Line strengths and transition dipole moment of the $v_2$ fundamental band of the methyl radical

G. D. Stancu and J. Röpcke
Institute of Low Temperature Plasma Physics-Greifswald, 17489 Greifswald, Germany

P. B. Davies
Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, United Kingdom

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The line strengths of nine $Q$-branch lines in the $v_2$ fundamental band of the methyl radical in its ground electronic state have been measured by diode laser absorption spectroscopy. The vibration–rotation spectrum of methyl was recorded in a microwave discharge in ditertiary butyl peroxide heavily diluted in argon. The absolute concentration of the radical was determined by measuring its kinetic decay when the discharge was extinguished. The translational, rotational, and vibrational temperatures, also required to relate the line strengths to the transition dipole moment, were determined from relative integrated line intensities and from the Doppler widths of the lines after allowing for instrumental factors. The line strengths of the nine $Q$-branch lines were used to derive a more accurate value of the transition dipole moment of this band, $\mu_2 = 0.215(25)$ D. Improved accuracy over earlier measurements of $\mu_2$ (derived from line strengths of single lines) was obtained by integrating over the complete line profile instead of measuring the peak absorption and assuming a Doppler linewidth to deduce the concentration. In addition, a more precise value for the rate constant for methyl radical recombination than available earlier was employed. The new value of $\mu_2$ is in very good agreement with high-quality $ab$ initio calculations. Furthermore, the ratio of the transition dipole moments of the $v_2$ and $v_3$ fundamental bands in the gas phase is now in highly satisfactory agreement with the ratio determined for the condensed phase.

INTRODUCTION

The methyl radical plays a fundamental role in many chemical systems, such as combustion,\textsuperscript{1} chemical-vapor deposition,\textsuperscript{2} and atmospheric chemistry.\textsuperscript{3} Furthermore, it is present in the interstellar medium\textsuperscript{4} and in the atmospheres of Saturn\textsuperscript{5} and Neptune.\textsuperscript{6} It has no electric-dipole-allowed rotational transitions because of its $D_{3h}$ symmetry and IR spectroscopy has become one of the most suitable methods for its detection. The determination of methyl radical concentrations in terrestrial and astronomical sources using IR spectroscopy relies on the availability of accurate line strengths and transition dipole moments. The $v_2$ band of CH$_3$ is the strongest of its IR active fundamentals and particularly useful for quantitative measurements. The first experimental value of the $v_2$ fundamental band transition dipole moment $\mu_2$ determined over 20 years ago,\textsuperscript{7} has a stated experimental uncertainty of 17%. The need for a more accurate and precise value of $\mu_2$ has been highlighted by the measurements of CH$_3$ in the atmosphere of Neptune,\textsuperscript{8} where the main contribution to the discrepancy between model concentrations and measurements is believed to arise from the uncertainty in $\mu_2$.

Infrared tunable diode laser absorption spectroscopy (TDLAS) has proven to be a convenient and reliable technique for concentration measurements in discharges as well as under ambient conditions. The high spectral resolution, absolute calibration, time-resolved capability, and different modulation methods are some of the advantages of TDLAS compared with other techniques. Substantial spectroscopic and mechanistic results have been obtained using TDLAS to detect the methyl radical.\textsuperscript{6-9} Furthermore, great improvements have been made in recent years with respect to data acquisition so that microsecond-resolved measurements of integrated absorption coefficients can be achieved. This strongly suggested that a new measurement of $\mu_2$ for methyl would be worthwhile. In their seminal work on the infrared laser spectroscopy of the $v_2$ band of CH$_3$ using TDLAS, Yamada et al.\textsuperscript{9} assumed a value of 0.1 D for the transition dipole moment of the $v_2$ fundamental based on the absolute intensity of their data and by analogy with the $v_2$ band of ammonia (0.3 D). Shortly afterwards, Yamada and Hirota\textsuperscript{7} made the first quantitative measurement of $\mu_2$, using the facile dissociation of ditertiary butyl peroxyde (DTBP) in a low-pressure dc discharge to form the radical. The decay of the peak absorption of the $Q_{(4,4)}$ line was used to determine the absolute [CH$_3$] required to deduce the line strength and ultimately $\mu_2$. This method assumes that the main removal process for methyl is its bimolecular recombination to C$_2$H$_6$.

Wormhoudt and McCurdy\textsuperscript{10} made a further measurement, also using TDLAS, but employed a different method...
for producing CH$_3$, namely, the reaction of fluorine atoms with methane in a discharge flow system. The change in methyl concentration as a function of the methane injection position permitted the absolute methyl concentration to be determined. The principal methyl removal process was again assumed to be the self-recombination of the radicals. The second derivative recordings of the $Q_{(8,8)}$ line were converted into optical depth, $\ln(I_0/I)$, by calibrating them against an unmodulated absorption signal from an intense CH$_3$ line. The line strength was measured as $(3.2 \pm 1.0) \times 10^{-19}$ cm molecule$^{-1}$ at room temperature, which corresponds to a band strength of $(2.5 \pm 0.8) \times 10^{-17}$ cm molecule$^{-1}$ and a transition dipole moment $\mu_2$ of 0.315 ± 0.05 D.

A theoretical calculation of $\mu_2$ in 1983 by Botschwina et al. complements these experimental results. They calculated the potential-energy surface appropriate for the symmetric stretch and out-of-plane bending motion for CH$_3$ using unrestricted Hartree–Fock self-consistent electron pair (UHF) wave functions. They obtained $\mu_2=0.218\pm0.022$ D for the fundamental transition. Further theoretical work was reported by Pacansky et al. in connection with calculations of the IR and Raman spectra of hydrocarbon radicals. Their calculated $v_2$ band intensities were 80.3 km/mol (UHF/6-311G) or 1.33 \times 10^{-17}$ cm molecule$^{-1}$, and 82.74 km/mol (UMP2 (unrestricted Möller–Plesset second-order perturbation) 6-311G) or 1.37 \times 10^{-17}$ cm molecule$^{-1}$, and for the $v_3$ band, 11 km/mol and 4.13 km/mol, respectively.

