J. Phys. Chem. A **2000,** *104,* 5444−5450

Time-Resolved IR−IR Double Resonance Measurements in Methane Excited to $2\nu_3(F_2)$

F. Menard-Bourcin,* L. Doyennette, J. Menard, and C. Boursier

Laboratoire de Physique Moléculaire et Applications,[†] *CNRS, Université Pierre et Marie Curie,*
Tour 13-Bte 76 4, place Jussieu, 75252 Paris Cedex 05, France

Received: January 14, 2000; In Final Form: April 3, 2000

Time-resolved double resonance (DR) measurements have been performed in neat methane in order to investigate the rovibrational energy transfer processes occurring in CH_4 upon inelastic collisions. The CH_4 molecules were excited to the $2\nu_3(F_2)$ vibrational state by an optical parametric oscillator pumped by a Nd:YAG laser and tuned around 1.66 μm, and the low power beam of a tunable diode laser emitting around 3.4 μm was used to probe diad−octad, pentad−tetradecad, and transitions with the tetradecad as the lower level. The transitions involving the tetradecad are not yet well-known, but our DR measurements have allowed, in numerous cases, the assignment of $2\nu_3(F_2) \leftarrow \nu_3$ transitions, their frequencies being measured with a precision of ± 0.01 cm^{-1}, which should be useful for the spectroscopists who are analyzing the $2\nu_3$ vibrational state. Several rate constants have been deduced from the time evolution of the DR signals. A rate constant of 20 ± 2 μs^{-1} Torr^{-1} was obtained for the rotational energy transfer within $2\nu_3(F_2)$ occurring between levels of the same nuclear spin modification. Following the rotational equilibration, the $2\nu_3(F_2)$ levels relax first with a rate constant of 6 ± 2 μs^{-1} Torr^{-1} corresponding to rovibrational energy transfer within the tetradecad, then with a rate constant of 1.7 ± 0.2 μs^{-1} Torr^{-1} corresponding to the deexcitation of the tetradecad due to near-resonant energy transfer coupling the tetradecad to lower polyads. Other rate constants concerning the relaxation of the pentad and the diad have also been determined.

Introduction

There is great interest in obtaining reliable data on rovibrational energy transfer occurring in methane upon molecular collisions. Indeed, methane is a minor atmospheric constituent, but it is a major greenhouse gas, which participates in the global warming of the earth and, consequently, plays an important role in atmospheric physics. Its concentration being rather uniform in the low atmosphere, the CH_4 molecule could be used as a probe of its environment by laser techniques with appropriate airborne equipment, but this needs a good knowledge of the rovibrational relaxation of CH_4.[1] Methane is also present in atmospheres of giant planets such as Jupiter and Saturn. Recently, emissions of methane at 3.3 μm, due to nonlocal thermodynamic equilibrium effects, have been observed in spectra of these planets obtained by the ISO satellite, but the modeling of these spectra requires data on the collisional processes of vibrational energy transfer occurring in methane.[2] Of course, for such applications, the relaxation of CH_4 must be investigated in mixtures of CH_4 with the main atmospheric constituents (terrestrial or in giant planets).

In a previous work,[1] we have investigated rovibrational energy transfer occurring in CH_4−N_2/O_2 mixtures by using the laser-induced fluorescence method: CH_4 was excited to the $2\nu_3(F_2)$ vibrational state by an optical parametric oscillator (OPO) pumped by a Nd:YAG laser, and fluorescence emission from hot bands was detected at about 3.3 and 7.5 μm corresponding to the wavelengths of the two infrared active fundamental bands ν_3 and ν_4. But it is not possible to derive detailed information on the relaxation pathways from the time evolution of such a global fluorescence emitted by several states. For thorough study of the relaxation one needs to monitor the populations of selected vibrational states using IR−IR time-resolved double resonance experiments. So we have undertaken such double resonance (DR) experiments. Our first measurements have been performed in neat methane, which is necessary prior to further investigations in order to obtain a good knowledge of relaxation mechanisms connecting the energy levels up to 6000 cm^{-1}. It is the purpose of the present work. Methane is excited to the $2\nu_3(F_2)$ state by an OPO, as in our previous work, and a tunable diode laser is used to probe transitions around 3.4 μm. To analyze state-to-state energy transfer measurements, reliable spectroscopic assignments of probed transitions are needed. Unfortunately, because of the complexity of the spectroscopy of CH_4, the vibrational states higher than those of the octad are not yet well-known and assigned frequencies are not always available in the databases.[3,4] However, besides the determination of energy transfer rate constants, we have been able to assign probed levels and to deduce the corresponding probed transitions.

Experimental Section

The experimental setup used for our double resonance measurements is schematically shown in Figure 1. The CH_4 molecules are pumped to overtone levels of the $2\nu_3(F_2)$ asymmetric stretching vibration by a powerful tunable IR optical parametric oscillator (OPO) from Continuum (model Mirage 3000) pumped by a pulsed Nd:YAG laser. The characteristics of this laser system have already been indicated in a previous paper.[1] Let us recall that the OPO output consists of single longitudinal mode pulses about 7 ns in duration; the emission produced by the signal wave (~5 mJ in power) is tunable from 1.45 to 2.12 μm with a 0.02 cm^{-1} line width, which allows

---

* Corresponding author. Fax: 33 (0)1 44 27 70 33. E-mail: menard@ccr.jussieu.fr.

[†] Laboratoire associé à l'Université Pierre et Marie Curie.

