

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231397086>

Transition dipole moment of the ν_3 band of CH_3

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY · JUNE 1994

Impact Factor: 2.78 · DOI: 10.1021/j100074a009

CITATIONS

20

READS

6

6 AUTHORS, INCLUDING:



I. Tanarro

Spanish National Research Council

89 PUBLICATIONS 867 CITATIONS

SEE PROFILE



D. Bermejo

Spanish National Research Council

88 PUBLICATIONS 1,191 CITATIONS

SEE PROFILE

THE TRANSITION DIPOLE MOMENT OF THE ν_3 BAND OF CH_3

I. Tanarro, M. M. Sanz, C. Domingo, D. Bermejo, J. Santos, J. L. Domenech.

Inst. de Estructura de la Materia, CSIC, Serrano 123, 28006 Madrid, Spain.

ABSTRACT

The transition dipole moment of the ν_3 band of the methyl radical has been measured for the first time. A new discharge laser amplitude double modulation method with a difference frequency laser spectrometer and a hollow cathode discharge cell has been used. The CH_3 concentration has been estimated from the absorption decay when the discharge is turned off. The transition dipole moment is found to be $\mu_{\nu_3} = 0.029 \pm 0.005$ D.

INTRODUCTION

Methyl radicals play an important role in many chemical processes. They participate in most combustion systems¹, they are involved in atmospheric chemistry through the reaction of methane with OH, Cl and O(¹D)², and moreover, it is thought that CH₃ may be one of the most abundant free radicals in the interstellar medium³.

In its ground state the methyl radical is a planar molecule belonging to the D_{3h} point group. Because of its symmetry, no electrical dipole rotational transitions in the millimeter or far-infrared regions are expected for this radical^{4,5}, and optical emission in the visible or UV spectrum is also forbidden for most of its states^{6,7}. Laser induced fluorescence (LIF) and Resonance-enhanced multiphoton ionization (REMPI) spectroscopy via predissociative states are usually significantly quenched⁸. The observation of the IR vib-rotational transitions is thus a very suitable way of detecting this radical and for that purpose the IR spectrum of the ν_2 out of plane bending vibration⁹, at 606.45 cm⁻¹, whose band strength has been reported before¹⁰, is usually employed.

The ν_3 in-plane degenerate C-H stretching band of CH₃ is much weaker than the ν_2 band in the IR spectrum. Zeeman and frequency modulation spectroscopic techniques were required in order to achieve enough sensitivity to obtain its high resolution spectrum for the first time^{11,12}. In spite of that, the understanding of this spectrum is very interesting for population distribution and dynamic studies^{8,13}; moreover, since this band lies in the 3 μ m atmospheric window, it may provide a very useful tool to achieve the expected detection of the methyl radical in the stratosphere and in the space. Nevertheless, measurements of absolute concentration require a precise knowledge of the dipole moments, and there is very little information for the ν_3 band of CH₃. The only datum reported about its intensity was that from a Ne matrix experiment¹⁴, which showed that its absorbance was around nine times weaker than that of the ν_2 band; this datum, together with the theoretical¹⁵ and

experimental values¹⁰ of the ν_2 band dipole moment, allows to estimate the intensity of the ν_3 band. However, indirect estimations from Zeeman spectroscopy^{11,12} and emission measurements^{16,17}, suggest an even smaller value for this intensity¹⁸.

In this work the measurement of the dipole moment of the ν_3 band of CH_3 is reported for the first time. In order to obtain it, the absorption intensities of several vib-rotational transitions of this band have been measured. The radical has been produced in a hollow cathode discharge cell, by using a CH_4 discharge, and the spectrum has been obtained by means of a discharge and laser amplitude double modulation spectroscopic technique, with a difference frequency laser spectrometer and a double phase sensitive detection method^{19,20}. To measure the CH_3 density, one of the ν_3 vib-rotational transitions has been selected. Its absorption decay with time, due mainly to diffusion and recombination of the radicals in the gas phase, has been observed when the discharge is turned off. The required data about the gas phase recombination rate constants have been obtained from the literature^{1,21-25}.