Two experimental determinations of the transition dipole moment of the $v_3$ band should also be mentioned here. First, Tanarro et al. used an electric discharge in methane at 1 mbar as a source of CH$_3$ and measured the absorption of the $rQ_{(4,0)}$ line of the $v_3$ fundamental by IR difference frequency spectroscopy. Double modulation detection was employed to enhance the weak absorption and minimize overlapping with lines of other plasma species. The absolute concentration of CH$_3$ was again determined following the decay of the peak absorption coefficient. The measured value of $\mu_3$ was 0.029 ± 0.005 D. Second, Bethardy and Macdonald determined $\mu_3$ by producing methyl radicals in a flow tube using laser flash photolysis and measuring their spectra using transient infrared absorption spectroscopy with an F-center laser. The methyl radical concentration was deduced by assuming that it was formed stoichiometrically from the reaction CN + CH$_3$ = CH$_3$ + HCN (at 5.3 mbar and 295 K). The absorption profile was assumed to arise from both the Doppler effect and pressure broadening. The pressure broadening parameters for methyl lines were measured from which they obtained $\mu_3=0.0327\pm0.0021$ D, satisfactorily close to the result of Tanarro et al. Last, Snelson measured both bands simultaneously in the condensed phase. The methyl radical was formed in the gas phase by pyrolysis of CH$_3$I or Hg(CH$_3$)$_2$ and then trapped in a Ne matrix. The ratio of the peak absorbances of the $v_2$ and $v_3$ bands was obtained for a variety of experimental conditions and found to be approximately 9:1.

This article describes a new measurement of $\mu_2$ for the $v_2$ fundamental band of the methyl radical in order to resolve the differences between earlier experimentally measured values and between experiment and theory. The method used for determining the absolute methyl radical concentrations was the same as that used by Yamada and Hirota. However, integrated intensities and many more lines were used. Furthermore, the kinetic conditions were more precisely specified and the temperature determined more quantitatively. The resulting value of $\mu_2$ is now in much better agreement with theory.

**THEORY**

Under conditions of weak absorption, the radiation intensity $I(v)$ transmitted through a homogeneous sample is given by the Beer–Lambert law,

$$I(v)=I_0(v)\exp[-k(v)L],$$

where $I_0(v)$ is the incident intensity, $k(v)$ is the absorption coefficient, and $L$ is the absorption length. The integrated value of the absorption coefficient $K_v$ is given by

$$K_v=\int k(v)dv=S(T)N,$$

where $S(T)$ is the line strength of a specific absorption line at the temperature $T$ and $N$ is the total concentration of particles in all states. The profile of an actual absorption line can be included by expressing $k(v)$ as

$$k(v)=S(T)Nf(v-v_{nm}),$$

where $f(v-v_{nm})$ is the normalized line-shape function and $v_{nm}$ is the resonance frequency of the transition. In this study $S(T)$ is determined from the experimentally measured integrated absorption coefficient [Eq. (2)].

An alternative approach, which was used by Yamada and Hirota and by Wormhoudt and McCurdy, is to measure $(I_0/I)$ at the maximum of the absorption line and to assume that the absorption profile is determined by Doppler broadening so that the line shape is Gaussian. Then $K_v$ becomes

$$K_v=\frac{1}{L}\sqrt{\frac{\pi}{\ln 2}}\Delta v_D\ln\left(\frac{I_0}{I_{\text{max}}}\right),$$

where $\Delta v_D$ is the Doppler half width at half maximum,

$$\Delta v_D=3.581 \times 10^{-7} v_{nm} \sqrt{T/M}.$$

$M$ is the molar mass and $T$ is the temperature. This method is less accurate than integrating over the full line profile, however, because it is well known that other factors like laser noise can also contribute to the Gaussian line shape.

The relationship between the line strength $S(T)$ and the dipole moment matrix element of the transition $|R_{\nu_3 J K}^{\nu_2 J' K'}|^{2}$ is given by

$$S_{\nu_3 J K}^{\nu_2 J' K'}(T)=\frac{8\pi^2}{3hc}v_{\nu_3 J K}^\nu v_{\nu_2 J' K'}^\nu N_{\nu_3 J K}^\nu N_{\nu_2 J' K'}^\nu |R_{\nu_3 J K}^{\nu_2 J' K'}|^2 \times \left[1-\exp\left(-\frac{hc v_{\nu_3 J K}^\nu}{kT}\right)\right],$$

(6)
where \( v, J, \text{and } K \) are the quantum numbers of the lower (\( \nu \)) and upper (\( \nu' \)) rovibrational levels, \( v_{\nu' \nu J' K'} \) is the transition frequency, and \( N_{\nu' \nu J' K'} \) is the population density of the lower level. The last factor in square brackets on the right side of (6) allows for stimulated emission as well as absorption. At thermal equilibrium, the population density distribution is governed by Boltzmann’s law,

\[
\frac{N_{\nu' \nu J' K'}}{N} = \frac{g_{\nu' \nu J' K'}}{Q(T)} \exp \left( \frac{-E_{\nu' \nu J' K'}}{kT} \right),
\]

where \( g_{\nu' \nu J' K'} \) is the total statistical weight, \( Q(T) \) is the total partition function, and \( E_{\nu' \nu J' K'} \) is the energy of the lower level. The transition dipole moment matrix element \( |R_{\nu' \nu J' K' K}^J| \) is related to the transition dipole moment \( \mu_{\nu' \nu} \) by the Hön–London factor \( H_{\nu' \nu J' K'} \).

\[
|R_{\nu' \nu J' K'}| = (\mu_{\nu' \nu})^2 H_{\nu' \nu J' K'}.
\]

The \( \text{CH}_3 \) radical absorption lines measured in the present work were almost all \( Q \)-branch lines for which

\[
H_{\nu' \nu J' K'} = \frac{K^2}{J(J + 1)}.
\]

Combining Eqs. (6)–(9) gives the relationship between the line strength and the transition dipole moment \( \mu_{\nu' \nu} \) in units of cm molecule \(^{-1}\),

\[
S_{\nu' \nu J' K'}(T) = \frac{8 \pi^3}{3\hbar c} v_{\nu' \nu J' K'} \frac{g_{\nu' \nu J' K'}}{Q(T)} \exp \left( \frac{-E_{\nu' \nu J' K'}}{kT} \right) (\mu_{\nu' \nu})^2 
\]

\[
\times \frac{K^2}{J(J + 1)} \left[ 1 - \exp \left( -\frac{\hbar c v_{\nu' \nu J' K'}}{kT} \right) \right].
\]

The transition dipole moment is then obtained from (10) using the experimentally measured line strengths [Eq. (2)]. Conversely, once \( \mu \) has been determined, it permits the line strength of any line to be calculated and hence the absolute methyl radical concentration can be obtained using Eq. (2).

