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# Measurement of the Transition Dipole Moment of the First Hot Band of the $\nu_2$ Mode of the Methyl Radical by Diode Laser Spectroscopy

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The line strengths of five Q-branch lines of the first hot band of the out-of-plane bending vibration ($2_1^2$) of the methyl radical, $CH_3$, have been measured using infrared laser absorption spectroscopy. The spectra of the radical were measured in situ in a microwave discharge using ditertiary butyl peroxide, diluted in argon as the precursor. The line strengths were used to determine the transition dipole moment of the hot band. Absolute concentrations of the radical were required for this purpose, and these were determined kinetically from the measured decays of the spectral lines after the discharge was extinguished. The translational, rotational, and vibrational temperatures were also determined spectroscopically from measured integrated line intensities and line widths. The transition dipole moment of the first hot band was determined to be 0.31(6) D. This value is in satisfactory agreement with the value of 0.27(3) D from a high-precision *ab initio* calculation using the self-consistent electron pairs (SCEP) method reported by Botschwina, Flesch, and Meyer [Botschwina, P.; Flesch, J.; Meyer, W. *Chem. Phys.* **1983**, *74*, 321].

## 1. Introduction

The methyl radical is one of the most important of the aliphatic free radicals and plays a central role in hydrocarbon combustion processes and discharges. It is also present in planetary atmospheres and in the interstellar medium.[2,3] Its structural and spectroscopic parameters have been the subject of numerous studies.[4–12] A number of different spectroscopic techniques have been used to determine its absolute concentration in the gas phase, including UV/visible, infrared, and Raman spectroscopies. In the infrared region, its intense out-of-plane bending mode, $\nu_2$, located at $\sim$606 cm$^{-1}$, provides a convenient band for concentration measurements, and this feature has been used extensively for this purpose.[13,14] However, this method requires a numerical value for the transition dipole moment, $\mu_2$, of the $\nu_2$ band. This has been determined experimentally for the fundamental band using diode laser absorption spectroscopy, which relies on finding absolute concentrations of the radical by kinetic spectroscopy using a method introduced by Yamada and Hirota.[15] The procedure is based on the well-established mechanism for the removal of the radicals by self-recombination. Earlier uncertainties in the experimentally derived values of $\mu_2$ have been considerably reduced with the availability of new kinetic data on the self-recombination of the radical, combined with more extensive measurements. Consequently, there is now good agreement between the latest experimental value[16] and an accurate *ab initio* calculation by Botschwina, Flesch, and Meyer[1] for the fundamental band.

The infrared laser absorption spectra of the methyl radical recorded in electric discharges consist not only of fundamental band lines but also of weaker hot band lines suggesting the possibility of determining the transition dipole moments of the hot bands for comparison with theory. This article describes the determination of the transition dipole moment of the first hot band of the $\nu_2$ mode employing the same experimental method as used earlier for the fundamental band.[16]

## 2. Experimental Section

A planar, pulsed microwave (2.45 GHz) reactor equipped with a multipass White cell and diode laser IR source was used to record spectra of the radical in the region of the $\nu_2$ band around 600−700 cm$^{-1}$. The radical was produced by discharging a mixture of ditertiary butyl peroxide heavily diluted in argon at a total pressure of 1 mbar. The measurements involved recording the line profiles of the transitions of interest to derive experimental values of the integrated absorption coefficients and complementary kinetic decays of these lines when the plasma was turned off. The latter provided an absolute concentration of the radical for evaluating the line strength and subsequently the transition dipole moment. The details of the kinetic measurements and the derivation of the absolute methyl concentration are described fully in ref 16. A survey spectrum of some of the Q-branch lines of the first hot band is shown in Figure 1.