EXPERIMENTAL SET-UP

The spectroscopic technique used in this work is based on an IR difference frequency laser spectrometer and on the well known modulation of concentration method, in a modulated electrical discharge. This method, at discharge frequencies above 1 kHz, where background noise is low, has been employed usually without laser amplitude modulation for detecting fast disappearing unstable species^{26,27}. However CH_3 is one of the more stable hydrocarbon radicals, so that a low modulation frequency ($\sim \text{Hz}$) of the discharge is essential to obtain an effective modulation of its concentration. Unfortunately, at low modulation frequencies background noise grows up, making very difficult any signal recovery, even when employing phase sensitive detection. Besides, the ν_3 band of CH_3 is so

weak that, for the concentration values reached in the discharge, its absorptions remain buried under noise in the transmittance spectrum. Furthermore, numerous transitions belonging to the CH_4 precursor or to other stable reaction products ($\text{C}_2\text{H}_4, \text{C}_2\text{H}_6$) appear in the spectral region of the ν_3 band of CH_3 , where the C-H stretching hydrocarbon bands are found²⁸⁻³⁰. For this reason a double modulation and phase sensitive detection method has been employed in this work .

The description of the experimental set-up used here is reported in ref.19. Briefly, the IR radiation is generated by a difference frequency laser spectrometer built in our laboratory³¹ following the design of Pine³². The infrared beam is amplitude modulated at 15 kHz by an electro-optic modulator and polarizer arrangement in the ring dye laser path; travels several times through the absorption cell and is detected with phase sensitive detection. One part of the beam is split before the cell and used for noise reduction and IR power normalization purposes, as is usually done to obtain the transmittance spectra of stable species. Two lock-in amplifiers and one analog divider are used. The time constant of this whole system is 1 ms.

The methyl radical is produced by a low frequency modulated, hollow cathode discharge, in a White configuration multipass cell. The cathode is a copper cylinder, 70 cm long and 5 cm wide. The stainless steel anode is mounted on a side arm, in front of a hole drilled in the mid point of the cathode. The electrodes are water-cooled. The discharge is established in a continuous flow rate of methane. In order to ensure an uniform methyl radical distribution inside the cathode, CH_4 was supplied through a glass tube of the same length than the cathode, placed inside it, with a diameter of 1 cm and small holes along it. The optical path of the laser beam, with its multiple traversals was located as close to the axis of symmetry of the cathode as possible, in such a way that it was contained in the region of the negative glow discharge, where the values of luminosity and electric potential are nearly constant. To detect CH_3 , a second phase sensitive detection stage, with another lock-in amplifier collecting the transmittance signal given by the first stage and synchronized at the

modulation frequency of the discharge, is used. We measure in this way the modulated variations in transmittance signal due to the modulation of concentration. Discharge modulation frequencies above 80 Hz showed a significative decrease in CH_3 absorption signals up to their complete disappearance, so a square wave at 18.2 Hz has been selected to modulate the discharge. The time constant of the third lock-in is chosen at 1 s.

Being a zero level detection method, the output of the second phase sensitive detection stage measures only the transmittance variations modulated at the frequency of the discharge and, at the same time, the transmittance signal is recovered from the first phase sensitive detection stage. In opposition to Zeeman¹¹ or source frequency³³ modulation techniques, this method gives an absorption-like lineshape, so that a quantitative estimation of absorption values is easily obtainable.

For the stable species involved in the discharge, transmittance variations due to thermal population variations are also observed in the third lock-in output. These variations are especially significative for transitions from high lying levels. In fact, the discharge and laser amplitude double modulation has proved to be a good method for identifying weak lines from excited levels of such species¹⁹. Nevertheless, for the stable organic compounds other than CH_4 produced in the discharge, these signals decrease when He is added, even up to total disappearance, while the CH_3 signals, belonging to transitions from low energy levels and depending on concentration variations, remain unchanged. In this way CH_3 transitions may be identified even when they overlap with lines from the stable compounds. This property of He as a suitable buffer gas in hydrocarbon discharges has been reported before³⁴.

The temporal evolution of CH_3 density, due to the modulation of the discharge, has been studied with a digital oscilloscope (Tektronix 2430A) working in the average mode, located at the output of the first phase sensitive detection stage. This oscilloscope records the transmittance variation with time

when the laser frequency is locked to the peak of the CH_3 line. At the low frequency used for modulation, the internal DC filter of the oscilloscope distorts the signal; to avoid this, an external high pass filter with a time constant of 10 s has been used to remove the DC component. The temporal evolution of the CH_3 density is obtained from the oscilloscope signal after averaging 256 sweeps and deconvoluting with the response of the first phase sensitive detector stage, with a 1 ms time constant.