For stable molecules, the evaluation of \( S(T) \) from Eq. (2) is straightforward because the concentration \( N \) is readily obtained, but for unstable species like methyl, determining \( N \) is more difficult. In this work a kinetic method of determining the methyl radical concentration, originally introduced by Yamada and Hirota,\(^7\) was used and is described in the Results section.

**EXPERIMENT**

Details of the diode laser spectrometer and discharge absorption cell have been reported elsewhere\(^20\) and only a brief account of them is given here. The methyl radical was produced in a 2.45-GHz discharge in mixtures of diteritary butyl peroxide and argon at total pressures around 1 mbar and microwave powers of 1.5 kW. Argon was chosen as the carrier gas because of the extensive data available on methyl radical recombinations using Ar as the third body. The mixtures used here were composed of at least 90% Ar. The absorption cell was fitted with White-type optics, providing 48 passes through the discharge. The visible emission from the plasma was uniformly distributed below the horizontal quartz window (through which the microwaves were coupled into the reactor). The discharge length was 45 cm. Due to inhomogeneities in the plasma edges, an uncertainty of 10% was estimated for the overall absorption path length of 2160 cm.

Two kinds of experiments were performed: (a) time-dependent measurement of the decay of the absorption coefficient when the discharge was turned off to obtain absolute methyl concentrations and (b) measurements of the absorption coefficients of different rovibrionic lines. Line positions for the \( \nu_2 \) band of \( \text{CH}_3 \) were taken from the work of Yamada et al.\(^8\) and identified using \( \text{N}_2 \text{O} \), \( \text{CO}_2 \), and \( \text{C}_2 \text{H}_2 \) reference spectra.\(^9\) Interpolation and relative wave-number calibration was provided by an air-spaced etalon with a free spectral range of 0.0096 cm\(^{-1}\). Recordings were made on two channels simultaneously. One channel for the etalon and the other for the reference and plasma spectra recorded either simultaneously or sequentially. A survey spectrum in the \( \nu_2 \) fundamental band of \( \text{CH}_3 \) is shown in Fig. 1.

Several sources of experimental error were identified and minimized in making the measurements. Since the tuning rate of the diodes is slightly nonlinear, it was essential to frequency calibrate each methyl line with an absolute frequency in order to obtain accurate line profiles and absorption coefficients. The integrated absorption coefficient is less sensitive to \( I_0(\nu) \) and frequency calibration than the line profile where both factors strongly influence the numerical values. Other factors that have to be considered are power saturation effects, when the population distribution is strongly perturbed by the laser intensity, overlapping laser mode, and instrumental broadening. All these factors change the line profile. In particular, instrumental broadening (considered in detail later) changes the line profile leading to errors in determining the temperature. Typical instrumental contributions to the linewidth were of the order of 10\(^{-3}\) cm\(^{-1}\). In total, ten lines were studied in the fundamental band \( \{Q(1,1) \cdot Q(2,2) \cdot Q(3,3) \cdot Q(4,4) \cdot Q(5,5) \cdot Q(6,6) \cdot Q(8,8) \cdot Q(5,3) \cdot Q(4,4) \cdot Q(6,6) \cdot Q(8,8) \cdot Q(7,5) \cdot Q(6,6) \cdot Q(8,8) \cdot Q(7,5) \cdot Q(6,6) \cdot Q(8,8) \cdot Q(7,5) \cdot Q(6,6) \cdot Q(8,8) \cdot Q(7,5) \cdot Q(6,6) \cdot Q(8,8) \cdot Q(7,5) \} \).
Q_{(10,10)}, Q_{(12,12)}, and R_{(0,0)}, seven in the first hot band [Q_{(4,2)}, Q_{(9,8)}, Q_{(10,9)}, Q_{(11,12)}, Q_{(12,11)}, P_{(3,0)}, and P_{(4,2)}], and one from the second hot band [P_{(2,1)}].

RESULTS

In order to derive accurate line strengths using Eq. (2), it is first necessary to obtain the absolute concentration of the methyl radical (N) and its temperature in the discharge.

A. Absolute CH_3 concentrations

The plasma was switched on and off for periods of 10 s and the decay of the methyl radical signal was measured during the off period. The Q_{(8,8)} line, which had the highest signal-to-noise ratio, was selected for measuring decays. The laser frequency was swept over the absorption line at a rate of a few kilohertz and the spectrum was recorded every millisecond. Sweep integration was used for data acquisition, i.e., the laser frequency sweeps over the full absorption profile and the area of the absorption coefficient determined by integration of the nonlinear least-squares fit to the known spectral line profile. Finally, the software plots the integrated absorption coefficient as a function of time.