## 3. Results

The integrated absorption coefficient, $K_\nu$, is related to the absolute concentration $N$ and the line strength $S(T)$ of an individual resolved vibration−rotation line at temperature $T$ by[4,17]

$$K_\nu = \int_\nu k(\nu)\mathrm{d}\nu = S(T)\,N \qquad (1)$$

The experimental approach necessary to measure an absolute concentration of $CH_3$, and hence enable eq 1 to be used, was the so-called decay method. The plasma was switched on and off for 10 s periods, and the decay of the absorption coefficient

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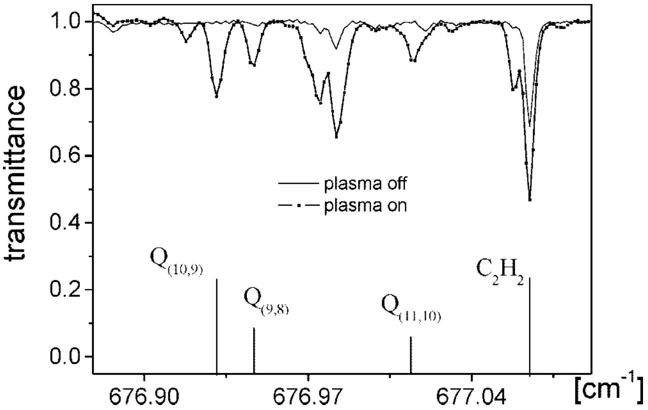

**Figure 1.** Survey spectrum showing Q-branch lines from the first hot band. Several lines of stable species are also observed, both inside and outside the plasma.

**TABLE 1: Measured Line Strengths of Q-Branch Lines of the $\nu_2$ First Hot Band of the Methyl Radical at 600 K**

| line | $Q_{(4,2)}$ | $Q_{(9,8)}$ | $Q_{(10,9)}$ | $Q_{(11,10)}$ | $Q_{(12,11)}$ |
|---|---|---|---|---|---|
| $S^a$ | 0.92(7) | 2.88(22) | 6.96(51) | 1.83(10) | 1.56(10) |

[a] S in units $10^{-20}$ cm molecule$^{-1}$. One standard deviation is given in parenthesis.

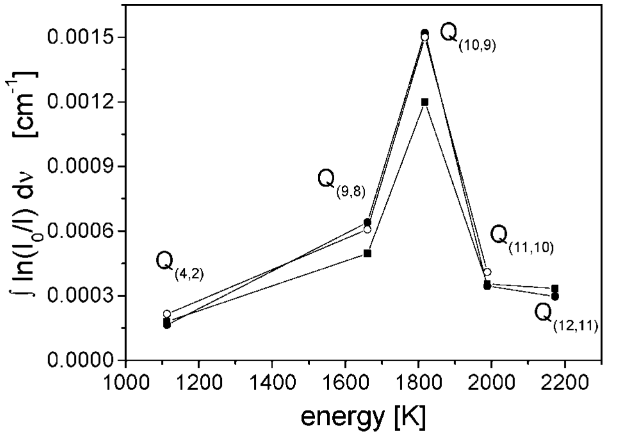

**Figure 2.** Integrated absorbances of the Q-branch lines of the first hot band $2_1^2$ as a function of the energy of the lower rovibrational level of each transition.

of the Q(8,8) line of the fundamental band when the plasma was switched off followed with millisecond resolution over 10 or more milliseconds. Second-order decay plots were obtained from which the absolute concentration of the radical during the plasma "on" period was then derived. The required methyl recombination rate coefficient in the presence of argon and at the experimental temperatures is available from the literature. The measured line strengths for the $\nu_2$ first hot band Q-branch transitions are given in Table 1. The values in brackets are the statistical standard deviations. It should be noted that the uncertainties in the line strengths of the Q(4,2), Q(11,10), and Q(12,11) lines are the largest because they overlap with lines of stable species produced in the plasma. Assuming a Boltzmann population distribution, then the relationship between the line strength and the transition moment is given (in centimeter−gram−second (cgs) units) by[4,17,18]

$$S_{v''J''K''}^{v'J'K'}(T) = \frac{8\pi^3}{3hc}\nu_{v''J''K''}^{v'J'K'} \frac{g_{v''J''K''} \exp\left(-\frac{E_{v''J''K''}}{kT}\right)}{Q(T)} \times (\mu_{v''}^{v'})^2 H_{J''K''}^{J'K'}\left[1 - \exp\left(-\frac{hc\nu_{v''J''K''}^{v'J'K'}}{kT}\right)\right] \quad (2)$$

