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EXPERIMENTAL STUDY OF CH₄ (ν₃) DEACTIVATION IN METHANE PLUS ADDED RARE GASES

M.Y. Perrin

Groupe de Recherches Thermiques du C.N.R.S., associé à l'Ecole Centrale des Arts et Manufactures, Grande Voie des Vignes, 92290 Châtenay-Malabry, France

Résumé - La technique photoacoustique est utilisée pour étudier la relaxation vibrationnelle du mode ν₃ de la molécule CH₄. Le schéma de relaxation adopté est en accord avec celui donné par des mesures de fluorescence. En diluant fortement CH₄ dans un gaz rare (He-Ne-Ar), nous déterminons pour la première fois les constantes (ν₃→T/R) de déactivation des niveaux supérieurs.

Abstract - The photoacoustic technique is applied to study the CH₄(ν₃) deactivation. The relaxation pathway deduced agrees with that deduced from fluorescence measurements. By diluting CH₄ with rare gases (He-Ne-Ar) we can determine (ν₃→T/R) deactivation constants from upper levels.

The spectrophone (the name sometimes given to the photoacoustic apparatus) has revealed to be very usefull for the study of vibrational relaxation /1-6 and references therein/. All the referred studies have been possible due to the great sensitivity of this technique which allows the use of thermal sources. In the present work the use of an infrared laser enable us to take even better advantage of the possibility of this technique. Thus even for an extensively studied molecule like CH₄ we can determine unknown constants.

I - PRINCIPLE AND EXPERIMENTAL SET-UP

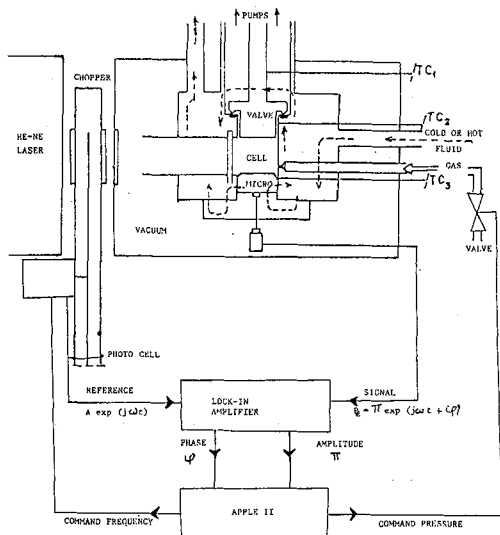


Fig. 1 - Experimental set up

The gas under study, placed in a small cell (≈10 cm³), is excited by a infrared beam modulated at frequency ω. To pump the ν₃ level of CH₄, we use a He-Ne laser working at ν_L = 2947,9 cm⁻¹ with an output power of 4 mW. The vibrational energy is transferred by collisions to the translation-rotation degrees of freedom. It results in a periodic variation of the temperature and consequently of the pressure P_e at the modulation frequency ω

$$P_e = \bar{P} \exp\left[j\left(\omega t + \frac{\pi}{2} - \psi\right)\right]$$

Here ψ is the phase shift between the incident radiative power and the dynamic pressure. The overpressure P_e is measured by a capacitive microphone with sensitivity 50 mV/N m⁻². The signal is processed by a lock-in amplifier to obtain the phase shift ψ. At a fixed frequency, the phase shift ψ is recorded as a function of the filling pressure P and stored by an acquisition system.

The great sensitivity of the experimental apparatus allows us to dilute CH₄ as low as x = 10⁻⁵ in concentration. Below this concentration the acoustic signal arising from scattered light on the cell walls is no longer negligible compared to the acoustic signal associated with the gas absorption.

II - KINETIC MODEL

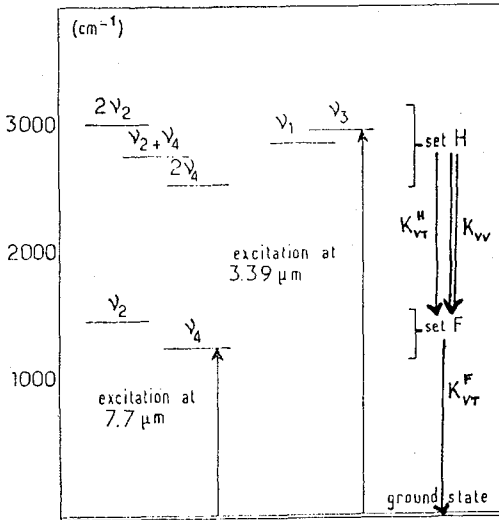
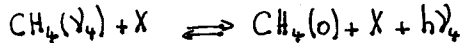