10.1021/jp0002087 CCC: \$19.00

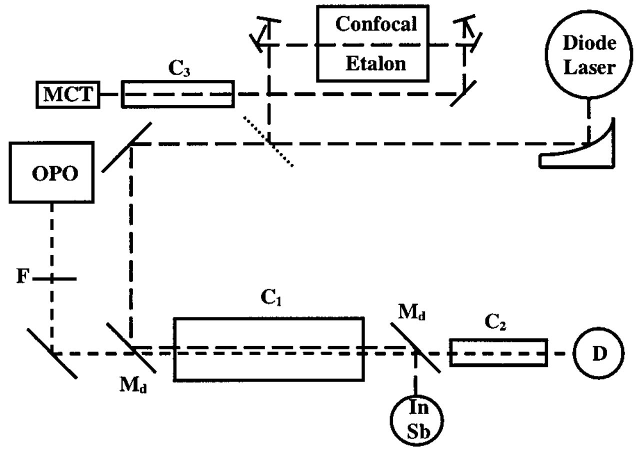

Figure 1. Schematic diagram of the experimental setup used for double resonance measurements in methane excited to $2\nu_3(F_2)$ rovibrational levels by an optical parametric oscillator (OPO). C_1 is the double resonance cell, C_2 and C_3 are absorption cells filled with CH_4 and C_2H_4, respectively, M_d are dichroic mirrors, *F* is a filter, and D is a pyroelectric detector.

excitation of well-isolated lines or a group of lines of the overtone $2\nu_3$ band near 1.66 μm.

The low power continuous wave (cw) probe beam is produced by a L5621S MBE tunable diode laser (TDL) from Laser Photonics. This TDL is liquid nitrogen cooled in a dewar (L5736), and its temperature can be set between 78 and 86 K and stabilized by a L5830 controller from Laser Photonics. It runs on a >92% single mode and can be quasi-continuously tuned over the 2938−2983 cm^{-1} frequency range. Its output power is ~0.1 mW, and its line width has been found[5] equal to 2×10^{-3} cm^{-1}. Tested on a diode laser interferometer system developed in the laboratory,[6] the TDL frequency appeared to be very stable.

As shown in Figure 1, a small part of the collimated TDL beam is reflected through a confocal Etalon (AL6000 from Aerolaser), which provides optical interference fringes, allowing the control of the TDL frequency. This reference beam then passes through a 30 cm long absorption cell (C_3) containing ethylene at 60 Torr pressure and is focused onto a MCT infrared detector. The signal from this detector, resulting from the modulation of the current passing through the TDL, allows monitoring of the interference fringes and of the C_2H_4 absorption lines. These C_2H_4 lines are numerous in the 2938−2983 cm^{-1} range, and their frequencies have been precisely measured.[7] The TDL frequency was determined by interpolation of the C_2H_4 line frequencies with a precision estimated to ±0.01 cm^{-1}.

The probe TDL beam is reflected by a dichroic mirror M_d, which transmits ~85% of the OPO pump beam intensity at about 6000 cm^{-1}. The probe and pump beams overlap at a small angle in a Pyrex double resonance cell (C_1) 60 cm in length and 3.8 cm in diameter. A second dichroic mirror ensures the separation of the two beams after passing through the sample cell: the probe beam is reflected to an InSb infrared detector, and the pumping beam is transmitted through a 60 cm long absorption cell (C_2) containing methane at 100 Torr pressure. This part of the pumping beam is then detected by a pyroelectric energy meter (D). The signal from this detector is amplified by a lock-in amplifier, which allows a continuous control of the excitation wavelength.

The double resonance signal (DR signal) carried on the probe beam is detected by the InSb detector and preamplified with a bandwidth between 10 kHz and 20 MHz. Then it is sampled, averaged, and recorded by a Tektronix DSA 610, the trigger pulse being derived from a photodiode ET2000 that receives a part of the scattered pump laser signal. The averaged DR signals are transmitted for analysis to a microcomputer.

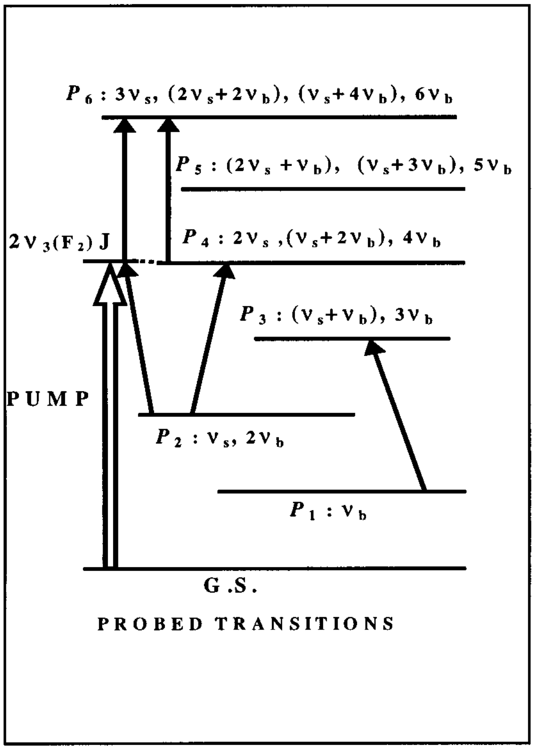

Figure 2. Simplified diagram of the CH_4 vibrational energy levels. These levels are gathered in polyads of interacting states. Each polyad P_N gathers all the states such as $N = n_b + 2n_s$ where n_s and n_b are the numbers of stretching and bending excitation quanta. For instance, the pentad P_2: (ν_s, $2\nu_b$) gathers the ν_1 and ν_3 levels ($n_s = 1$) and the $2\nu_2$, $2\nu_4$, and $\nu_2+\nu_4$ levels ($n_b = 2$).

The CH_4 gas with purity >99.995%, provided by Air Liquide, was introduced in the sample cell at pressures ranging from 15 mTorr to 1 Torr. The pressure was monitored by a 1 Torr MKS capacitance manometer.