The absolute concentration was obtained from the decay data of the integrated absorption coefficient and the recombination rate constant determined following the method of Yamada and Hirota. For the purpose of the methyl concentration measurements, it was assumed that the radical was confined to the visible plasma region in the reactor. It is well known from numerous kinetic studies that the main loss channel under the conditions used here, i.e., pressure of 1 mbar, is self-recombination via a three-body reaction [hereafter called reaction (i)]

\[ \text{CH}_3 + \text{CH}_3 + M \rightarrow \text{C}_2\text{H}_6 + M. \]

Literally hundreds of experiments have been reported showing that the recombination rate constant depends on the nature and concentration of the third body and on the temperature. However, it is assumed that the temporal change in the methyl radical concentration, \([\text{CH}_3] = N\), follows the more general relationship:

\[ -\frac{dN}{dt} = 2k_1N^2 + k_2N, \tag{11} \]

where \(k_1\) is the self-recombination rate constant and \(k_2\) is a rate constant encompassing all first-order losses like diffusion and surface recombination. \(k_1\) is actually a composite rate constant for the third-order reaction (ii) which under our conditions is in the intermediate pressure regime between the low- and high-pressure limits. Its value under our conditions is discussed later. With \(N_{(t=0)} = N_0\), Eq. (11) can be converted to

\[ N(t) = \frac{k_2N_0}{(k_2 + 2N_0k_1)\exp(k_2t) - 2k_1N_0}. \tag{12} \]

If the first-order processes are the main steps in removing CH_3, then only the second term in (11) is needed and the time dependence, \(N(t)\), reduces to

\[ N(t) = N_0 \exp(-k_2t), \tag{13} \]

i.e., an exponential decay. If instead the recombination reaction is the dominant process, then

\[ N(t) = \frac{N_0}{1 + 2N_0k_1t}. \tag{14} \]

Figure 2 shows typical decay data for methyl, which has been fitted with the functions in Eqs. (12)–(14). The functions in (12) and (14) not only fit the data more satisfactorily than function (13) but essentially coincide with each other over the complete time frame confirming that reaction (i) is the main loss channel. Rearrangement of Eq. (14) yields

\[ N_0 = \sqrt{\left| \frac{K_v}{|K_v|} \right| - 1} \frac{1}{2k_1t}. \tag{15} \]

It follows from Eq. (2), since \(S(T)\) is constant, that \(K_v = \int k(v)dv\) is proportional to \(N\) and Eq. (15) converts to

\[ N_0 = \left| \frac{K_v}{|K_v|} \right| - 1 \frac{1}{2k_1t}. \tag{16} \]

or

\[ \left| \frac{K_v}{|K_v|} \right| = 1 + 2k_1N_0t. \tag{17} \]

Hence by measuring the time dependence of the integrated absorption coefficient and knowing the value of \(k_1\), the absolute concentration of the methyl radical, \(N_0\), can be obtained from (16). Figure 3 shows the data from Fig. 2 plotted according to Eq. (17) and fitted linearly. This plot confirms the bimolecular nature of the loss process and provides a means for obtaining \([\text{CH}_3] = N_0\) from the slope.

The rate constant \(k_1\) for the self-recombination reaction of methyl radicals has been extensively investigated between \(10^{-1}\) and \(10^{3}\) mbar and from 200 to 1700 K. Baulch et al. compiled all the experimental data available up to 1994. In order to use this data for the specific temperature and argon
concentrations used here, the following functions were employed. Based on the Troe\textsuperscript{22} model, the constant \(k_1\) can be expressed as:\textsuperscript{21}

\[
k_1 = \frac{k_0 k_\infty [M]}{k_0 [M] + k_\infty F},
\]

where \(k_0\) is the recombination rate constant in the low-pressure limit ((\(M\)) \(\rightarrow 0\)), \(k_\infty\) is the high-pressure limiting value ((\(M\)) \(\rightarrow \infty\)), and \(F\) is a broadening factor. Taking logs of (18),

\[
\log(k_1) = \log\left(\frac{k_0 [M] k_\infty}{k_0 [M] + k_\infty}\right) + \log(F),
\]

with \(\log(F)\) given by

\[
\log(F) = \frac{\log(F_C)}{1 + \frac{\log\left(\frac{k_0 [M]}{k_\infty}\right)}{n}},
\]

where \(n = 0.75 - 1.27\log(F_C)\). The recommended values for calculating \(k_1\) as a function of temperature and pressure have been given by Baulch \textit{et al.}\textsuperscript{21} as \(k_\infty = 6 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}\), \(k_0 = [\text{Ar}] 3.5 \times 10^{-7} T^{-7} \exp(-1390/T) \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}\), and \(F_C = 0.38 \exp(-T/773) + 0.62 \exp(-T/1180)\). The resulting dependence of \(k_1\) on [\text{Ar}] calculated at the same temperatures reported by Baulch \textit{et al.}\textsuperscript{21} is shown in Fig. 4.

It remains to find the temperature under the conditions used in this study to be able to find \(k_1\). It has been shown that the gas temperature in pulsed microwave discharges returns to room temperature on the microsecond time scale after the discharge is extinguished.\textsuperscript{23} In the present work the methyl decay was followed over 20 ms and the first data point recorded after 1 ms. It is therefore safe to assume that the temperature has returned to an equilibrium room temperature for the period of the measurement. The gas temperature in the discharge off period was measured from the Doppler width of a methane line (corrected for instrumental broadening) as 340 K. This is a reasonable value given that the temperature of the aluminum walls of the reactor was measured as 320 K. The curve for \(k_1\) at 340 K has been included in Fig. 4. The argon concentration used here was 1.2\times 10^{16} \text{molec} \text{cm}^{-3}, which corresponds to a value of \(k_1 = 2.1 \times 10^{-11} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1}\).

Many measurements of the methyl radical decay were made under different plasma conditions and plasma compositions. The linear dependence of \(1/K_v\) versus time was also observed using CH\(_4\) or C\(_2\)H\(_2\) instead of DTBP as the CH\(_3\) precursor and H\(_2\) instead of argon as the third body. However, the requirement of maximum signal-to-noise ratio and the data available on the recombination rate constant meant that all quantitative results for \([\text{CH}_3]_0\) were obtained using DTBP as the methyl radical source and argon as the third body. An average from about 15 decays was used to determine each \([\text{CH}_3]_0\) and Fig. 5 shows some of the decay plots of the reciprocal of \(K_v\) values as a function of time and their corresponding linear fits.

