



ELSEVIER

24 June 1994

**CHEMICAL
PHYSICS
LETTERS**

Chemical Physics Letters 223 (1994) 305–312

The $\text{CH}_3 3p_z \ ^2A_2'' \leftarrow \tilde{X} \ ^2A_2'' \ 0_0^0$ band at temperatures up to 1700 K investigated by REMPI spectroscopy

J. Heinze, N. Heberle, K. Kohse-Höinghaus¹*DLR Institut für Physikalische Chemie der Verbrennung, Pfaffenwaldring 38–40, D-70569 Stuttgart, Germany*

Received 5 April 1994

Abstract

The 0_0^0 band of the $\text{CH}_3 3p_z \ ^2A_2'' \leftarrow \tilde{X} \ ^2A_2''$ Rydberg transition has been recorded using the (2+1) resonance-enhanced multiphoton ionization (REMPI) of CH_3 at 333 nm. CH_3 was generated in a discharge flow reactor at room temperature and in a hot-filament-assisted chemical vapor deposition (HFCVD) reactor at temperatures of 820 to 1700 K. By means of spectral simulation the rotational constants, B'_0 and C'_0 , and the rotational state-dependent predissociation rates of the $3p_z \ ^2A_2''$ state were determined. Based on these constants and the well-known rotational and vibrational ground-state constants, relative intensities of the CH_3 REMPI spectra were calculated for temperatures up to 2300 K. These spectra were used to evaluate relative CH_3 concentrations from measured REMPI peak intensities of the dominant Q branch.

1. Introduction

Since the methyl radical CH_3 is an important species in combustion as well as in CVD processes for diamond formation [1–5], non-intrusive concentration measurements in these environments are of great interest to the kinetic modeling of gas phase chemistry and for process control. Therefore, a quantitative detection technique with sufficient sensitivity, and spatial and temporal resolution is required. As known from the earliest work [6,7], strong predissociation of all excited states prevents fluorescence detection. IR and UV absorption, mass spectrometry and resonance-enhanced multiphoton ionization (REMPI) have been successfully used for sensitive CH_3 detection in flames or CVD environments. Absorption measurements [8–10] enable determination of ab-

solute concentrations, but drawbacks of this technique include limited sensitivity and spatial resolution. The highly sensitive mass spectrometry technique requires a pressure much lower than that typically used in flames or CVD processes. Only indirect detection of the CH_3 radical via a microprobe and scavenging [11,12] or detection near to the entrance of a mass spectrometer [13] is possible. Detection of CH_3 with REMPI has been demonstrated to be a technique of high sensitivity and good spatial and temporal resolution [14–19].

The intense (2+1) REMPI transitions of CH_3 at 333.4 and 286.2 nm were first reported by DiGiuseppe et al. [20]. Hudgens et al. [21] have identified the vibronic structure of the two-photon resonances to be the vibrationless $3p_z \ ^2A_2'' \leftarrow \tilde{X} \ ^2A_2''$ and $4p_z \ ^2A_2'' \leftarrow \tilde{X} \ ^2A_2''$ transitions of CH_3 . Chen et al. [22] resolved some rotational structures of the $3p_z \leftarrow \tilde{X}$ transition which were heavily broadened by predissociation of the $3p_z$ state. Chandler et al. [23] estimated the predissociation rates of the $3p_z$ state

¹ Present address: Fakultät für Physik, Institut für Angewandte Laserphysik, Universität Bielefeld, Universitätsstraße 25, D-33615 Bielefeld, Germany.

using a predissociation mechanism proposed by Black and Powis [24]. For the vibrationless $4p_z$ state, Black and Powis [24] found a similar predissociation which is partially caused by a perpendicular (x, y) -Coriolis interaction. These experiments were performed at temperatures up to 300 K, and the CH_3 radicals were generated by pyrolysis or photolysis.

For CH_3 monitoring at flame or CVD conditions, the $3p_z \leftarrow \tilde{X}$ transition at 333.4 nm is of particular interest because it shows no spectral interferences in these environments [15]. However, a quantitative interpretation of the REMPI spectra in terms of concentrations requires the analysis of the rotational structure and of the predissociation of the resonant excited $3p_z$ Rydberg state of CH_3 .