Spectroscopic Background

The main characteristics of the spectroscopy of CH_4 in connection with 1.6 μm laser excitation have been given in our previous paper.[1] Let us recall that CH_4 has two interacting bending modes with fundamental vibrations ν_2 and ν_4 at 1311 and 1533 cm^{-1} respectively, and two stretching modes with fundamental vibrations ν_1 and ν_3 at 2916.5 and 3019 cm^{-1}, which are roughly twice the two former ones. Because of Fermi ($\nu_1 \leftrightarrow 2\nu_2$, $\nu_1 \leftrightarrow 2\nu_4$, $\nu_3 \leftrightarrow 2\nu_4$, and $\nu_3 \leftrightarrow \nu_2 + \nu_4$) and Coriolis ($\nu_2$ and ν_4) resonances, the vibrational states are gathered in polyads of interacting states so that a polyad scheme is necessary to understand the vibration−rotation levels. The polyad P_N contains all harmonic or combination states such as $n_b + 2n_s = N$, where n_b and n_s are the numbers of bending and stretching quanta, respectively. The first polyads are a diad P_1 (ν_2 and ν_4), a pentad P_2 (ν_1, ν_3, $2\nu_2$, $\nu_2 + \nu_4$, $2\nu_4$), an octad P_3 ($\nu_1 + \nu_2$, $\nu_3 + \nu_2$, $\nu_1 + \nu_4$, $\nu_3 + \nu_4$, $2\nu_2 + \nu_4$, $\nu_2 + 2\nu_4$, $3\nu_2$, $3\nu_4$), and a tetradecad P_4. The following polyads called P_5 and P_6 have also been considered in this work. A simplified diagram of vibrational levels is given in Figure 2.

By pumping the $2\nu_3(F_2)$ state and probing in the 2938−2983 cm^{-1} range, one can expect to obtain DR signals corresponding

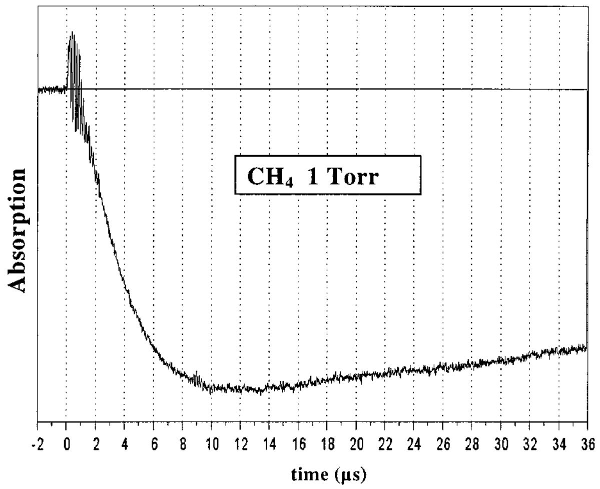

Figure 3. DR signal obtained by probing a diad → octad transition at 2949.11 cm^{-1} in methane at 1 Torr pressure. It shows a time decay in transmission of the probe beam due to an increase of population in the lower level of the probed transition, followed by a slow time rise back to equilibrium due to the V−T,R deexcitation of this level. This DR signal corresponds mainly to the time evolution of the populations in the states of the diad.

to various transitions involving vibrational levels of the tetradecad or of lower polyads, i.e.

•diad−octad transitions: P_1-P_3

•pentad−tetradecad transitions: P_2-P_4

•transitions in which the lower level is a level of the octad: P_3-P_5

•transitions in which the lower level is a level of the tetradecad: P_4-P_6

The diad−octad transitions are well-known and the frequencies and intensities of the corresponding lines are listed in methane spectroscopic databases.[3,4] But the levels of the tetradecad, and of course of higher polyads, are not well-known yet and the data on the frequencies and intensities of the lines corresponding to transitions involving levels of polyads higher than the octad are scanty and uncertain.

Results

To find the probe frequencies for which DR signals can be obtained, we have slowly scanned the frequency of the TDL while exciting CH_4 in the $2\nu_3(F_2)$ state with the pump frequency tuned to a given exciting line. Then, for a given probe, we have used various pump frequencies. Three main kinds of signals were thus observed.

(a) DR Signals Showing a Slowly Varying Absorption of the Probe Beam. These signals have been obtained at frequencies corresponding to diad−octad transitions, with many different pumping lines. As shown in Figure 3, they exhibit a quasi-exponential time decay followed by a much slower rise back to equilibrium. Some of these DR signals are very strong, as can be seen in Figure 3 for a probe line at 2949.11 cm^{-1}, with 1 Torr methane pressure. The value of the decay rate constant, $0.4 \pm 0.04\ \mu s^{-1}\ Torr^{-1}$, is independent of the pumped transition. The decay is due to an increase of population in the diad, which is the lower level of the probed transition; it results from near-resonant V−V transfer involving the exchange of a bending quantum between the collision partners. These V−V transfer processes effectively gather the excited molecules in the diad. Let us notice that our result of $0.4\ \mu s^{-1}\ Torr^{-1}$ for the decay rate constant (corresponding to the filling of the diad) is comparable to the value found in our laser-induced fluorescence measurements[1] for the decay rate constant of the fluorescence emitted around the ν_4 frequency in hot bands that corresponds to the depletion of the upper polyads.

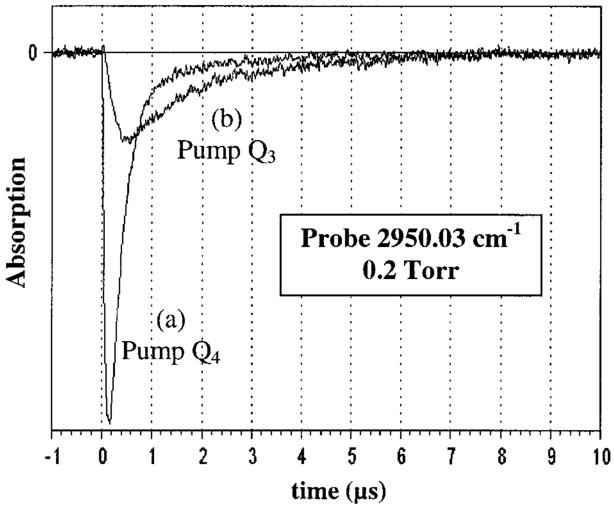

Figure 4. DR signals obtained by probing a transition at 2950.03 cm^{-1} and tuning successively the pump laser to the Q_3 and Q_4 lines in methane at 0.2 Torr pressure. With the Q_4 pump line (a), a very strong signal is obtained, showing a decrease in transmission of the probe beam in the time scale of the laser pulse followed by a fast rise up to an equilibrium value. The $2\nu_3(F_2)$, $J = 4$ level directly populated by the pump laser is then the lower level of the probed transition. With the Q_3 pump line (b), a much weaker signal is obtained (this signal has been magnified by a factor 2). The lower level of the probed transition is now populated by rotational energy transfer from the $2\nu_3(F_2)$, $J = 3$ level directly excited by the pump laser.