CONCENTRATION OF CH_3

The only significant gas phase chemical reaction for CH_3 disappearance in a discharge of methane is $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ ^{10,21}. Therefore, the temporal evolution of the methyl radical concentration, $[\text{CH}_3]=n$, can be expressed as

$$dn/dt = - 2 K_1 n^2 - K_2 n \quad (1)$$

where K_1 is the rate constant for CH_3 recombination into C_2H_6 in the gas phase and K_2 is the diffusion and surface loss constant. When the recombination reaction is the dominant route for removing CH_3 , as it is most usually found in the literature, the solution of this equation can be approximately given by

$$n = n_0 / (1 + 2 n_0 K_1 t) \quad (2)$$

and if diffusion and surface reactions were the dominant causes of CH_3 disappearance, the solution would be approximately

$$n = n_0 e^{-k_2 t} \quad (3)$$

The general solution of the differential equation (1) when both processes are taken into account is given by

$$n = \frac{n_0 K_2 e^{-k_2 t}}{2 n_0 K_1 (1 - e^{-K_2 t}) + K_2} \quad (4)$$

It can be seen that due to the second order character of bimolecular recombination the temporal evolution given by eq. (4) is sensitive to the initial density n_0 .

Fig.1 shows the temporal evolution of the normalized CH_3 density after the hollow cathode discharge is turned off, as it is obtained in this work from the absorption decay of the ${}^1\text{Q}_0(4)$ transition. As can be seen in fig.1.B, in contrast to other works on the decay of CH_3 concentration, obtained under quite different physical conditions^{10,11,21,25}, this curve could not be fitted just by assuming the limiting case of total recombination in the gas phase, given by equation (2); in order to adjust it the complete equation (4) was needed (fig.1.A). A similar behavior was found by Itabashi et al³⁵ for the SiH_3 radical in a silane plasma.

Three decay curves, being each one the average of 256 cycles, were recorded at the same experimental conditions; the mean values of them gave

$$2 n_0 K_1 = 149 \pm 23 \text{ s}^{-1} \quad \text{and} \quad K_2 = 144 \pm 27 \text{ s}^{-1}$$

The errors are expressed as the standard deviation of the set of three results and are in good agreement with the statistical errors obtained from the fit of each decay curve to equation (4).

Data on the recombination rate constant K_1 of CH_3 have been published before, as well as its dependence with temperature, pressure and the nature of the third collider (mainly Ar and He). In our case, neutral species in the hollow cathode discharge were estimated to be close to ambient temperature¹⁹, as it was deduced from Doppler broadening and relative line absorption strengths. For this temperature a good agreement can be found among the CH_3 rate constants reported without buffer gas^{21,25} and those using buffer gases in the fall-off region^{1,22-24}. The value that we have used,

$K_1 = (4.5 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, has been obtained extrapolating the data of refs. 22, 23 and 24 to zero Ar pressure for $T = 300 \text{ K}$, and agrees with the mean value of refs. 21 and 25 measured without buffer gases (4.3×10^{-11} and $4.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively). Thus the CH_3 density turns out to be

$$n_0 = (1.7 \pm 0.3) \times 10^{12} \text{ molecules cm}^{-3}$$

equivalent to a CH_3 partial pressure of $6.3 \times 10^{-5} \text{ mbar}$.

From the measurement of the K_2 value, some useful information about the diffusion and deposition processes of CH_3 can be inferred, if a more complete characterization of the plasma composition and surface conditions is done. This kind of measurements are now important because methyl radicals are considered to be the key active species in chemical vapor deposition of diamond (CVD) and other carbonated thin films³⁶. The measurement of the CH_3 sticking coefficient in our laboratory using this method is in progress.