In this Letter we present CH_3 REMPI spectra of the vibrationless $3p_z \leftarrow \tilde{X}$ transition recorded at room temperature in a discharge flow reactor and at high temperatures in a HFCVD reactor. The local gas temperatures in the HFCVD reactor are evaluated from LIF spectra of the $\tilde{A}^2\Sigma \leftarrow \tilde{X}^2\Pi$ transition of NO [25–27] seeded into the feed gas. The CH_3 REMPI spectra enable determination of the rotational constants and predissociation rate of the $3p_z$ state with sufficient accuracy to permit simulation of the REMPI spectra in detail. For temperatures up to 2300 K the temperature dependence of the REMPI spectra is calculated and summarized in a temperature scaling factor which allows the direct determination of relative CH_3 concentrations from REMPI peak intensities, if the local gas temperature is known.

2. Experimental

The experiments were performed in a discharge flow reactor and in a HFCVD reactor. At room temperature and a pressure of 5 mbar, CH_3 was generated in the discharge flow reactor using the reaction [28]



The H atoms were produced by a microwave discharge in He doped with a small amount of H_2 . CH_3I as a minor component of the reaction was added into the flow reactor. Its mole fraction fixed the CH_3 concentration at about 10^{12} cm^{-3} . This well-defined CH_3 source enables not only a spectroscopic investigation

but also an absolute calibration of CH_3 REMPI signals. At the high temperatures in the HFCVD reactor, CH_3 was primarily generated by the fast bimolecular reaction [29]



Here the H atoms were mainly produced by dissociation of H_2 at the resistively heated filament which consisted of a 60 mm long tantalum wire of 2 mm diameter. The filament temperature of 2550 K was measured by a single-color pyrometer. Typically the feed gas contained 0.8% CH_4 in H_2 and the gas pressure in the HFCVD reactor was 25 mbar. For gas temperature measurements, less than 0.1% NO was seeded into the feed gas. The absolute CH_3 concentration was of the order of 10^{13} cm^{-3} .

For the CH_3 (2+1) REMPI excitation, the frequency-doubled output of a Nd:YAG pumped dye laser was focused into the reactor parallel to the filament with a 50 cm lens. Laser pulse energies were attenuated to less than 1 mJ at 333 nm to avoid saturation of the two-photon transition. The tip of the REMPI probe was placed at a distance of 2 mm from the laser focus. To collect the photoelectrons probe voltages of 20–40 V were applied. The REMPI signals at the load resistor of 150 k Ω were amplified by a factor of 10–100 and registered by a boxcar integrator. The laser pulse energy was monitored by a fast vacuum photodiode and also fed to a boxcar integrator. For gas temperature measurements in the HFCVD reactor the $\tilde{A}^2\Sigma \leftarrow \tilde{X}^2\Pi$ (0, 0) band of NO was excited. In order to generate tunable laser radiation at 225 nm, the frequency-doubled output of the dye laser was Raman shifted in a cell filled with H_2 . The pulse energy of the second anti-Stokes radiation at 225 nm was attenuated to less than 100 μJ to allow weak focusing for sufficient spatial resolution without saturating the NO transition. The laser-induced fluorescence (LIF) was spectrally filtered using a 10 cm monochromator, detected by a photomultiplier and registered by a boxcar integrator. The signals of the REMPI probe, photomultiplier and vacuum photodiode were stored on a PC for further analysis.

3. Results

Normalized REMPI spectra of the CH_3 $3p_z \leftarrow \tilde{X} 0_0^0$

band are shown in Fig. 1 for different temperatures. Since the spectral structure is determined by the two-photon resonance, the spectra are given as a function of twice the laser frequency.

The spectra are dominated by the Q branch ($\Delta N=0$) which is about 100 times more intense than the weak O, P, R and S branches ($\Delta N=-2, -1, 1, 2$). The rotational structure arises from the two-photon selection rules for a parallel band:

$$\begin{aligned} \Delta K &= 0, \\ \Delta N &= 0, \pm 2, \quad \text{for } K=0, \\ \Delta N &= 0, \pm 1, \pm 2, \quad \text{for } K \geq 1. \end{aligned} \quad (3)$$

The high intensity of the Q branch is caused by the great number of overlapping lines and by the more than 20 times higher rotational line strength in comparison with that of the other branches [30]. With increasing temperature the Q branch is significantly broadened. However, the high density of lines and their lifetime-broadened linewidth prohibit the resolution of single transitions. Direct information on the rotational structure and predissociation of the $3p_z$ state may be obtained from the other, weak branches.