The following slow rise to equilibrium observed on the DR signals results from the V−T,R deexcitation of the states of the diad, which occurs with a rate constant at least 2 orders of magnitude smaller than the previous one.[8]

(b) DR Signals Exhibiting a Fast Initial Absorption of the Probe Beam. These signals exhibit a fast initial decay in transmission of the probe beam followed by a slower rise back to equilibrium. The time variation of these signals, which is due to a fast initial increase in population of the lower level of the probed transition, is a clear indication that this lower level belongs to the tetradecad. The intensity and the decay time corresponding to this increase of population depend on the line used to pump the gas. This is illustrated in Figure 4 by the DR signals obtained for a 2950.03 cm^{-1} probe frequency with the pump laser tuned to the frequencies of the Q_3 and Q_4 lines of the $2\nu_3$ band, the gas pressure being 0.2 Torr in both cases. With the pump laser tuned to the Q_4 line, the DR signal given in Figure 4a is very intense and shows an initial time decay too fast to be determined with the bandwidth of our detector, even at very low pressures, and must be considered as occurring in the time scale of the pumping pulse. It appears clearly that the lower level of the probed transition is the $2\nu_3(F_2)$, $J = 4$ level directly populated by the laser pump, the upper level being of course a level of the P_6 polyad. Considering the large intensity of the signal, this upper level is probably a $3\nu_3$ level. The following increase of the signal is mainly due to rotational energy transfer depleting the pumped level. With the pump tuned to the Q_3 line, the same probed transition leads to a weaker DR signal with a slower decay, as shown in Figure 4b. The $2\nu_3(F_2)$, $J = 4$ probed level is then populated by rotational energy transfer from the $2\nu_3(F_2)$, $J = 3$ pumped level, then it relaxes at a slower rate.

Other DR signals showing a very fast and intense absorption of the probe beam intensity have been obtained for different

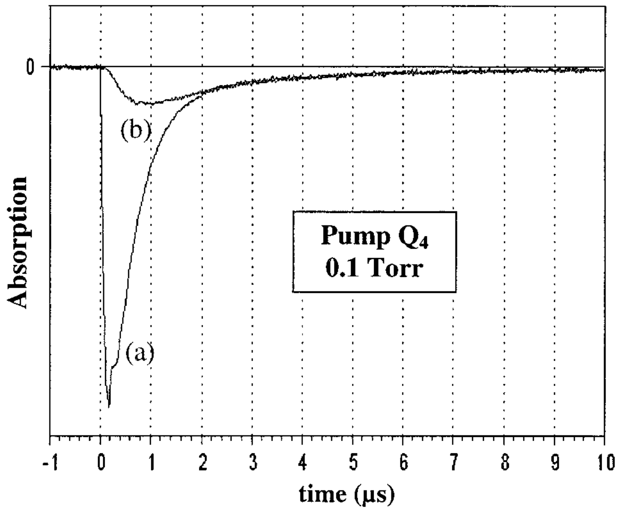

Figure 5. DR signals obtained by probing two different transitions at 2939.79 and 2939.70 cm^{-1} and pumping at the frequency of the Q_4 line in methane at 0.1 Torr pressure. The first signal (a) at 2939.79 cm^{-1} exhibits a decrease in transmission in the time scale of the laser pulse, demonstrating that the lower level of the probed transition is the $2\nu_3(F_2)$, $J = 4$ level excited by the pump laser. The second signal (b) at 2939.70 cm^{-1} is much weaker and shows a slower time decrease with a rate constant close to the first rise rate constant of signal a, demonstrating that the lower level of the probed transition is populated by rotational energy transfer from the laser-excited level.

TABLE 1: Frequencies of Some $P_6 \leftarrow 2\nu_3(F_2)$ Probed Transitions[a]

probe frequency (cm^{-1})	pump line	lower level of the probed transition
2939.79	Q_4	$2\nu_3(F_2)$, $J = 4$, A_2
2944.82	Q_3	$2\nu_3(F_2)$, $J = 3$, A_1
2945.27	Q_4	$2\nu_3(F_2)$, $J = 4$
2950.03	Q_4	$2\nu_3(F_2)$, $J = 4$, F_1
2950.13	Q_4	$2\nu_3(F_2)$, $J = 4$

[a] For each of them, the lower level of the transition is given along with the pump line populating this level.

probe and pump frequencies. In some cases we have been able to determine the symmetry of the probed level from the DR signals observed by pumping at different frequencies. For example, with a probe frequency at 2950.03 cm^{-1}, the very intense DR signal of Figure 4a is obtained only when the pump is tuned to the F symmetry component of Q_4 at 6003.837 cm^{-1}. When the pump is tuned to different lines having a F symmetry component, the DR signals are similar to that shown in Figure 4b. The lower level of the probed transition is then the $2\nu_3(F_2)$, $J = 4$ level of symmetry F_1. For the 2939.79 cm^{-1} probed transition, a very strong DR signal exhibiting a decay in the time scale of the pumping pulse is obtained with the pump tuned in this case to the high-frequency component of Q_4, at 6003.893 cm^{-1}, which corresponds to the A symmetry. Such a signal is shown in Figure 5a. It vanishes when the frequency is moved to the components of symmetry E or F. The lower level of the probed transition is then the $2\nu_3(F_2)$, $J = 4$ level of symmetry A_2. With the same probe and the pump tuned to the A symmetry components of the Q_3 and Q_6 lines, the DR signals are much weaker and exhibit a slower decay, as in Figure 4b. When the pump is tuned to the Q_2 and Q_5 lines, which have no component of A symmetry, no DR signal is detected, which confirms that state-to-state rotational energy transfer can only occur between levels of the same symmetry, in agreement with previous observations on CD_3H and CD_3Cl by Menard-Bourcin and Doyennette[9,10] and on CH_4 by Klaassen et al.[11]

The symmetry was determined in the same way for the 2944.82 cm^{-1} probed transition, the lower level of this transition being found to be the $2\nu_3(F_2)$, $J = 3$ level of symmetry A_1. Thus, the DR signals showing absorption of the probe beam intensity in the duration of the pumping pulse allow one to identify the lower level of the probed transition. The identified levels are summarized in Table 1.