$\nu_{v''J''K''}^{v'J'K'}$ is the transition frequency, $g_{v''J''K''}$ is the total statistical weight, $Q(T)$ is the total partition function, $E_{v''J''K''}$ is the energy of the lower level, $\mu_{\{v''\}}^{\{v'\}}$ is the transition dipole moment, and $H_{J''K''}^{J'K'}$ is the Hönl−London factor.

The translational, rotational, and vibrational temperatures are required to calculate the corresponding partition functions. Although the partition functions were deduced in the earlier study[16] on the fundamental band, they were also evaluated here from the hot band transitions using a more extended analysis. The translational temperature was obtained by fitting the line profiles to a Gaussian function since the line width is determined by Doppler broadening at the pressures used here. An additional Gaussian contribution to the line width arises from instrumental broadening (1−2 × $10^{-3}$ cm$^{-1}$), which was corrected for by using the lines of stable gas molecules to determine this broadening component. The net broadening due to the intrinsic Doppler broadening of the line corresponded to $T$ = 630 K. The pressure broadening contribution can be shown to be on the order of 2% under the conditions used here from the data for the pressure broadening of methyl by argon reported by Robinson et al.[19] The rotational temperature for a particular vibronic state is given by eq 3:

$$\exp\left(-\frac{E_{v''J''K''}}{kT_{\text{rot}}}\right) = \frac{Q(T)}{N}\frac{3hc\int k(\nu)\mathrm{d}\nu}{8\pi^3(\mu_{v''}^{v'})^2\nu_{v''J''K''}^{v'J'K'} H_{J''K''}^{J'K'}\left[1 - \exp\left(-\frac{hc\nu_{v''J''K''}^{v'J'K'}}{kT_{\text{vib}}}\right)\right]}\frac{1}{g_{v''K''J''}} \quad (3)$$

The rotational temperature can be obtained from this equation provided several different rotational lines from the same vibronic level are available. In practice, implementing eq 3 is most reliably achieved for Q-branch lines, and the rotational temperature was obtained using Q(4,2), Q(9,8), Q(10,9), Q(11,10), and Q(12,11). The integrated absorption coefficient for each line was measured three times under identical plasma conditions and plotted as a function of the lower rovibrational level energy (Figure 2). The effect of nuclear spin statistics is clearly visible for the line with $K = 3n$, i.e. Q(10,9). The closeness of the transition wavenumbers of the lines used means that the stimulated emission factor in eq 2 (the term in the square brackets) is, to a good approximation, constant. Equation 3 is then represented by

$$\exp\left(-\frac{E_{v''J''K''}}{kT_{\text{rot}}}\right) = \text{const} \times \frac{N_{v''J''K''}}{g_{v''J''K''}} \quad (4)$$

leading to

$$\ln\left(\frac{N_{v''J''K''}}{g_{v''J''K''}}\right) = \ln(\text{const}) - \frac{1}{T_{\text{rot}}}\frac{E_{v''J''K''}}{k} \quad (5)$$

The rotational energies in eq 5 were calculated from molecular constants reported by Yamada et al.[9] The data plotted according to eq 5 is shown in Figure 3 for the Q-branch data presented in Figure 2. It yields a rotational temperature of 590 ± 100 K, which is in good agreement with that obtained for the fundamental band, 600 ± 15 K, but with a much larger uncertainty.