Fig.2-Vibrational levels of CH₄

To extract the rate constants from the measured phase shift a critical attention must be paid to the establishment of a rigorous kinetic model. Theoretically we should include in our analysis at least 8 levels i.e. 7 vibrational levels and the translation-rotation degrees of freedom (see fig. 2). However a careful analysis of the different time scales allows us to reduce the number of coupled equations to be considered. The time scale of our experiments is typically $\omega/p = 2500 \text{ s}^{-1} \text{ torr}^{-1}$, the one of vibration to vibration (V→V) intermolecular transfers is $10^5 \text{ s}^{-1} \text{ torr}^{-1}$, the one of vibration to translation (V→TR) transfers is $10^3 \text{ s}^{-1} \text{ torr}^{-1}$. Thus in the time scale of our experiments we can assume that the levels in each set F (ν_2, ν_4) and H ($2\nu_2, 2\nu_4, \nu_2+\nu_4, \nu_3, \nu_1$) are in a quasi equilibrium distribution. The problem is reduced to a three levels scheme easily workable.

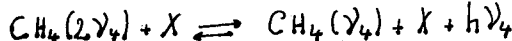
The rate constants involved are :

$-K_{VT}^F$ a V→TR constant which is a weighted sum of V→TR constants characterizing the deactivation of each level of set F like :



X being a CH₄ molecule or a rare gas atom.

$-K_{VT}^H$ a V→TR constant which is a weighted sum of V→TR constants characterizing the deactivation of each level of set H like :



$-K_{VV}$ a V→V constant which is a weighted sum of V-V intramolecular constants like :



However for high concentrations of CH₄ the V→V constant K_{VV} is much greater than K_{VT}^H . Thus all the vibrational levels are in a quasi equilibrium distribution. The only constant involved is K_{VT}^F .

Extended calculations of the resulting phase shifts can be found in ref /7/.

III -EXPERIMENTAL RESULTS

In a previous work, we have tested the proposed kinetic model in pure CH₄ and pure CD₄ as a function of the temperature /8/. In the present study we have worked at room temperature i.e. 300 K.

For each rare gas, 10 mixtures have been studied for concentrations in CH₄ between 1 and 10⁻⁵.

- For high concentrations of CH₄, 0.5 < x < 1, the kinetic scheme corresponds to a two levels scheme. The deactivation is characterized by K_{VT}^F . The values of K_{VT}^F deduced

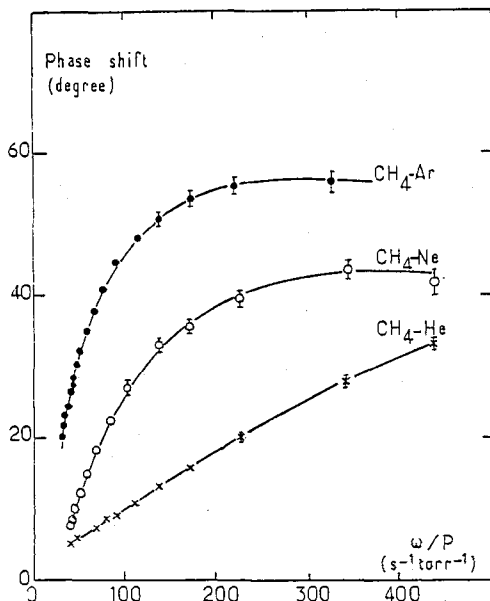


Fig. 3 - Experimental phase shift plots for CH_4 -X mixtures ($x = 10^{-4}$) following γ_3 excitation at 300K. The solid lines correspond to theoretical fits with:
 CH_4 -He : $K_{VT}^F = 630$, $K_{VT}^H = 1200$; CH_4 -Ne : $K_{VT}^F = 97$, $K_{VT}^H = 245$;
 CH_4 -A : $K_{VT}^F = 67$, $K_{VT}^H = 170$ and $K_{VV} = 10^6$

TABLE 1

Rate constants for $V \rightarrow \text{TR}$ transfers at 300 K in pure CH_4 and in mixtures of CH_4 with He, Ne, Ar. The rate constants are expressed in $\text{s}^{-1}\text{Torr}^{-1}$

	CH_4 - CH_4	CH_4 -He	CH_4 -Ne	CH_4 -A
K_{VT}^F (γ_4 excitation) /9/	855 ± 35	632 ± 33	93 ± 10	66 ± 7
K_{VT}^F (γ_3 excitation)	850 ± 35	630 ± 35	97 ± 10	65 ± 8
K_{VT}^H		1200 ± 200	245 ± 30	180 ± 30

are in excellent agreement with those deduced from the study of γ_4 deactivation /9/ (see table 1).