THE DIPOLE MOMENT

In the present work five lines of the ν_3 band of CH_3 at 3072.913, 3101.042, 3108.798, 3153.324 and 3154.746 cm^{-1} have been observed. Among them, only those at 3153.324 and 3154.746 cm^{-1} had been observed before¹¹. One example of the obtained spectra around the ${}^1Q_0(4)$ line of CH_3 ¹¹ at 3153.3240 cm^{-1} is illustrated in Fig.2. Fig.(2.a) shows the transmittance spectrum of the discharge cell. Fig.(2.b) shows the corresponding modulation of transmittance spectrum. The gain of the second phase sensitive detector stage was calibrated previously.

In this part of the transmittance spectrum, two weak transitions appear. In order to determine whether they belonged to the precursor CH_4 , a spectrum of 10 mbar of methane without discharge was recorded. Then they were identified as two R_6 lines of the $2\nu_2$ band of CH_4 at 3153.199 and 3153.447

cm^{-1} ³⁸. Their lower levels lie at an energy of $\sim 220 \text{ cm}^{-1}$. They appear also in fig.(2.b).

The absorption of the 3153.324 cm^{-1} transition of the ν_3 band of the methyl radical is so weak that with the present conditions its transmittance signals is completely buried in noise in the first spectrum and it can be observed only in the modulation of transmittance spectrum. Its detection in this case is possible just because the signals are collected by a zero method. In the same way, in fig.(2.b) two more CH_4 transitions at 3153.305 and 3153.389 cm^{-1} appear. They had not been experimentally observed before and do not appear in the methane spectrum at 10 mbar. They were identified thanks to the theoretical predictions of J. C. Hilico on hot bands of methane³⁹. The line observed at 3153.305 cm^{-1} was identified as a R_9 line of the $(\nu_3 + \nu_4 - \nu_4)$ band with a lower level energy of $\sim 1775 \text{ cm}^{-1}$ (calculated wavenumber $3153.311 \pm 0.01 \text{ cm}^{-1}$); the line observed at 3153.389 cm^{-1} was identified as a R_{14} line of the $(2\nu_2 + \nu_4 - \nu_4)$ band with a lower energy of $\sim 2400 \text{ cm}^{-1}$ (calculated wavenumber: $3153.399 \pm 0.01 \text{ cm}^{-1}$).

Since CH_4 is a stable species, an appreciable modulation in its concentration is not expected during each modulation period and its lines appearing in fig.(2.b) can all be explained as due to thermal population variations. This assumption is confirmed by the fact that the CH_4 signals observed in the modulation of transmittance spectra for transitions from high excited levels are large, while transitions from low energy levels change less if compared with the transmittance spectra, and show signals of opposite sign. This effect is explained in detail in ref.19. This is not the case for the methyl radical. Since the concentration of CH_3 vanishes after the discharge is turned off in every discharge modulation period, and the transitions studied here arise from levels of low energy, whose populations undergo small population variations with small changes of temperature, the CH_3 signals in the variation of transmittance spectrum can be attributed to a true variation in methyl radical concentration from zero to the steady state in the plasma. Therefore, they allow to obtain directly the absorption intensity of the CH_3 transitions. The temperature of the neutrals in the discharge was estimated to be

(315 ± 15)K by the measurement of Doppler broadening and line intensities variations¹⁹. The peak absorbance of the ¹Q₀(4) line was measured to be 0.0098 ± 0.0007 for the experimental conditions employed in this work. Then, for an optical path length along the hollow cathode in the multipass cell of 840 cm, an absorption coefficient of

$$\alpha = (1.17 \pm 0.08) 10^{-5} \text{ cm}^{-1}$$

may be inferred, with the assumption of an homogeneous CH₃ distribution within the light path inside the cathode during each semiperiod of discharge on, supported by time and geometrical considerations.

The absorption coefficient α of a transition ($n \leftarrow m$) with a frequency ν_{nm} and with a Doppler width $\Delta\nu_D$ (HWHM) is given by the expression¹⁰

$$\alpha = \frac{8\pi^3}{3hc} \frac{\nu_{mn}}{\Delta\nu_D} |\mu_{mn}|^2 (N_m - N_n) \sqrt{\frac{\ln 2}{\pi}} \quad (7)$$

where

$$N_m = [CH_3]_0 \frac{g_N g_I}{Q_r Q_{NS} Q_v} e^{\frac{-E_m}{KT}} \text{ is the population in the state } m ,$$