\section*{B. Temperature measurements}

\subsection*{1. Translational temperature}

The translational temperature or gas temperature \(T_{\text{trans}}\) was obtained by analyzing the profile of individual rovibrational lines. The line profile measurements were derived from signals averaged over a thousand spectra. At low pressure the line profile should be determined by Doppler broadening resulting in a Gaussian line shape. However, in practice, other contributions to the profile may occur, the most important of which in the present case is instrumental broadening. A determination of the temperature from the Doppler width of the absorption coefficient therefore requires these other contributions to be subtracted. Figure 6(a) shows the absorption coefficient profile of the \(Q_{(8,8)}\) line, which has the
highest signal-to-noise ratio. The signal-to-noise ratio is about 100:1 and the spectral resolution is $6 \times 10^{-4}$ cm$^{-1}$. Other fundamental band $Q$-branch lines used for temperature measurement were $Q_{(3,5)}$, $Q_{(6,6)}$, $Q_{(10,10)}$, and $Q_{(12,12)}$. Assuming a gas temperature of 600 K, the Doppler contribution to the linewidth [full width at half maximum (FWHM)] should be $\approx 2.75 \times 10^{-3}$ cm$^{-1}$. The measured widths were always greater than this, typically $(3.5 \pm 0.3) \times 10^{-3}$ cm$^{-1}$, and hence it was necessary to consider other broadening contributions before deriving $T_{\text{trans}}$. First, it should be noted that the Gaussian profile in Fig. 6(a) is an accurate representation of the experimental data. If significant pressure broadening was present, a Lorentzian contribution to the profile would be expected, introducing pronounced wings at the edges of the line. None were observed. Trial fits of the data using a Voigt line shape confirmed that the Lorentzian contribution was negligible. Finally, using the pressure broadening coefficient of methyl by argon measured by Robinson et al.,$^{24}$ the pressure broadening contribution at 1 mbar was estimated to be $\approx 6 \times 10^{-5}$ cm$^{-1}$, i.e., the pressure broadening contribution is less than 2%.

We now assume that the measured Gaussian width, $\Delta v_{\text{meas}}$ (FWHM), can be factorized into a contribution from the kinetic motion of the methyl radicals, $\Delta v_{\text{Doppler}}$, and an instrumental contribution, $\Delta v_{\text{inst}}$, which are related by

$$\Delta v_{\text{meas}}^2 = (\Delta v_{\text{Doppler}})^2 + (\Delta v_{\text{inst}})^2. \quad (21)$$

To determine $\Delta v_{\text{inst}}$, N$_2$O and CO$_2$ were used at room temperature, selecting lines for measurement closest in frequency to the CH$_3$ lines. It was found that in fact, $\Delta v_{\text{inst}}$ varied for different laser modes and different lasers. Generally $\Delta v_{\text{inst}}$ was found to be in the range $1 \times 10^{-3}$ to $2 \times 10^{-3}$ cm$^{-1}$. The derived values for the translational temperature of CH$_3$ in the discharge are in the range 630–830 K. Although this range of values is quite disperse, a translational temperature of 630 K is satisfactorily close to the rotational temperature, discussed later, namely, 600 K. The uncertainty in $T_{\text{trans}}$ can arise from several causes, in particular, the presence of unresolved spin–rotation splitting in $Q$-branch lines. Unfortunately the signal-to-noise ratio of $P$- and $R$-branch lines, in which the spin–rotation splitting is resolved [Fig. 6(b)], was too small to accurately determine their Doppler widths.

2. Rotational temperature

The rotational temperature $T_{\text{rot}}$ was deduced from $Q$-branch lines, namely, $Q_{(1,1)}$, $Q_{(2,2)}$, $Q_{(3,3)}$, $Q_{(4,4)}$, $Q_{(5,5)}$, $Q_{(6,6)}$, $Q_{(8,8)}$, $Q_{(10,10)}$, and $Q_{(12,12)}$ of the fundamental band. The integrated absorption coefficient of each line ($K_v$) was measured several times under the same plasma conditions. Each integrated absorption coefficient measurement was derived from signals averaged over a thousand spectra. The results, which were highly reproducible, are shown as a function of the rovibrational energy of the lower state of the transition in Fig. 7. As expected the integrated absorbance ($K_v L$) for $Q_{(3,3)}$, $Q_{(6,6)}$, and $Q_{(12,12)}$ is larger than for the other lines due to nuclear-spin statistical effects. Combining Eqs. (2), (7), and (10) gives

$$\ln \left( \frac{N_m}{g_m} \right) = \ln(\text{const}) - \frac{1}{T_{\text{rot}}} \frac{E_m}{k}. \quad (22)$$

The rotational temperature was then determined from a plot of the scaled population versus the rotational energy of the lower level (Fig. 8) yielding $T_{\text{rot}} = 600 \pm 15$ K. A similar procedure was applied to $Q$-branch lines in the first hot band, namely, $Q_{(4,2)}$, $Q_{(9,8)}$, $Q_{(10,9)}$, $Q_{(11,10)}$, and $Q_{(12,11)}$ and a rotational temperature of $750 \pm 150$ K obtained from an
analogous plot to Fig. 8. The rather higher uncertainty in $T_{\text{rot}}$ for this band was primarily due to the smaller data set.

Provided the translational temperature, i.e., $kT$, is higher than the energy of the rotational transition, the rotational and translational temperatures should be at equilibrium. Moreover, since CH$_3$ has no electric-dipole-allowed rotational transitions, the populations of the lowest rotational levels are controlled solely by collisions, making this more likely. This seems to be borne out here by the similarity of $T_{\text{trans}}$ and $T_{\text{rot}}$ and hence we have adopted $T_{\text{trans}} = T_{\text{rot}} = 600 \pm 15$ K. This result concurs with several observations in other studies that the rotational and translational temperatures in low-pressure discharges are $\sim 300 \, ^\circ\text{C}$ higher than room temperature.