- For low concentrations $10^{-5} \leq x \leq 10^{-4}$ the phase shift is sensitive to K_{VT}^F and K_{VT}^H (fig. 3). We determine then K_{VT}^H (see table 1).

- For intermediate concentrations we should be able to determine K_{VV} . Unfortunately $\gamma_4 \neq \gamma_3$ and $K_{VT}^H = 2 K_{VT}^F$. The phase shift is not very sensitive to K_{VV} . We obtain :

$$8 \cdot 10^4 \leq K_{VV} \leq 5 \cdot 10^6 \text{ s}^{-1} \text{ torr}^{-1}$$

IV - DISCUSSION

An extensive study of CH_4 has been made using the fluorescence technique [10,11 and references therein]. A lot of informations have been obtained on $V \rightarrow V$ transfers. The value of K_{VV} obtained in this work is in agreement with these fluorescence measurements. However since in the photoacoustic method we observe the appearance of translation energy in the gas, we can obtain additional informations i.e. we can measure ($V \rightarrow TR$) constants from upper levels. The two techniques are complementary.

The kinetic model proposed is valid for experimental conditions corresponding to ω/P lower than $2500 \text{ s}^{-1} \text{ torr}^{-1}$. For higher values the hypothesis of quasi equilibrium repartition needs to be reconsidered and additive information should be available. The upper limit of ω/P arises from our upper one for ω and lower one for P . For relaxation measurements it is better to work at frequencies lower than the first resonance frequency to avoid interferences effects. At low pressure ($P < 10 \text{ torr}$) the molecules diffuse towards the cell wall. The probability of deactivation is close to one. The microphone being itself a cell wall, the phase shift is modified. Presently another photothermal technique is under study to look for an extension of the time scale ω/P . We detect the deviation of a light beam produced by the modulation of refractive index in the cell.

The experimental ratio $r = K_{VT}^H / K_{VT}^F$ corresponds to 1.9, 2.5, 2.7 for He, Ne, Ar respectively. These ratios are in agreement with theoretical calculations made using the SSH theory [12]. However the absolute values of K_{VT}^H and K_{VT}^F are not correctly predicted by this theory. This is due to the influence of rotation transfers which are not taken into account. To clarify this influence, we presently carry out an experimental study of the CD_4 molecule, and a theoretical study of the vibrational relaxation of CH_4 and CD_4 .

- 1 - F. Lepoutre, G. Louis, J. Taine, J. Chem. Phys. 70 (1979) 2225
- 2 - J. Taine, F. Lepoutre, Chem. Phys. Lett. 65 (1979) 554
J. Taine, F. Lepoutre, Chem. Phys. Lett. 75 (1979) 448
- 3 - F. Cannemeije, A.E. De Vries, Physica 70 (1973) 135
- 4 - M.H. De Vasconcelos, A.E. De Vries, Physica 86 A (1977) 509
- 5 - E. Avramides, T.F. Hunter, Chem. Phys. 57 (1981) 441
- 6 - M. Rebello da Silva, M.H. Vasconcelos, Physica 106 C (1981) 142
- 7 - M.Y. Perrin, Chem. Phys. Lett. 94 (1983) 434
- 8 - M.Y. Perrin, Chem. Phys. Lett. 93 (1983) 515
- 9 - M.Y. Perrin, Chem. Phys. Lett. 85 (1982) 521
- 10 - P. Hess, C.B. Moore, J. Chem. Phys. 65 (1976) 2339
- 11 - P. Hess, A.H. Kung, C.B. Moore, J. Chem. Phys. 72 (1980) 5525
- 12 - R.N. Shwartz, Z.I. Slawsky, R.T. Herzfeld, J. Chem. Phys. 20 (1952) 1591