In Figure 5, the very fast DR signal obtained by probing at 2939.79 cm^{-1} and tuning the pump laser to the component of A symmetry of the Q_4 line is compared to a signal obtained with the same pump and at the same methane pressure, but by probing at 2939.70 cm^{-1}. For this probe, the DR signal, given in Figure 5b, is much weaker and shows a slower decay. In this case, the lower level of the probed transition is no longer populated directly by the laser pulse but by rotational energy transfer from the laser-excited $2\nu_3(F_2)$, $J = 4$ level.

From the time evolution of these DR signals several rate constants, corresponding to different relaxation pathways, have been deduced. First, all the DR signals obtained by pumping the lower level of the probed transition exhibit a similar time evolution and the signal increase can be fitted essentially by a single-exponential function of time from which a rate constant, corresponding to rotational energy transfer, is deduced and found equal to $\beta_1 P^{-1} = 20 \pm 2\ \mu s^{-1}\ Torr^{-1}$, for all the probed transitions. Concerning the other DR signals, they exhibit first an initial decay with a rate constant close to $\beta_1 P^{-1}$, then a rise that can be well fitted by a sum of two exponential functions of time from which two rate constants are deduced: the largest rate constant $\beta_2 P^{-1} = 6 \pm 2\ \mu s^{-1}\ Torr^{-1}$ corresponds certainly to a redistribution of the rovibrational energy among the states of the tetradecad, and the other rate constant $\beta_3 P^{-1} = 1.7 \pm 0.2\ \mu s^{-1}\ Torr^{-1}$ corresponds to the global deexcitation of the tetradecad due to V−V transfer coupling the polyads.[1]

(c) DR Signals Showing an Amplification of the Probe Beam. These signals exhibit a fast initial increase followed by a slower decay, at the end of which the probe beam becomes weakly absorbed, and then a rise back to equilibrium. The time variation of these signals shows that a fast increase in population occurs in the upper level of the probed transitions that may be then assigned as pentad−tetradecad transitions. The signal presented in Figure 6 was obtained by tuning the OPO to the Q_4 line frequency and probing at 2963.99 cm^{-1} for 0.2 Torr methane pressure. The intensity and the rise time corresponding to this increase of population were found to be dependent on the pump line used. As shown by the signal of Figure 7 obtained with 0.015 Torr methane pressure, when the pump is tuned to the R_0 line frequency, the DR signal is very intense and shows an initial rise so fast that it cannot be measured with the bandwidth of our detector, even for very small gas pressures. This rise, which corresponds to the increase in population of the upper level of the probed transition, occurs in the time scale of the pumping pulse. Clearly, in this case, the upper level is the $2\nu_3(F_2)$, $J = 1$, A_2 level, which is directly populated by the R_0 laser line, giving rise to a quasi-instantaneous large amplification of the probe beam intensity in the time scale of the pumping pulse. From the energies given in the literature[3,4] for the levels of the ν_3 and $2\nu_3(F_2)$ states, this probed transition at 2963.99 cm^{-1} can be assigned to the $2\nu_3(F_2)$, $J = 1$, $A_2 \leftarrow \nu_3$, $J = 2$, A_1 transition.

Another example is the transition probed at 2944.69 cm^{-1}. When the pump is tuned to the Q_3 line, a very intense DR signal is obtained with a rise in the time scale of the pumping pulse, as shown in Figure 8. In this case, the upper level is the $2\nu_3(F_2)$, $J = 3$ level, which is directly populated by the Q_3 laser

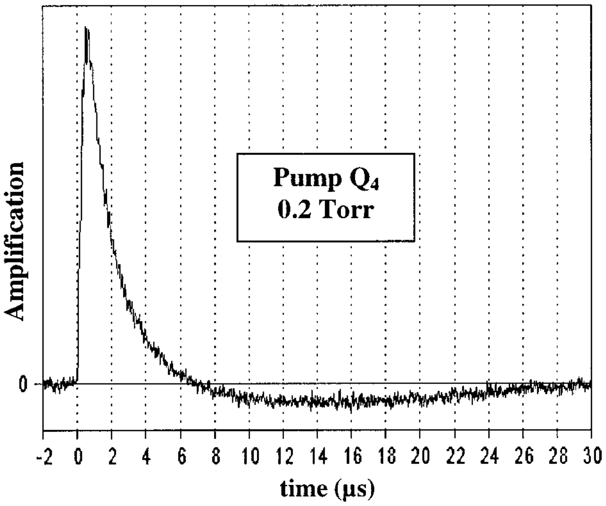

Figure 6. DR signal obtained by tuning the OPO to the Q_4 line and probing with the diode laser tuned to 2963.99 cm^{-1} in 0.2 Torr methane. The very fast initial rise in transmission is due to an increase of population in the upper level of the probed transition, which is assigned as a pentad → tetradecad transition. Then the signal shows a time decrease due to the global depletion of the tetradecad and the filling of the pentad, followed by a much slower increase back to equilibrium due to the relaxation of the pentad.