3. Vibrational temperature

The vibrational temperature $T_{\text{vib}}$ was the most difficult one to determine experimentally primarily because of the need to know the transition dipole moments of the first and second hot band transitions to be able to compare rotational lines from different bands. Two sources of the transition dipole moment for different $\nu_2$ bands of methyl are available. First Yamada et al.\textsuperscript{5} assumed that $\mu$ for the first hot band was twice that of the fundamental. In contrast Botschwina et al.\textsuperscript{11} obtained $\mu(2_1^1) = 1.25 \times \mu(2_0^1)$ and $\mu(2_2^1) = 1.41 \times \mu(2_0^1)$. The following rovibrational lines were used: $Q_{(10,10)}$, $Q_{(10,9)}$ from $2_1^1$, and $P_{(2,1)}$ from $2_2^1$. They were scaled using Eqs. (2), (6), and (7) before plotting them according to Eq. (22), with $T_{\text{vib}}$ replacing $T_{\text{rot}}$ and $E_m$ becoming the lower rovibrational energy of the $2_1^1$, $2_2^1$, and $2_3^1$ transitions (Fig. 9). We obtain $T_{\text{vib}} \sim 850$ K from the result of Botschwina et al. and $T_{\text{vib}} \sim 500$ K from the Yamada et al. value. The vibrational temperatures in discharges are usually found to be higher than the translational and rotational temperatures. However, the methyl out-of-plane bending potential is quite shallow so that the first excited vibrational level lies at 606 cm$^{-1}$. This corresponds to a temperature of about 860 K, which is comparable to the gas temperature. It is therefore a reasonable approximation to assume that the vibrational temperature is in equilibrium with the translational and rotational temperatures, i.e., $T_{\text{vib}} = 600$ K, which falls between the $T_{\text{vib}}$ values mentioned above.

C. Line strength

Equation (10) relating the line strength and the transition dipole moment contains the total partition function $Q(T)$ and the total statistical weight, $g_{v,n^j n^k n^m}$, where $Q(T) = Q_E Q_V Q_K Q_{NS}$ and $g_{v,n^j n^k n^m} = g_v g_n g_j g_k g_m$. Under the experimental conditions used here, it can be safely assumed that only the ground electronic state is populated as the first excited state lies at 46 305 cm$^{-1}$. Hence $Q_E = 1$ and, provided the spin–rotation splitting is not resolved, $g_s = 1$ also. The vibrational partition function is a product of the partition functions of all four normal modes,

$$Q_V = \prod_i \left[ 1 - \exp \left( -\frac{h \nu_i}{kT} \right) \right]^{-g_v},$$

where $g_v$ is the vibrational mode degeneracy. The wave numbers and degeneracies of the fundamental modes of CH$_3$ used to calculate $Q_V$ are $\nu_1 = 3004.8$ cm$^{-1}$ ($g_v = 1$), $\nu_2 = 606.4531$ cm$^{-1}$ ($g_v = 1$), $\nu_3 = 3160.821$ cm$^{-1}$ ($g_v = 2$),
and \( \nu_k = 1396 \, \text{cm}^{-1} \) \((g_s = 2)\). The vibrational partition function for methyl has often been calculated using only the \( \nu_2 \) and \( \nu_3 \) modes. Above 1000 K this assumption begins to significantly underestimate the vibrational partition function.

Each rotational level of a symmetric top molecule has a rotational degeneracy \( g_J \) and \( g_K \), where \( g_J = 2J + 1 \) and \( g_K = 1 \) for levels with \( K = 0 \) and \( g_K = 2 \) for levels with \( K = 1, 2, 3, \ldots \). However, because \( \text{CH}_3 \) is a planar molecule of \( D_{3h} \) symmetry, the reflection of the nuclei in the center of mass produces a configuration that can be obtained by simple rotation of the molecule. The inversion doubling of the levels then does not occur with the result that \( g_k = 1 \) for all values of \( K \). The rotational partition function \( Q_R \) for a planar symmetric top (\( D_{3h} \) symmetry) in which nuclear-spin effects are ignored is given by

\[
Q_R = \sum_{J=0}^{\infty} \sum_{K=0}^{J} (2J+1) \times \exp \left\{ \frac{- [B(2J+1) + (C-B)K^2]}{kT} \frac{\hbar c}{kT} \right\}.
\]  

(24)

At sufficiently high rotational temperatures this expression approximates to

\[
Q_R \approx \sqrt{\frac{\pi}{B^2C}} \left( \frac{kT}{\hbar c} \right)^3 ,
\]  

(25)

where \( B \) and \( C \) are the rotational constants. At high temperature the nuclear-spin effects can be included through the nuclear-spin partition function \( Q_{ns} \).

\[
Q_{SUM} = Q_R Q_{ns} = (2J+1) \frac{1}{\sigma} \sqrt{\frac{\pi}{B^2C}} \left( \frac{kT}{\hbar c} \right)^3 ,
\]  

(26)

where we have assumed three equivalent nuclei with nonzero spin, i.e., \( \text{CH}_3 \). \( \sigma \) is the symmetry number, which is 6 for \( D_{3h} \) symmetry. Specifically then for \( \text{CH}_3 \)

\[
Q_{SUM} = \frac{8}{6} \sqrt{\frac{\pi}{B^2C}} \left( \frac{kT}{\hbar c} \right)^3 .
\]  

(27)

The nuclear-spin degeneracy \( g_{ns} \) associated with each rotational level is included implicitly in the approximate Eq. (27). At low temperatures this equation is no longer valid and must be replaced by the exact sum [Eq. (24)], modified to include the specific \( g_{ns} \) for each level. The value of \( g_{ns} \) depends on the \( K \) quantum number of the rotational level: \( g_{ns} = 4 \) for \( K = 3n \), \( g_{ns} = 2 \) for \( K \neq 3n, n = 1, 2, 3, \ldots \), and \( g_{ns} = 4 \) for \( K = 0 \) and \( J \) even. Since \( A_2 \) rotational levels are not allowed, then \( K = 0 \) and \( J \) odd levels are missing. At low temperature then

\[
Q_{SUM} = \sum_{J=0}^{\infty} \sum_{K=0}^{J} g_{ns} (2J+1) \times \exp \left\{ \frac{- [B(2J+1) + (C-B)K^2]}{kT} \frac{\hbar c}{kT} \right\}.
\]  

(28)

The rotational partition functions for \( \text{CH}_3 \) (actually \( Q_{SUM} \)) calculated from Eqs. (27) and (28) are indistinguishable over a wide temperature range (<1% divergence) but deviate below 100 K (Fig. 10). As expected Eq. (27) tends to zero as \( T \to 0 \) while (28) tends to 4, the nuclear statistical weight of the lowest allowed rotational level \( J = K = 0 \). The actual effect of the nuclear-spin statistical weights on the appearance of the spectra has already been mentioned (Fig. 7).