$$E_m : E(N, K) \text{ the rotational energy of the state } m (E_n - E_m = h\nu_{mn}) ,$$

$$Q_r = \frac{1}{\sigma} 1.02704 \sqrt{\frac{T^3}{B^2 C}} \text{ is the rotational partition function and}$$

$$Q_v = \prod_i (1 - \exp(-\omega_i hc / KT))^{-d_i} \text{ the vibrational partition function ;}$$

$$Q_{NS} \text{ is the nuclear spin function (8 for CH}_3\text{),}$$

$$\mu_{mn} = \langle m | \mu | n \rangle \text{ the dipole moment matrix element,}$$

$$g_I = 4 \text{ (K = 0, J even) , } g_N = 2N+1 \text{ and } |\mu_{mn}|^2 = A_{NK} \mu^2$$

$$(A_{NK} : \text{Hönl-London Factor, } \mu : \text{vibrational transition moment})$$

In the vibrational partition function, Q_v , only the two lowest normal modes of CH_3 , $\omega_2 = 606 \text{ cm}^{-1}$, $\omega_4 = 1396 \text{ cm}^{-1}$, are taken into account. By substituting in Eq.(7) α and $[\text{CH}_3]_0$ from this work, and appropriate tabulated values for the other parameters, the transition dipole moment of the ν_3 band of CH_3 has been calculated to be

$$\mu_{\nu_3} = (0.029 \pm 0.005) D$$

where for the estimation of the error in μ_{ν_3} , uncertainties in CH_3 concentration, absorbance, temperature and rate constant, have been taken into account.

DISCUSSION

To the best of our knowledge the transition dipole moment of the ν_3 band of the methyl radical had not been estimated either experimentally, nor theoretically up to now. On the contrary the dipole moment of the ν_2 band of CH_3 was measured by Yamada and Hirota¹⁰ giving $\mu_{\nu_2} = 0.280$

$\pm 0.049 \text{ D}$; it seemed to be in reasonable agreement with the value inferred from the ν_2 band strength measured by Wormhoudt and McCurdy⁴⁰ and slightly higher than the theoretical value,

$\mu_{\nu_2} = 0.22 \text{ D}$, determined by Botschwina et al¹⁵, using ab initio calculations. On the other hand,

Snelson¹⁴ reported the absorbance ratio between the ν_2 and ν_3 fundamental bands of CH_3 in a neon matrix, measured by Fourier Transform IR Spectroscopy, giving $A_2 / A_3 \sim 9$. This result implied

$\mu_{\nu_2} / \mu_{\nu_3} \sim 3$. Then, taking into account the experimental μ_{ν_2} datum of Yamada and Hirota,

a value $\mu_{\nu_3} \sim 0.09 \text{ D}$ would be inferred. Nevertheless, up to now it has been thought that

the μ_{ν_3} value would be notoriously smaller than this one^{17,18,40} and our result tends to confirm this assumption.

In an attempt to clarify the origin of this disagreement, one fact concerning the experimental μ_{ν_2} value must be taken into account. As Wormhoudt and McCurdy⁴⁰ suggest in their work on the strength of the ν_2 band of CH_3 , the recombination rate constant, K_1 , used by Yamada and Hirota in order to estimate the CH_3 concentration, might not be appropriate enough if data about CH_3 recombination published afterwards are considered. They used a value of $K_1 = 4.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from Laguna and Baughcum²⁵, who measured it at 300 K in 2 - 20 Torr of Ar and He and found no measurable pressure or third-body dependence. More recent data reported in the literature show that these kinds of dependence do exist and are significant. Such measurements suggest that, under the conditions of the Yamada and Hirota study, which used di-ter-butyl peroxide (DTBP) as a third body and reported a temperature of 600 K, the true recombination rate coefficient might be smaller. The actual value for the rate constant applicable to the Yamada and Hirota study is difficult to determine since to our knowledge there are no measurements of the third-body collision efficiency in DTBP; but in order to be able to compare the μ_{ν_2} value with our μ_{ν_3} result, we have estimated a value for $K_1 \approx (1.0 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the conditions of ref.10. This estimation is based on refs.22-24 employing azomethane/argon^{22,23} and acetone/argon²⁴ mixtures at 577 K, and measuring it at the fall-off region. From this recalculated value of K_1 , a value $\mu_{\nu_2} = 0.129 \pm 0.022 \text{ D}$ would be obtained.