Fig. 2 shows the normalized spectrum taken at 295 K on an enlarged scale. Now the O, P, R, and S

branches can be seen clearly. Their transitions are marked above the measured spectrum. According to (3), each line of a branch consists of a set of transitions with different quantum number $K \leq \min(N', N'')$. Only the R(1) and P(2) lines consisted of one transition, i.e. $K=1$. Using the molecular constants of Table 1, the energy splittings of the K transitions are always smaller than the lifetime-broadened linewidth. In addition, Fig. 2 shows the simulation of the CH_3 spectrum and the residual of the experimental and simulated spectra. The spectral structure at 60155 cm^{-1} or 332.4 nm was observed not to be caused by CH_3 or residual CH_3I , but could not be assigned.

Due to the strong predissociation of the excited CH_3 , almost none of the indicated transitions were resolvable. Therefore, the rotational constants and the predissociation rates of the $\text{CH}_3 3p_z$ state were determined by fitting the simulated spectra to the measured REMPI spectra at room and elevated temperatures. In the spectral simulation, the transition frequencies were calculated using the following expression:

$$\nu = \nu_0 + E'_{\text{rot}}(N', K') - E''_{\text{rot}}(N'', K''). \quad (4)$$

The quantities indicated by single and double prime belong to the excited or ground state, respectively. The

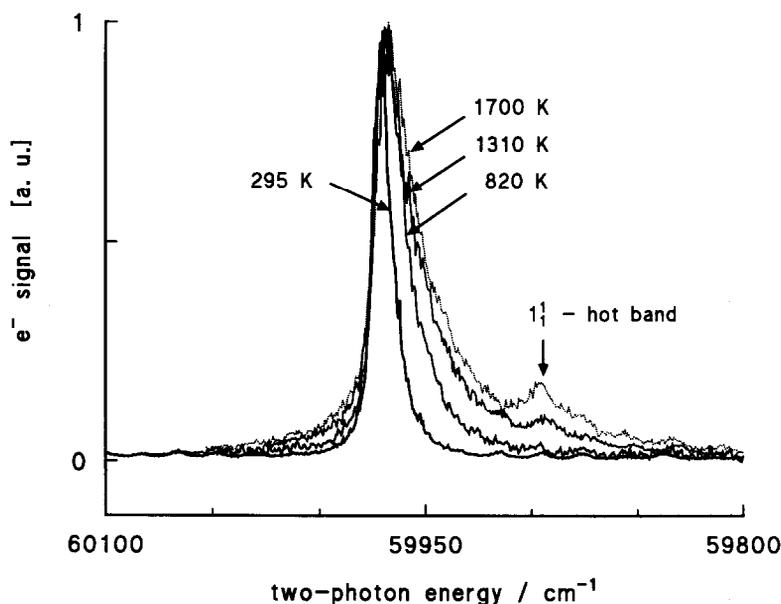


Fig. 1. CH_3 REMPI spectra of the $3p_z \leftarrow \bar{X} 0g$ band taken at 295, 820, 1310 and 1700 K. The normalized spectra are dominated by the Q branch which exhibits a significant broadening with increasing temperature.

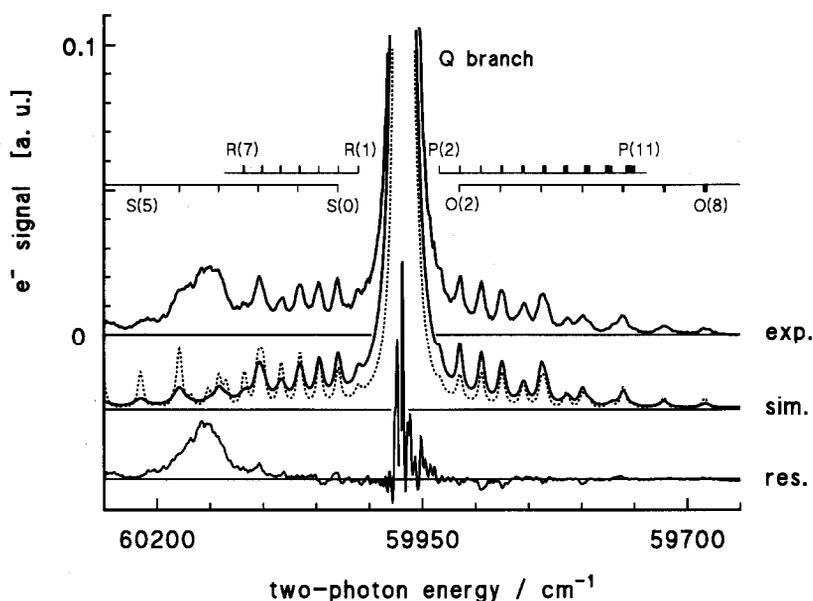


Fig. 2. CH_3 REMPI spectra of the $3p_z \leftarrow \bar{X} 0_0^+$ band taken at 295 K with enlarged scale. The experimental spectrum is compared with the simulated spectrum using the molecular constants of Table 1. To demonstrate the influence of the heterogeneous predissociation, also a simulation without a state-dependent predissociation (···) is shown.