The line strengths were calculated from the experimental data using Eq. (2) and then scaled to a reference temperature, \( T_{ref} = 296 \, \text{K} \), using Eq. (29).\(^{17}\)

\[
S(T) = S(T_{ref}) \frac{Q(T_{ref})}{Q(T)} \exp \left\{ \frac{- E_m}{kT_{ref}} \right\} \left[ 1 - \exp \left\{ \frac{- \hbar c v_{mn}}{kT_{ref}} \right\} \right] ,
\]  

(29)

where \( Q(T_{ref}) \) and \( Q(T) \) refer to the reference and measurement temperatures, respectively. Figure 11 shows how the line strengths vary with temperature for the fundamental
band. The specific values at 296 K are given in Table I. Finally \( \mu \) for the \( \nu_2 \) fundamental band was calculated from Eq. (10).

**DISCUSSION**

The experimental and theoretical values reported for the band strength and transition dipole moment of the \( \nu_2 \) fundamental of \( \text{CH}_3 \) are collected in Table II. In order to compare their measured line strength for the \( Q_{(8,8)} \) line and the transition dipole moment value obtained by Yamada and Hirota,\(^7\) Wormhoudt and McCurdy\(^11\) converted the transition dipole moment into a band strength \( S_{\text{band}} \) defined by

\[
S_{\text{band}} = \frac{8 \pi^3}{3hc} v_{\text{band}} \mu^2,
\]

(30)

where \( v_{\text{band}} \) is 606.453 cm\(^{-1}\), and the line strength into the band strength by

\[
S_{\text{band}} = \frac{S(T)Q(T)}{g_{v''''k'''} \exp \left( -\frac{E_{v''''k'''}}{kT} \right) H^5_{v''''k'''} \left[ 1 - \exp \left( -\frac{\hbar c v_{\nu''''k'''}^\text{rot}}{kT} \right) \right]}.
\]

(31)

These definitions have been adopted here. The present result for \( \mu_2 \) is lower than the two earlier gas phase values\(^7,10\) but in excellent agreement with the \textit{ab initio} calculation of Botschwina \textit{et al.}\(^11\). The most likely source of the discrepancy with the earlier experiments lies in the choice of the value of \( k_1 \), the \( \text{CH}_3 \) self-recombination rate constant. Many measurements of this constant have been made and its dependence on temperature and the nature and concentration of the third body have been quantified. However, several of the more precise results were obtained from measurements made subsequent to the work by Yamada and Hirota\(^7\) and by Wormhoudt and McCurdy.\(^10\) The present study has been able to take advantage of this latter data and, in particular, experimental conditions were chosen to ensure that argon made up the highest proportion of the gas present in the discharge.

In Yamada and Hirota’s\(^7\) determination of \( \mu_2 \), several simplifying assumptions were adopted. Some of these have been validated in the present work such as the likely rotational and vibrational temperatures in the discharge. However, although they used a discharge in pure DTBP, they adopted a value of \( k_1 = 4.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) chosen from the results of Laguna and Baughcum,\(^25\) the most appropriate data at that time. This is an average from measurements of \( k_1 \) using \( \text{CH}_3 \text{I} \) heavily diluted in helium or argon. (No distinction was made between the measurements from the two different third bodies.) On the other hand, Wormhoudt and McCurdy,\(^10\) using helium as the third body, calculated \( k_1 \) for their specific temperature and pressure from the data then available. This gave a value of \( k_1 = 3.85 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). In 2002, Cody \textit{et al.}\(^26\) made new measurements of the recombination rate constant at pressures between 0.8 and 2.7 mbar and temperatures from 202 to 298 K and reviewed the previous data on methyl recombination in helium. For the conditions used by Wormhoudt and McCurdy, this data yields a revised value of \((2.15 \pm 0.42) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\). We have used this value to recalculate \( \mu_2 \), and the new value is \( 0.24 \pm 0.04 \text{ D} \), which is in much closer agreement with our result and lower than that of Yamada and Hirota’s. Both Yamada and Hirota, and Wormhoudt and McCurdy, performed their measurements using only the peak of the absorption curve and assumed that the line profile was entirely due to the Doppler effect of methyl itself. From the present work and a number of recent studies, it is now known that there are significant contributions to the line profile in addition to Doppler broadening. As well as laser noise (frequency jitter), there is evidence that the unresolved spin–rotation splitting might also contribute to the line broadening. Bethardy and Macdonald\(^14\) have mentioned this effect as a major contribution to the linewidth in their study of the \( \nu_3 \) fundamental band.

Bethardy and Macdonald\(^14\) and Tanarro \textit{et al.}\(^13\) measured \( \mu_3 \) to be much smaller than \( \mu_2 \), namely, \( 0.0327 \pm 0.0021 \) or \( 0.029 \pm 0.005 \text{ D} \), respectively. Tanarro \textit{et al.} combined their result with a ratio of \( \mu_2 / \mu_3 = 3:1 \), deduced from the peak absorbance ratio measured in the condensed phase by Snelson,\(^15\) \( A_2/A_3 = 9:1 \). To conclude that the value of \( \mu_2 \) reported by Yamada and Hirota was too large by a factor of 3. This apparent anomaly arises because Tanarro \textit{et al.} made an approximation for the relationship between \( \mu \) and \( A \). The vibrational band intensity is given by Eq. (32), which follows from Eq. (10) by summing over the rotational transitions of the fundamental band.