Now, if we compare this transition dipole moment with that of the ν_3 fundamental band obtained in this work, a ratio

$$\mu_{\nu_2} / \mu_{\nu_3} = 4.4 \pm 1.6$$

is inferred. It is in reasonable agreement with Snelson's¹⁴ result, between the error limits, and confirms the predictions of refs.17 and 18 about a value of μ_{ν_3} lower than believed, although

taking into account that the μ_{ν_2} value seems also to be lower than it was believed until now.

CONCLUSIONS

In this work the dipole moment of the weak ν_3 band of CH_3 has been obtained for the first time. The comparison with a revised value of the experimentally obtained dipole moment of the ν_2 band shows a fair agreement with the absorbance ratio between the ν_2 and ν_3 bands, measured in ref. 14. Nevertheless, more detailed studies about recombination rate constants would be useful in order to have a more precise value of μ_{ν_2} and some theoretical support in the calculation of the intensity of the ν_3 band would be convenient.

ACKNOWLEDGMENTS

We wish to thank Dr. J. C. Hilico for sending us the whole relation of the CH_4 hot band transitions belonging to the observed regions and Dr. R. Escribano for the careful revision of this manuscript.

We also acknowledge the financial support of the Spanish DGICYT (Project PB91-0128).

BIBLIOGRAPHY

- ¹W. Tsang and R. F. Hampson, *J. Phys. Chem. Ref. Data* **15**, 1087 (1986).
- ²A. R. Ravishankara, *Ann. Rev. Phys. Chem.* **39**, 367 (1988).
- ³H. Suzuki, *Prog. Theor. Phys.* **62**, 936 (1979).
- ⁴G. Herzberg, *Proc. R. Soc. London* **A262**, 291 (1961).
- ⁵S. C. Foster and T. A. Miller, *J. Phys. Chem.* **93**, 5986 (1989).
- ⁶J. W. Hudgens, T. G. Guiseppe and M. C. Lin, *J. Chem. Phys.* **79**, 571 (1983).
- ⁷D. F. Davidson, A. Y. Chang, M. M. di Rosa and R. K. Hanson, *J. Quant. Spectrosc. Radiat. Transfer* **49**, 559 (1993).
- ⁸T. Suzuki and E. Hirota, *J. Chem. Phys.* **98**, 2387 (1993).
- ⁹C. Yamada, E. Hirota and K. Kawaguchi, *J. Chem. Phys.* **75**, 5256 (1981).
- ¹⁰C. Yamada and E. Hirota, *J. Chem. Phys.* **78**, 669 (1982).
- ¹¹T. Amano, P. F. Bernath, C. Yamada, Y. Endo and E. Hirota, *J. Chem. Phys.* **77**, 5284 (1982).
- ¹²T. Amano, P. F. Bernath and C. Yamada, *Nature* **296**, 372 (1982).
- ¹³J. O. Chu, G. W. Flynn, C. J. Chen and R. M. Osgood Jr., *Chem. Phys. Lett.* **119**, 206 (1985).
- ¹⁴A. Snelson, *J. Phys. Chem.* **74**, 537 (1970).
- ¹⁵P. Botschwina, J. Flesh and W. Meyer, *Chem. Phys.* **74**, 321 (1983).
- ¹⁶D. J. Donaldson and S. R. Leone, *J. Chem. Phys.* **85**, 817 (1986).
- ¹⁷D. J. Donaldson and S. R. Leone, *J. Phys. Chem.* **91**, 3128 (1987).
- ¹⁸T. Amano, *Bull. Soc. Chim. Belg.* **92**, 565 (1983).
- ¹⁹I. Tanarro, M. M. Sanz, D. Bermejo, C. Domingo and J. Santos, *J. Chem. Phys.* **100**, 238 (1994).
- ²⁰I. Tanarro, M. M. Sanz, C. Domingo, D. Bermejo and J. Santos, XXII International Symposium on Free Radicals, Doorwerth, The Netherlands (1993)
- ²¹H. Toyoda, H. Kojima and H. Sugai, *Appl. Phys. Lett.* **54**, 1507 (1989).
- ²²M. T. MacPherson, M. J. Phylling and M. J. C. Smith, *J. Phys. Chem.* **89**, 2268 (1985).
- ²³M. T. MacPherson, M. J. Phylling and M. J. C. Smith, *Chem. Phys. Lett.* **94**, 4941 (1983).