Table 1
Molecular constants of the $\text{CH}_3 3p_z \ ^2A_2'' - \bar{X} \ ^2A_2' 0_0^+$ band

	$3p_z \ ^2A_2''$	$\bar{X} \ ^2A_2'$	Units
ν_0	59972 ^a		cm^{-1}
B_0	9.51 (7)	9.57789 ^c	cm^{-1}
C_0	4.62 (3)	4.74202 ^c	cm^{-1}
D_N	7.7 ^b	7.699 ^c	10^{-4}cm^{-1}
D_{NK}	-13.6 ^b	-13.58 ^c	10^{-4}cm^{-1}
D_K	6.3 ^b	6.34 ^c	10^{-4}cm^{-1}
$\Delta\nu_0$	4.2 (6)		cm^{-1}
C	0.05 (2)		
F/E	0.7 (1)		

^a Ref. [21].

^b Fixed to the ground-state values of Ref. [31].

^c Ref. [31].

simplified rotational energy level expression includes the rotational constants B , C , D_N , D_{NK} and D_K .

$$E_{\text{rot}}(N, K) = BN(N+1) + (C-B)K^2 - D_N N^2(N+1)^2 - D_{NK} N(N+1)K^2 - D_K K^4. \quad (5)$$

Due to the limited experimental resolution, higher-order correction terms as well as the spin-rotation interaction [31] were neglected. The value of the

band origin ν_0 was fixed at 59972 cm^{-1} as given by Hudgens et al. [21]. For the ground state the well established values of Yamada et al. [31] were used. The intensity of a rotational line was determined by the Boltzmann factor of the ground-state level, its nuclear spin and statistical weights [32], and the two-photon rotational linestrength [30]. The Lorentzian lineshape was convoluted with the Doppler and laser lineshapes.

The comparison of measured and simulated spectra in Fig. 2 gave evidence for a quantum state-specific, i.e. heterogeneous, predissociation within the vibrationless $3p_z$ state. If in the simulation only a state-independent, i.e. homogeneous, predissociation was considered (see Fig. 2, dotted line), the simulated lines with high N -quantum number had higher intensities than the measured lines. To quantify the effect of the heterogeneous predissociation of the intermediate state on the REMPI signal, we followed the concept of Ashfold et al. [33,34] which describes the predissociation of the $\bar{C} \ ^1B_1$ state of water and the $\bar{C} \ ^1A_1'$ of ammonia. According to this model, the ionization quantum yield Φ is given by the ratio of the ionization rate k_i of the intermediate state and its total decay rate k_T ,

$$\Phi \equiv k_1/k_T \approx k_1/[\omega_0 + \omega_{\text{het}}(N', K')]. \quad (6)$$

Because predissociation is the dominant decay process of the $3p_z$ state, the total decay rate k_T can be approximated by the sum of the homogeneous and heterogeneous predissociation rates, ω_0 and $\omega_{\text{het}}(N', K')$ respectively. The lifetime-broadened linewidth $\Delta\nu$ of the REMPI transition is proportional to the predissociation rate. With Φ_0 , $\Delta\nu_0$ and h_0 denoting the quantum yield, the linewidth and the height of the homogeneous broadened transition, respectively, the additional heterogeneous predissociation $\omega_{\text{het}}(N', K')$ influences these quantities as follows:

$$\Phi = \Phi_0/F,$$

$$\Delta\nu = \Delta\nu_0 F,$$

$$h = h_0/F^2. \quad (7)$$

The ratio of the total and the homogeneous predissociation rate is abbreviated by F ,

$$F \equiv 1 + \omega_{\text{het}}(N', K')/\omega_0 = 1 + cf(N', K'). \quad (8)$$