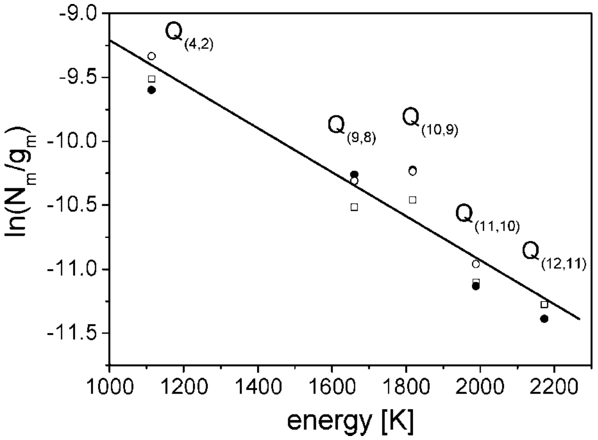

**Figure 3.** Scaled rotational population of the lower-energy level of the Q-branch transitions of the first hot band ($2_1^2$) as a function of the energy of that level.

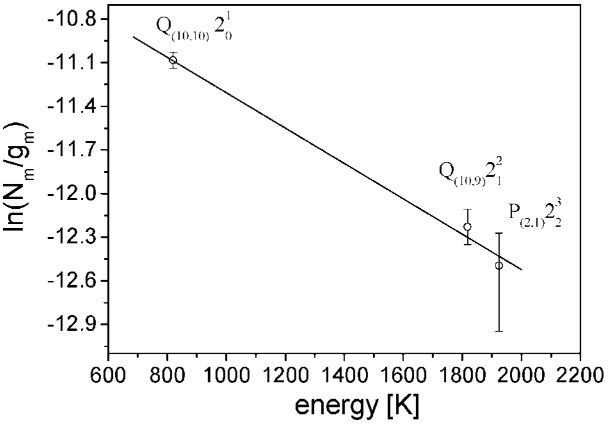

**Figure 4.** Scaled vibrational population as a function of the lower state rovibrational energy for three transitions from different vibrational levels.

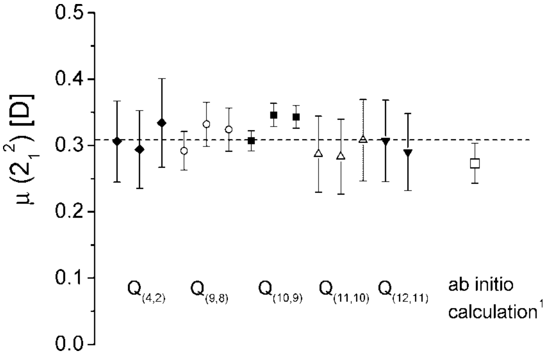

**Figure 5.** The transition dipole moment of the $\nu_2$ first hot band. Multiple determinations from the five measured transitions are compared with the *ab intio* calculation[1].

Experimentally, the vibrational temperature is obtained from measured integrated absorption coefficients of resolved vibration–rotation transitions in the fundamental and the hot bands. The temperature $T_\text{rot}$ in the Boltzmann factor on the left-hand side of eq 3 is replaced by $T_\text{vib}$, and the transition dipole moment $\mu$ has to be given for each vibrational band. The vibrational equation analogous to eq 5 for rotation is

$$\ln\left(\frac{N_{v''J''K''}}{g_{v''J''K''}}\right) = \ln(\text{const}) - \frac{1}{T_\text{vib}}\frac{E_{v''J''K''}}{k} \qquad (6)$$