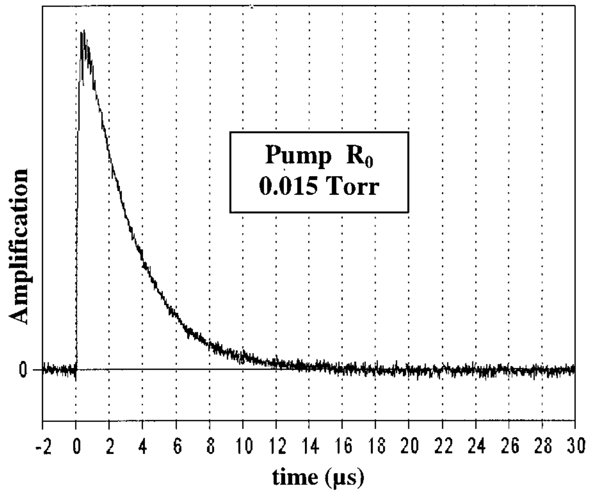

Figure 7. DR signal obtained by tuning the OPO to the R_0 line and probing with the diode laser tuned to 2963.99 cm^{-1}, the same transition as indicated in Figure 6. The methane pressure is 0.015 Torr. This very intense signal exhibits first, in the time scale of the laser pulse, a rise corresponding to an increase of population in the upper level of the probed transition, this level being obviously the $2\nu_3(F_2)$, $J = 1$, A_2 level directly excited by the pump laser. The following time decrease is due to the depletion of this level, mainly by rotational energy transfer, then by rovibrational energy transfer within the tetradecad.

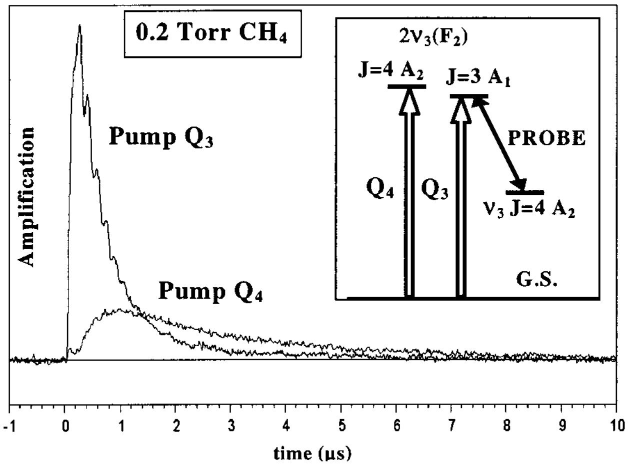

Figure 8. DR signals obtained by probing a transition at 2944.69 cm^{-1} and pumping successively at the frequencies of the Q_3 and Q_4 lines. In both cases, the methane pressure is 0.2 Torr. With the pump line tuned to Q_3, a very intense signal, similar to that given in Figure 7, is obtained, showing that the upper level of the probed transition is the $2\nu_3(F_2)$, $J = 3$, A_1 level directly excited by laser. With the pump line tuned to Q_4, a much weaker signal is obtained; the upper level of the probed transition is populated by rotational energy transfer from the $2\nu_3(F_2)$, $J = 4$, A_2 level directly excited by the laser.

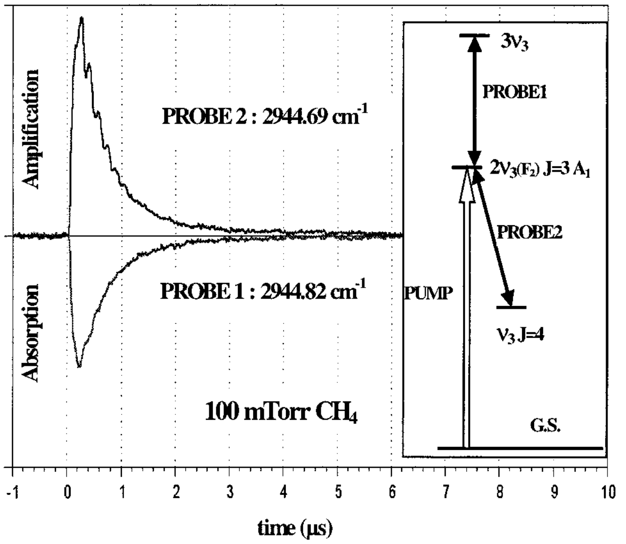

Figure 9. DR signals obtained by pumping at the frequency of the A component of the Q_3 line, i.e., at 6004.29 cm^{-1}, and probing the transitions at 2944.69 and 2944.82 cm^{-1}. They exhibit respectively, in the time scale of the laser pulse, a rise and a decay in the transmitted intensity of the probe beam. Both the probed transitions have in common the $2\nu_3(F_2)$, $J = 3$, A_1 level, which is the upper level for the transition at 2944.69 cm^{-1} and the lower level for the transition at 2944.82 cm^{-1}.

line. With the pump laser tuned to the Q_4 line and the same probed transition at 2944.69 cm^{-1}, the observed DR signal is less intense with a slower rise. Indeed, with this pump line, the molecules are now excited into the $2\nu_3(F_2)$, $J = 4$ level while the probed $2\nu_3(F_2)$, $J = 3$ level is then populated by rotational energy transfer from $J = 4$ to $J = 3$. It has been also possible to determine experimentally the symmetry of the levels of this transition at 2944.69 cm^{-1}. First, the previous signals are obtained when the frequency of the pump is tuned to the components of A symmetry, i.e., at 6004.293 cm^{-1} for the Q_3 line and at 6003.893 cm^{-1} for the Q_4 line. Then, with the Q_2 and the Q_5 lines, which have no component of A symmetry, no signal is obtained. Accordingly, this probed transition at 2944.69 cm^{-1} can be assigned to the $2\nu_3(F_2)$, $J = 3$, $A_1 \leftarrow \nu_3$, $J = 4$, A_2 transition. This assignment is consistent with the experimental determination of the symmetry of the levels involved in the probed transition.

Thus, the upper level of the probed transition at 2944.69 cm^{-1} is the $2\nu_3(F_2)$, $J = 3$, A_1 level. As seen above, this level is also the lower level of the probed transition at 2944.82 cm^{-1}. Both these DR signals, obtained by laser-exciting methane at 0.1 Torr, are given on the same scale in Figure 9. During the pumping pulse, probing the $2\nu_3(F_2)$, $J = 3$, A_1 level gives rise to an intense amplification of the probe beam when it is tuned to 2944.69 cm^{-1}, and to an intense absorption when it is tuned to 2944.82 cm^{-1}. In both cases, the level is relaxing essentially upon rotational energy transfer with the same rate constant of about 20 μs^{-1} Torr^{-1}.