<table>
<thead>
<tr>
<th>Line</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>8</th>
<th>10</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S (10^{-19} \text{ cm molecule}^{-1}) )</td>
<td>0.874</td>
<td>1.73</td>
<td>4.637</td>
<td>2.58</td>
<td>2.55</td>
<td>5.23</td>
<td>1.49</td>
<td>0.751</td>
<td>0.619</td>
</tr>
</tbody>
</table>

Table I. Measured line strengths of \( (J=K) Q \)-branch lines of the \( \nu_2 \) fundamental band of the methyl radical at 296 K.
TABLE II. Band strengths ($S_{\text{band}}$) and transition dipole moments ($\mu_2$) for the $v_2$ fundamental band of the methyl radical.

<table>
<thead>
<tr>
<th></th>
<th>$S_{\text{band}}$ (10$^{-12}$ cm molecule$^{-1}$)</th>
<th>$\mu_2$ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yamada and Hirota (Ref. 7)</td>
<td>0.28±0.049</td>
<td>1.979±0.69</td>
</tr>
<tr>
<td>Wormhoudt and McCurdy (Ref. 10)</td>
<td>0.315±0.05</td>
<td>2.5±0.8</td>
</tr>
<tr>
<td>Present (Ref. 18)</td>
<td>0.215±0.025</td>
<td>1.167±0.28</td>
</tr>
<tr>
<td>Theoretical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Botschwina et al. (Ref. 11)</td>
<td>0.218±0.022</td>
<td>1.2±0.24</td>
</tr>
<tr>
<td>Pacansky et al. (Ref. 12)</td>
<td>0.229</td>
<td>1.33</td>
</tr>
<tr>
<td>Pacansky et al. (Ref. 12)</td>
<td>0.232</td>
<td>1.37</td>
</tr>
</tbody>
</table>

$$S_{\text{vib}} = \frac{8\pi^3}{3hc} \frac{\exp(-E_{\text{lower}}/kT)}{Q(T)} \left[ 1 - \exp\left(-\frac{h\nu_{\text{band}}}{kT}\right) \right] \times \mu_2^2,$$

(32)

where $\exp(-E_{\text{lower}}/kT)/Q(T)[1-\exp(-h\nu_{\text{band}}/kT)]$ is about unity for both bands at the matrix temperature in Snelson’s work. Hence $S_{\text{vib}} \propto (\nu_{\text{band}})^2\mu_{\text{band}}^2$, giving $\mu_2/\mu_3 = 6.85:1$ from the matrix work. This is in very satisfactory agreement with the gas phase ratio using the present value of $\mu_2$ in combination with the $\mu_3$ of Bethardy and Macdonald (Ref. 14) $\mu_2/\mu_3 = 6.58:1$ or with the $\mu_3$ from Tanarro et al.13 of 7.4:1. The result is supported by the calculations of Pacansky et al.12 The ratio from their work is 6:1 or 10:1 depending on whether the UHF or UMP2 method is used. Figure 12 shows that their theoretical value of $\mu_2$ and Wormhoudt and McCurdy’s corrected value agree with the present result to better than 10%.

The uncertainty of 0.025 D assigned to the value of $\mu_2=0.215$ D measured here was arrived at from a comprehensive error analysis. Although this uncertainty (12%) is not significantly better than that quoted by Yamada and Hirota (17.5%); this is because the present measurement still involves several steps with significant uncertainties which have been explicitly included in the error analysis. We have conservatively estimated these as 20% for the recombination rate constant $k_1$, 10% for the path length, 5% for measuring the kinetic decays, and 5% in the partition functions and stimulated emission contribution arising from temperature uncertainties. The new data on the line strengths (Table I) should replace earlier values based on the $Q_{(8,8)}$ value determined by Wormhoudt and McCurdy. In addition, the earlier values of the line strengths derived by Fan27 and by Lombardi et al.28 omitted the effect of stimulated emission. This leads to an overestimate of the line strength of 6% at room temperature, 17% at 500 K,27 and 65% at 2000 K.28 The neglect of stimulated emission is certainly not justified for the more accurate line strength measurements reported here.

The choice of vibration rotation line to optimize the sensitivity of infrared absorption spectroscopy for detecting the methyl radical is an important consideration in practical applications. The temperature dependence of the line strengths given in Fig. 11 has already been presented in Table I using a reference temperature of 296 K. The most intense of the measured $Q$-branch lines, due to nuclear-spin statistics, are $Q_{(3,3)}$, $Q_{(6,6)}$, and $Q_{(12,12)}$. At temperatures up to about 300 K, the $Q_{(3,3)}$ line has the highest line strength and would be the most appropriate for astronomical use. This has been confirmed by the observation that the most intense line in Neptune’s atmosphere at 170 K is $Q_{(3,3)}$. Between 300 and 1100 K, typical kinetic flow tube, and plasma temperatures, the $Q_{(6,6)}$ line should be used, while in thermal diamond deposition studies, the $Q_{(12,12)}$ line is the line of choice.

CONCLUSION

Several factors have contributed to the improved accuracy of the measured $\mu_2$ transition dipole moment of the ground state of the methyl radical described here. The most important are the improved accuracy of the recombination
rate constant and the defined nature of the third body involved in the methyl radical recombination reaction at specific temperatures and pressures; the use of integrated instead of peak absorbances, which automatically includes any unresolved broadening due to the spin–rotation interaction; and the derivation of more accurate temperatures by examining a large number of lines. Further improvements might be achieved in the present experiment by determining the vibrational temperature more accurately and by better definition of the absorption path length. However, the largest contributing uncertainty is the recombination rate constant $k_1$, which is not amenable to study in the present experimental arrangement. The convergence of the experimental result with high-quality theoretical calculations is further confirmation of the improvement in the accuracy of the experimental result. Finally, there is now good agreement between the ratio of the transition dipole moment values of the $\nu_2$ and $\nu_3$ fundamentals measured in the gas and condensed phases.

ACKNOWLEDGMENTS

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