In order to determine $T_\text{vib}$, *a priori* knowledge of the transition dipole moment of the fundamental and hot bands is required. We used two sources of data for this purpose. First, Yamada et al.[9] suggested that $\mu$ for the first hot band was twice that of the fundamental. Botschwina et al.[1] calculated that the transition dipole moments were factors of 1.25 and 1.41 greater than that for the fundamental for the first and second hot bands, respectively. The individual lines used in the experiments here to derive $T_\text{vib}$ were Q(10,10) from the fundamental band, Q(10,9) from the first hot band, and P(2,1) from the second hot band. They were scaled using eq 3 before-plotting them according to eq 6. The result is presented in Figure 4. The corresponding values of $T_\text{vib}$ are 500 or 800 K using the transition dipole moment increase suggested by Yamada et al.[9] ($\mu(2_1^2) = 2 \times \mu(2_0^1)$) or by Botschwina et al.[1] ($\mu(2_1^2) = 1.25 \times \mu(2_0^1)$, and $\mu(2_2^3) = 1.41 \times \mu(2_0^1)$), respectively. These widely spread values imply a considerable uncertainty in $T_\text{vib}$. Since the value from Yamada et al.[9] is based on an estimated transition dipole and is, in any case, lower than the translational and rotational temperatures, the higher value for the vibrational temperature seems more reasonable. It is well-known that vibrational temperatures in plasmas are generally higher than either the rotational or translational ones.[20,21] However, the first excited vibrational level lies at 606 cm$^{-1}$, i.e. about 860 K in temperature terms. Thus, Boltzmann equilibrium over the first vibrational levels is expected, because the vibrational energy is comparable with the kinetic energy. Moreover, the higher figure of 800 K has a large uncertainty associated with it due to the reduced number of data points and the errors arising in the calculated transition dipole moments. Hence it is reasonable to assume, as in the analysis of the fundamental band, that the vibrational temperature is in equilibrium with the rotational and translational temperatures and that $T_\text{trans} = T_\text{rot} = T_\text{vib} = 600$ K. The transition dipole moment was deduced to be 0.31(6) D from the measured line strengths of the five Q-branch hot band lines given earlier. Figure 5 shows the transition dipole moment values of the first hot band obtained from the experimental line strength measurements of the different transitions.

## 4. Discussion

All four normal modes were considered in calculating the vibrational partition function, although the $\nu_2$ mode makes the largest contribution. The wavenumbers and degeneracies of the modes[8–12] are $\nu_1 = 3004.417$ cm$^{-1}$ ($g_\nu = 1$), $\nu_2 = 606.4531$ cm$^{-1}$ ($g_\nu = 1$), $\nu_3 = 3160.8212$ cm$^{-1}$ ($g_\nu = 2$), and $\nu_4 = 1396$ cm$^{-1}$ ($g_\nu = 2$). At the experimental temperatures, only the ground state levels, the first six excited vibrational levels of $\nu_2$, one each for $\nu_1$ and $\nu_3$, and three for $\nu_4$, are required here. The contributions of higher vibrational levels to the partition function are negligible at experimental temperatures. The $\nu_2$ vibration is strongly anharmonic, and the contribution of the anharmonicity has also been considered here.

Yamada et al.[9] measured transitions from the fundamental band, $2_0^1$, and two hot bands, $2_1^2$ and $2_2^3$, and evaluated the energy separation between the corresponding vibrational levels as $E_1 - E_0 = 606.4531$ cm$^{-1}$, $E_2 - E_1 = 681.637$ cm$^{-1}$, and $E_3 - E_1 = 731.076$ cm$^{-1}$. A large negative anharmonicity is clearly indicated by these values. They have considered two potential functions in calculating the vibrational energy. First, a power series expansion in $x$, where $x$ is the displacement of the carbon atom from the plane containing the hydrogen atoms:

$$V_2(x) = \frac{1}{2}k_2x^2 + \frac{1}{4\,!}k_4x^4 + \frac{1}{6\,!}k_6x^6 \qquad (7)$$

The potential constants obtained are $k_2 = 0.3475$ mdyn/Å, $k_4 = 35.61$ mdyn/Å$^3$, and $k_6 = -1496$ mdyn/Å$^5$. Yamada et