TABLE 2: Frequencies of the $2\nu_3(F_2) \leftarrow \nu_3$ Probed Transitions[a]

probe frequency (cm^{-1})	pump line	transition assignment
2942.48	R_2	$2\nu_3(F_2)$, $J = 3$, E $\leftarrow \nu_3$, $J = 4$, E
2942.56	R_2	$2\nu_3(F_2)$, $J = 3$, $F_1 \leftarrow \nu_3$, $J = 4$, F_2
2944.60	Q_3	$2\nu_3(F_2)$, $J = 3$, $F_1 \leftarrow \nu_3$, $J = 4$, F_2
2944.69	Q_3	$2\nu_3(F_2)$, $J = 3$, $A_1 \leftarrow \nu_3$, $J = 4$, A_2
2951.24	P_3	$2\nu_3(F_2)$, $J = 2$, $A_1 \leftarrow \nu_3$, $J = 3$, A_2
2963.99	R_0	$2\nu_3(F_2)$, $J = 1$, $A_2 \leftarrow \nu_3$, $J = 2$, A_1
2981.20	Q_6	$2\nu_3(F_2)$, $J = 6$, $A_2 \leftarrow \nu_3$, $J = 6$, A_1
2981.82	Q_5	$2\nu_3(F_2)$, $J = 5$, $F_2 \leftarrow \nu_3$, $J = 5$, F_1

[a] For each of them, the pump line populating directly the upper level of the transition and the assignment for the probed transition are given.

Several other DR signals showing a fast amplification of the probe beam intensity have been obtained for different transitions. For the probe beam frequency tuned to 2942.48 cm^{-1}, we have determined, as previously, the upper level of the probed transition, which is the $2\nu_3(F_2)$, $J = 3$ level, while the lower level should be ν_3, $J = 4$, both being of E symmetry. In the same way, the upper levels of several other probed transitions have been determined by pumping with different line frequencies and the transitions have been assigned. These results are summarized in Table 2, giving for each probe beam frequency the pump line with which the upper level has been determined, the assignment of the probed transition, and the corresponding line in the $2\nu_3(F_2) \leftarrow \nu_3$ band.

All the DR signals obtained by laser-exciting the upper level of the probed transition are similar. After a quasi-instantaneous rise, each signal decreases first rapidly, showing that the excited level relaxes mainly upon rotational energy transfer to other rotational levels with a rate constant $\beta_1 P^{-1} \sim 20\ \mu s^{-1}\ Torr^{-1}$; then the signal is decreasing more slowly upon intermode transfer occurring between the states of the tetradecad as well as V−V transfer coupling the tetradecad to lower states. When the upper level of the probed transition is another level of the same symmetry as the laser-excited level, the DR signal exhibits first an initial rise corresponding to the filling of the upper level upon rotational energy transfer from the laser-excited level; then it shows a decay from which two rate constants can be deduced. They are found very close to $\beta_2 P^{-1}$ and $\beta_3 P^{-1}$ measured from the DR signals corresponding to tetradecad−P_6 transitions, i.e., $\sim$6 and $\sim$1.7 $\mu s^{-1}\ Torr^{-1}$.

Finally, after a weak absorption of the probe beam intensity, as shown in Figure 6, the rise to equilibrium is relatively slow with a rate constant $\beta_4 P^{-1} = 0.25 \pm 0.05\ \mu s^{-1}\ Torr^{-1}$, corresponding to the relaxation of the lower level of the probed transition, i.e., the ν_3 state.

Discussion

From the DR signals obtained by probing diad−octad transitions, a rate constant of $0.4 \pm 0.04\ \mu s^{-1}\ Torr^{-1}$ was found for the increase of population in the diad, due to near-resonant V−V energy transfer in which a bending quantum is exchanged between the collision partners. A smaller rate constant of $0.25 \pm 0.05\ \mu s^{-1}\ Torr^{-1}$ is found for the relaxation of the ν_3 state. This last result is in good agreement with the value of 0.25 $\mu s^{-1}\ Torr^{-1}$ reported by Hess and Moore[12] for the vibrational relaxation of the ν_3 state. These authors have also found a rate constant of 0.36 $\mu s^{-1}\ Torr^{-1}$ for the increase of population in the diad by energy transfer from ν_3, a value comparable to what is measured in our experiments for the increase of population of the diad after an excitation to $2\nu_3$.

The time evolution of the DR signals corresponding to pentad−tetradecad or tetradecad−P_6 transitions shows that very fast rotational energy transfer occurs with a rate constant of $20 \pm 2\ \mu s^{-1}\ Torr^{-1}$ from the laser-excited level to other levels of the same symmetry, A, E, or F, i.e., of the same nuclear spin modification. It is thus confirmed that rotational equilibration occurs for all levels of the same rovibrational symmetry; this was previously observed in other molecules such as CD_3H[9] and CD_3Cl[10] and more recently in CH_4, within the $\nu_1 + \nu_4$ and $\nu_3 + \nu_4$ states of the octad, from DR measurements by Klaassen et al.,[11] who obtained for these states a rotational energy transfer rate constant close to the value determined in the present work.

