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On the laser snow effect

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Résumé. — On donne une explication simple de l'effet de neige laser. Cet effet se caractérise par la production de HCs cristallin dans un mélange gazeux Cs-H₂ sous l'effet d'un laser à argon ionisé.

Abstract. — A simple explanation of the laser snow effect is given. This photochemical effect consists in the production of crystalline HCs in a Cs-H₂ gas mixture under the effect of a ionized argon laser.

The purpose of this note is to explain an amusing photochemical effect which has been first reported by Tam, Moe and Happer and is commonly described as the snow laser effect [1]. In this experiment, the radiation from a neon laser passes through a gas mixture made of vapour caesium (at the saturation pressure) and hydrogen. Typical temperatures are from 250 to 400 °C, and a typical H₂ pressure is 10⁻¹ atm. Some buffer gas such as helium may be added to hydrogen. The caesium doublet lines at 4 555 and 4 593 Å are broadened enough by collisions under such pressures to overlap with the laser lines at 4 545 and 4 579 Å, so that many caesium atoms are excited from the 6s fundamental state to a 7p state. What is observed is rather spectacular : small crystals (i.e. snow) are produced in the laser beam, scattering the incoming light. Through variation of the buffer composition, it can be ascertained that these crystals are made of CsH.

It turns out that the effect can be explained in an elementary fashion if one retains only the leading terms that behave exponentially with temperature. In fact, there is no point in trying to build a more sophisticated theory since some of the parameters which enter into the exponentials contain too large experimental uncertainties and since the basic cross sections are unknown. Nevertheless, the numbers we shall obtain will be clearcut enough to explain the effect.

We take the system as consisting of two parts : the first part (subsystem 1) consists of everything that lies within the laser beam. The rest of the container (subsystem 2) will be treated as a thermostat at temperature T . The extension of thermodynamics

to such an out-of-equilibrium system has been treated by Levine and Ben-Shaul [2] but the starting point we shall need is quite simple and easily derived from the second principle of thermodynamics, viz. that the state of minimum Gibbs potential will be produced. We therefore proceed as follows : compute the Gibbs potential G_v of CsH vapour in the system 1, as if the solid phase were absent, and compare it to the Gibbs potential G_c in the crystalline state. Snow will be produced if $G_v > G_c$.

To compute G_v , let us first note that the vapour pressure of caesium is given by the simplified Clausius-Clapeyron equation

$$P_{Cs} = P_0 \exp - \frac{\Delta H_0}{RT} \quad (1)$$

where $\Delta H_0 \simeq 70$ kJ/mole and $P_{Cs} = 1$ atm. at 690 °C.

We treat the equilibrium

under the conditions of extreme pumping as a chemical reaction : the ratio between the pressures of excited and non-excited Cs atoms is given by their statistical weights, i.e. 3/4 for Cs* (which is in a $l = 1$ state, $2l + 1 = 3$) and 1/4 for Cs (in a s-state, $2l + 1 = 1$). When this state of saturation is not realized, the ratio Cs/Cs* is an experimental parameter

$$0 \leq \beta \leq 3/4.$$

The partial pressure of Cs* is therefore given by

$$P_{Cs^*} = \beta P_0 \exp - \frac{\Delta H_0}{RT}. \quad (2)$$

With no radiation, the partial pressures of Cs, H₂ and CsH are related by the equilibrium equation

$$\frac{P_{\text{CsH}}^2}{P_{\text{Cs}}^2 P_{\text{H}_2}} = K \exp - \frac{\Delta H_1}{RT} \quad (3)$$

with $\log_{10} K = -17.81$ under normal conditions (pressures being measured in atmospheres) [3]. It is known that Eq. (3) can be derived from the Boltzmann equation using the Maxwell distribution for velocities and the cross sections for the reaction

and its inverse, these two cross sections being related by the principle of detailed balance (time reversal). The same analysis can be applied to the reactions

or whatever mechanism may be. The cross sections for the direct and inverse reactions are not any more simply related, but we shall assume that they are of the same order of magnitude as in the case of unexcited Cs. In fact, we should rather expect that the cross section for $\text{Cs}^* + \text{H}_2$ is larger than the cross section for $\text{Cs} + \text{H}_2$ so that the error we shall make will underestimate the partial pressure of CsH in the laser beam. We therefore write

$$\frac{P_{\text{CsH}}^2}{P_{\text{Cs}^*}^2 P_{\text{H}_2}} = AK \exp \left(- \frac{\Delta H_1 - 2\varepsilon}{RT} \right) \quad (4)$$

where A is some unknown factor (of the order of one), $\Delta H_1 = -86$ kJ/mole being the difference between the H-H bond (436 kJ/mole) and twice the Cs-H bond (175 kJ/mole), ε being the excitation energy of Cs (1.76 eV or 170 kJ/mole). Equation (4) is easily derived from the Arrhenius reaction-rate equation, the only point in the microscopic analysis being to ascertain the order of magnitude of A .

The Gibbs potential of vapour CsH is given, up to small corrections by [4]

$$G_v = RT \text{Log} \frac{P_{\text{CsH}}}{(kT)^{5/2}} \left(\frac{2\pi\hbar^2}{m_{\text{CsH}}} \right)^{3/2} \quad (5)$$

where m_{CsH} is the mass of a CsH molecule.

In order to compute G_c for the solid CsH state, we use the standard enthalpy value $H_0 = -84$ kJ/mole and the relations given by the Debye model [4]

$$G_c \simeq H_0 + 3R(T - T_0) - 3RT \left[\text{Log} \frac{T}{\Theta} + \frac{4}{3} \right] \quad (6)$$

where T_0 is the standard temperature and Θ the Fermi temperature of CsH which we take approximately as 100 K (its precise value is of no importance).

Typical numerical values are $T = 400$ °C, $P_{\text{H}_2} = 10^{-1}$ atm., $P_{\text{Cs}} = 3.6 \times 10^{-2}$ atm., $\beta = 3/4$ which give $G_v = -33$ kJ/mole, $G_c = -80$ kJ/mole. With no radiation, one finds G_v , as given by (3) and (5) equal to -203 kJ/mole. It is therefore clear that the solid state is produced when radiation is present, but not in its absence.

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