- ²⁴I. R. Slagle, D. Gutman, J. W. Davies and M. J. Philling, *J. Phys. Chem.* **92**, 2455 (1988).
- ²⁵G. A. Laguna and S. L. Baughcum, *Chem. Phys. Lett.* **88**, 568 (1982).
- ²⁶S. C. Foster and A. R. E. McKellar, *J. Chem. Phys.* **81**, 3424 (1984).
- ²⁷H. E. Warner, A. Fox, T. Amano and D. K. Bohme, *J. Chem. Phys.* **91**, 5310 (1989).
- ²⁸A. S. Pine, Report NSF/ASRA/DAR 78-24562, Washington (1980).
- ²⁹L. S. Rothman, R. R. Gamache, R. H. Tipping, C. P. Rinsland, M. A. H. Smith, D. Chris Benner, V. Malathy Devi, J. M. Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S. T. Massie, L. R. Brown and R. A. Toth, *J. Quant. Spectrosc. Radiat. Transfer* **48**, 469 (1992).
- ³⁰N. Husson, B. Bonnet, N. A. Scott and A. Chedin, *J. Quant. Spectrosc. Radiat. Transfer* **48**, 509 (1992).
- ³¹D. Bermejo, J. L. Domenech, P. Cancio, J. Santos and R. Escribano, *Laser Spectroscopy IX*, 126 (1989), Academic Press.
- ³²A. S. Pine, *J. Opt. Soc. Am.* **64**, 1683 (1974).
- ³³T. Oka, *Phys. Rev. Lett.* **45**, 531 (1980).
- ³⁴M. F. Jagod, "Laser Techniques for state-selected and state to state chemistry", Los Angeles, SPIE **1858**, 102 (1993).
- ³⁵N. Itabashi, K. Kato, N. Nishiwaki, T. Goto, C. Tamada and E. Hirota, *Jap. J. Appl. Phys.* **28**, L325 (1989).
- ³⁶F. G. Celii and J. E. Butler, *J. Appl. Phys.* **71**, 2877 (1992).
- ³⁷M.M. Sanz, L. Abad, V. J. Herrero and I. Tanarro, *J. Appl. Phys.* **71**, 5372 (1992).
- ³⁸R. H. Hunt, J. E. Lolck, A. G. Robiette, L. R. Brown and R. A. Toth, *J. Mol. Spect.* **92**, 246 (1982).
- ³⁹J. C. Hilico, private communication.
- ⁴⁰J. Wormhoudt and K. E. McCurdy, *Chem. Phys. Lett.* **156**, 47 (1989).

FIGURE CAPTIONS

Fig.1.- Decay of the CH_3 density after the discharge is turned off, obtained from the temporal evolution of the transmittance of the ${}^1\text{Q}_0(4)$ transition, at 3153.324 cm^{-1} . To measure it 1 mbar of pure CH_4 with 400 sccm gas flow rate was used. The hollow cathode discharge was operated at 18.2 Hz, 800 V and 90 mA. (1.B): The best fits of the equations (3) (short dashed line) and (2) (long dashed line) to the experimental curve. It can be seen the poor agreement between the pure recombination approximation of the long dashed line and the experimental result at the right hand side of the figure; conversely the pure diffusion approximation (short dashed line) and the experimental curve disagree mainly at the left hand side of the figure (near the origin of the time scale). (1.A): The best fit to the experimental curve of equation (4) (continuous regular line), where recombination and diffusion processes are taken into account.

Fig.2.-The obtained spectra around 3153.324 cm^{-1} of the methyl radical. (2.a) The transmittance spectrum. Two CH_4 lines may be seen. (2.b) The modulated variation of transmittance spectrum, showing the ${}^1\text{Q}_0(4)$ line of the ν_3 band of CH_3 . The same lines of CH_4 seen in (2.a) and two other lines belonging to CH_4 hot band transitions appear also in (2.b), due to a variation in thermal population with the discharge of the lower energy levels. The experimental conditions are the same that in fig.1.



