right), \quad (5)$$

then except for $K_{0 \rightarrow 1}$ and $K_{1 \rightarrow 0}$

$$Q' = \sum_{J=0}^{\infty} \frac{N_J}{N_0} \quad (6)$$

¹ C. H. Townes, Phys. Rev. **70**, 665 (1946).

² B. Bleaney and R. P. Penrose, Proc. Phys. Soc. **60**, 83 (1948).

³ R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948).

where N_i = number of molecules in state $J=i$, $K_{i \rightarrow J}$ = transition probability from $J=i$ to $J=J$, and Q' = non-equilibrium partition function for the general case.

However, in practice the only interesting case is the one where $\Delta J = \pm 1$, since "saturation" is only observed at low pressures. Thus for the special case discussed above, Eq. (6) becomes Eq. (3).

The deviation of the "saturated partition function," Q' (Eq. (3)) from the thermal equilibrium partition function Q (Eq. (1)) is temperature dependent and consequently this deviation will also be evident in the energy \bar{E}' , as well as the specific heat and other thermodynamic quantities. The average energy per mole, E' , of the saturated system must be calculated explicitly* as follows:

$$\bar{E}' = \frac{N \sum_J \epsilon_J Q_J'}{Q'} \quad (7)$$

where N = Avogadro's number, $\epsilon_J = J(J+1)\sigma$,

$$Q_J' = (2J+1) \exp\left[-\frac{J(J+1)-2}{kT}\right] \sigma \quad \text{for } J \geq 1$$

$$Q_J' = e^{(2\sigma/kT)} Q_J = q Q_J$$

for

$$J=0, \quad Q_J' = Q_J = 1.$$

Expressing Q' in terms of Q (the thermal equilibrium partition function) and since $\epsilon_{J=0}=0$, Eq. (8) becomes

$$\bar{E}' = \frac{Nq \sum_{J=1}^{\infty} \epsilon_J Q_J}{q(Q+\delta)}, \quad (8)$$

$$\bar{E}' = \frac{\bar{E}}{[1+(\delta/Q)]} \quad (9)$$

expanding $1+(\delta/Q)$ and neglecting second-order terms

* Under conditions of thermal equilibrium

$$C_v = \frac{dE}{dT} = \frac{d}{dT} \left[RT^2 \frac{d \ln Q}{dT} \right].$$

However, if one replaces Q by Q' in this expression one gets a quantity that differs from the modified specific heat, i.e.,

$$\frac{d}{dT} \left[RT^2 \frac{d \ln Q'}{dT} \right] = R \left[1 - \frac{4}{Q^2} \right].$$

Compare with Eq. (12).

in δ^2

$$\bar{E}' = \bar{E} [1 - (\delta/Q)] \quad (10)$$

expanding $e^{-2\sigma/kT}$ into a power series neglecting terms of second order and higher, and substituting the asymptotic value for the thermal equilibrium partition function,

$$Q = \frac{8\pi^2 I k T}{h^2} = \frac{kT}{\sigma}. \quad (11)$$

Then

$$Q' = Q \left(1 + \frac{2}{Q} - \frac{2}{Q^2} - \frac{4}{Q^3} \right)$$

or

$$\Delta Q = 2 \left(1 - \frac{1}{Q} - \frac{2}{Q^2} \right).$$

$$\bar{E}' = E \left[1 + \frac{2}{Q^2} \right]. \quad (12)$$

Calculating the specific heat

$$C_v' = \left(\frac{dE'}{dT} \right)_v = C_v \left[1 - \frac{2}{Q^2} \right]$$

or

$$C_v' = R \left[1 - \frac{2}{Q^2} \right]. \quad (13)$$

There is one additional approximation of interest, even though the correction is too small to be appreciable. As the temperature is raised, maintaining saturation will mean that additional energy of the order of $(\epsilon_1 \delta / Q^2)$ has been supplied by the radiation and consequently should be subtracted from Eq. (10) before C_v is calculated. Consider the specific case of HCN which has the smallest moment of inertia and consequently the smallest partition function Q , of any dipole linear molecule. At 100°K the change in C_v would be two parts in 10,000. Although it is possible to measure the specific heat of such a gas quite accurately by measuring the velocity of sound through it, it is improbable that one can measure the velocity of sound to two parts in 10,000 under these extreme conditions of 100°K and very low pressures. However, it is possible that the change in the velocity of sound in the gas when saturated with microwaves might be observable with a very good acoustic interferometer.