Following rotational relaxation, the $2\nu_3(F_2)$ levels relax first with a rate constant of $6 \pm 2\ \mu s^{-1}\ Torr^{-1}$, corresponding to fast rovibrational energy transfer from $2\nu_3(F_2)$ to other interacting states of the tetradecad, and then with a rate constant of $1.7 \pm 0.2\ \mu s^{-1}\ Torr^{-1}$, corresponding to the relaxation of the states of the tetradecad by near-resonant V−V energy transfers coupling the tetradecad to the lower polyads.[1]

Besides the improvement of the knowledge of rovibrational energy transfer in methane, our measurements are useful for the study of the spectroscopy of this molecule. Indeed, the transitions involving the states of the tetradecad are not yet well-known. The pentad−tetradecad transitions probed in our experiments have been assigned to $2\nu_3(F_2) \leftarrow \nu_3$ transitions. In numerous cases, our measurements have enabled us to determine the upper levels of the probed transitions and to deduce an exact assignment of the transitions, with their frequencies measured at $\pm 0.01\ cm^{-1}$. The probed tetradecad−P_6 transitions have been assigned to $P_6 \leftarrow 2\nu_3(F_2)$ transitions, most likely $3\nu_3 \leftarrow 2\nu_3(F_2)$ transitions because of their strength, and in some cases, our measurements have also allowed the determination of the lower levels of the probed transitions. These results provide new information for spectroscopists in their analysis of the tetradecad. Conversely, a good knowledge of the tetradecad levels should help us in further studies of rovibrational energy transfer coupling the $2\nu_3(F_2)$ state to the other states of the tetradecad.

Indeed, it should be very interesting to measure rovibrational energy transfer between the $2\nu_3$ sublevels of different vibrational symmetry by exciting methane in the $2\nu_3$ (F_2) state and probing a $2\nu_3$ (A_1) $\leftarrow \nu_3$ or a $2\nu_3$ (E) $\leftarrow \nu_3$ transition. In 1983, De Martino et al.[13] obtained, from double resonance spectra, frequencies and assignments of some lines of the $2\nu_3$ (A_1) $\leftarrow \nu_3$ band in the frequency range of our TDL, but attempts to obtain time-resolved DR signals at these frequencies have been unsuccessful.

On the basis of recent progress made at Dijon by Robert and Champion[14] in the analysis of the tetradecad, we hope to report soon time-resolved double resonance experiments probing pentad−tetradecad transitions other than those of the $2\nu_3$ (F_2) $\leftarrow \nu_3$ band. These new probed transitions should give better information about intermode energy transfer between the interacting states in the tetradecad and the pentad.

Conclusion

DR measurements have been performed in methane by pumping CH_4 molecules to $2\nu_3(F_2)$ levels with an OPO and probing transitions with a tunable diode laser emitting around 3.4 μm. Numerous DR signals corresponding to diad−octad, pentad−tetradecad, and tetradecad−P_6 transitions have been obtained, and assignments have been proposed.

The present measurements have been performed at room temperature in neat methane, which is the first step for a thorough understanding of rovibrational relaxation of CH_4. In view of atmospheric and planetologic applications, we plan to investigate soon the rovibrational energy transfer in mixtures of CH_4 with O_2 and N_2, the main atmospheric constituents, and with He and H_2, the main constituents in the atmosphere of giant planets. Of course, these DR measurements should be performed in the temperature range useful for such applications.

These future investigations (with new probed transitions and other collision partners) will allow us to refine the kinetic model presented in our previous paper[1] for the collisional relaxation of methane.

Acknowledgment. The authors are grateful to Dr. C. Camy-Peyret for helpful discussions and a careful reading of the manuscript. They thank also Dr. A. Henry for her help in the control of the stability of the diode laser wavelength and the determination of the characteristics of its emission with a TDL interferometer system. Support from the “Direction de la Recherche Et de la Technologie” is gratefully acknowledged.

References and Notes

(1) Doyennette, L.; Menard-Bourcin, F.; Menard, J.; Boursier, C.; Camy-Peyret, C. *J. Phys. Chem. A* **1998**, *102*, 3849.

(2) Encrenaz, T.; De Graauw, T.; Schaeidt, S.; Lellouch, E.; Feuchtgruber, H.; Beintema, D. A.; Bezard, B.; Drossart, P.; Griffin, M.; Heras, A.; Kessler, M.; Leech, K.; Morris, P.; Roelfsema, P. R.; Roos-Serote, M.; Salama, A.; Vandenbussche, B.; Valentijn, E. A.; Davis, G. R.; Naylor, D. A. *Astron. Astrophys. (Berl.)* **1996**, *315*, 397.

(3) Rothman, L. S.; Rinsland, C. P.; Goldman, A.; Massie, S. T.; Edwards, D. P.; Flaud, J.-M.; Perrin, A.; Camy-Peyret, C.; Dana, V.; Mandin, J.-Y.; Schroeder, J.; McCann, A.; Gamache, R. R.; Wattson, R. B.; Yoshino, K.; Chance, K.; Juks, K.; Brown, L. R.; Nemtchinov, V.; Varanasi, P. The HITRAN molecular spectroscopic database and HAWKS (HITRAN Atmospheric Workstation): 1996 edition. *J. Quant. Spectrosc. Radiat. Transfer (special issue HITRAN)* **1998**, *60*, 665.

(4) Wenger, Ch.; Champion, J.-P. Spherical Top Data Systems (STDS) software for the simulation of spherical top data, Université de Bourgogne, Dijon, France.

(5) Henry, A.; Hurtmans, D. *Spectrochim. Acta* **1999**, *A55*, 1967.

(6) Valentin, A. *Spectrochim. Acta* **1996**, *A52*, 823.

(7) Guelachvili, G.; Rao, K. N. *Handbook of infrared standards*; Academic Press: 1986.

(8) Yardley, J. T.; Moore, C. B. *J. Chem. Phys.* **1968**, *48*, 14; **1968**, *49*, 1111.

(9) Menard-Bourcin, F.; Doyennette, L. *J. Chem. Phys.* **1988**, *88*, 5506.

(10) Doyennette, L.; Menard-Bourcin, F. *J. Chem. Phys.* **1988**, *89*, 5578.

(11) Klaassen, J. J.; Coy, S. L.; Steinfeld, J. I.; Abel, B. *J. Chem. Phys.* **1994**, *101*, 10533.

(12) Hess, P.; Moore, C. B. *J. Chem. Phys.* **1976**, *65*, 2339.

(13) De Martino, A.; Frey, R.; Pradere, F. *Chem. Phys. Lett.* **1983**, *100*, 329.

(14) Robert, O.; Champion, J.-P. Private communication.