**TABLE 2: Reported Values of the Vibrational Band Origins of the $\nu_2$ Mode of the Methyl Radical**

| | $E_{v+1} - E_v$ [cm$^{-1}$] | | |
|---|---|---|---|
| vibrational band | present (calc.) | experimental | calculation[a] |
| $2_0^1$ | 606.492 | 606.4531[a] | 606.3601 |
| $2_1^2$ | 681.609 | 681.637[a] | 681.8487 |
| $2_2^3$ | 731.050 | 731.076[a] | 730.9084 |
| $2_3^4$ | 766.972 | 772 ± 4[b] | 766.9622 |
| $2_4^5$ | 793.425 | | |
| $2_5^6$ | 812.323 | | |

[a] Reference 9. [b] Reference 25.

al.[9] attributed the anharmonicity to the vibronic interaction between the electronic ground state ($\tilde{X}^2A_2''$) and the electronically excited $\tilde{B}^2A_2''$ state. Assuming this interaction is of the type $ax$, the resulting out-of-plane potential function in the ground electronic state is given by

$$V_2(x) = \frac{1}{2}k_2^{(0)}x^2 + \frac{1}{2}\Delta E - \frac{1}{2}(\Delta E^2 + 4\,a^2x^2)^{1/2} \qquad (8)$$

where $k_2^{(0)} = 2.7888$ mdyn/Å, $a = 1.0599$ mdyn, and $\Delta E = 46205$ cm$^{-1}$. Both these potentials have been used here to calculate the vibrational energies. Since the one-dimensional Schrödinger equation cannot be solved analytically for either of these potentials, the eigenvalues were calculated using the Numerov−Cooley method.[22–24] The eigenvalues, $E_v$, were calculated up to level $v = 6$, for which the two potential functions 7 and 8 are still identical ($|x| < 0.9$ b $\rightarrow |x| < 0.5$ Å). The present calculated vibrational band origins of $\nu_2$, together with the earlier reported values, are given in Table 2. The experimental value for the $2_3^4$ hot band reported by Hermann and Leone[25] shows good agreement with the present calculations. Finally, the measured and calculated vibrational energy values have been used to determine a more accurate vibrational partition function. The present approach lowers the value of the vibrational partition function by 1.3% at 600 K and has a small effect on the transition dipole moment ($\mu \sim (Q_V)^{1/2}$). However, at higher temperatures, the use of anharmonic potentials in the calculations will lead to decreases of $Q_V$, of about 10% at 2000 K and a corresponding increase of up to 10% in the line strength ($S \sim 1/Q_V$). (The partition function and line strength values at elevated temperatures including anharmonicity and other factors will be published elsewhere.) One further check on the accuracy of the calculated partition function was made, namely, the assumed factorization into vibrational, rotational, and nuclear spin terms. The partition function from an exact sum over all vibration−rotation levels was identical to that using the conventional formulas to about 1%.

The present value of the transition dipole moment of the first hot band is 1.44 times that of the fundamental band and lies between the factor of 2 suggested by Yamada et al.[9] and the factor of 1.25 calculated by Botschwina and co-workers.[1] Given the excellent agreement between the measured and *ab initio* values for the fundamental band, the source of the divergence of theory and experiment for the first hot band has been considered further. The explanation lies in part in the experimental error associated with the hot band measurement, shown for individual determinations in Figure 5. The accumulated error in the measurement is, not surprisingly, considerably higher than that for the fundamental band, and is estimated to be 19% versus 11%. The main contributions arise from the temperature uncertainties for calculating the partition function, the overlapping of lines, and the small number of data acquisitions. Botschwina et al.[1] estimate their error as 10% for the fundamental band. Assuming a similar error for the hot band, an upper limit of 0.30 D is obtained for the calculated value. This largely falls within the experimental error range, which has a lower bound of 0.25 D. The self-consistent electron pairs (SCEP) results imply that the transition dipole moment has an approximately $(v + 1)^{0.3}$ dependence, much smaller than the linear dependence suggested by Yamada et al.[9] and also assumed by Hermann and Leone.[25] The experimental result obtained here suggests an intermediate value following a $(v + 1)^{0.5}$ dependence, i.e., that expected for a harmonic oscillator.

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