It is convenient to factorize $\omega_{\text{het}}/\omega_0$ in terms of a functional dependence $f(N', K')$ and an adjustable parameter c for the strength of the heterogeneous predissociation. The assumption that this predissociation is caused by a perpendicular (x, y)-Coriolis interaction leads to [33]

$$f = N(N+1) - K^2. \quad (9)$$

Assuming this functional dependence, a good agreement between measurement and simulation was achieved using an appropriate value for c . If we examine different, physically plausible assumptions on the mechanism for the heterogeneous predissociation, like predissociation due to parallel Coriolis coupling, we observed a significantly lower agreement between measurement and simulation. Under the assumption made above, the heterogeneous predissociation due to perpendicular Coriolis coupling was unambiguously an appropriate choice and was applied to fit the molecular constants including the parameter c .

The constants of the CH_3 $3p_z$ state determined in this work are listed in Table 1 together with the constants of the ground state. The strong predissociation limited the accuracy especially for the constant B'_0 ,

and led to high correlation of the centrifugal constants D'_N, D'_K, D'_{NK} and the constants B'_0 and C'_0 . Therefore, the centrifugal constants were fixed at the ground-state values. Nevertheless, even at elevated temperatures the contour of the dominant Q branch is well represented by the simulation as seen in Fig. 3. The highly excited rotational states contribute only a small amount to the total signal due to the fast predissociation of these states.

In Table 1 the ratio F/E is also given. The ratio of the electronic–vibronic matrix elements E and F scales the two-photon linestrength of the Q branch with respect to the linestrength of the other branches [30]. If the reasonable assumption of a branch-in-

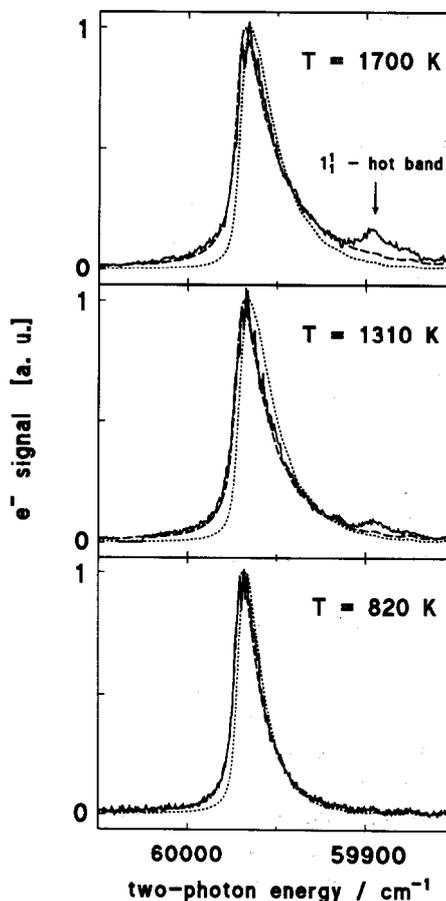


Fig. 3. CH_3 REMPI spectra of the Q branch at 820 K (lower part), 1310 K (middle part) and 1700 K (upper part). In addition to the measured spectra (—) the simulated spectra with (---) and without heterogeneous predissociation (···) are shown, omitting the 1_1 hot band.

dependent ionization quantum yield is made [35], the ratio of F and E can be determined from the intensity ratio of the Q branch to the other branches.

At elevated temperatures a spectral feature appeared at 59895 cm^{-1} which we assigned as the Q branch of the $1\frac{1}{2}$ band (see Fig. 3). Using 3004.8 cm^{-1} [36] for the energy spacing between $\nu''_1=1$ and $\nu''_1=0$ in the ground state, the energy spacing between $\nu'_1=1$ and $\nu'_1=0$ in the excited state is determined to $2928(5)\text{ cm}^{-1}$. This value is in agreement with the observation of Chandler et al. [23], and the value of 2914 cm^{-1} of Hudgens et al. [21] is somewhat smaller.

4. Discussion

The result of the previous section can be summarized as follows: the molecular constants given in Table 1 enable a detailed simulation of the CH_3 REMPI spectra of the $3p_z^2A_2''-\tilde{X}^2A_2''0_0^0$ band at temperatures from 295 to 1700 K. In this section, we first want to compare the molecular constants, especially the predissociation rates, with results of previous studies and discuss their physical implications. In the second part of the discussion, the influence of the temperature dependence of the REMPI spectra on the quantitative CH_3 detection at temperatures up to 2300 K is examined.

The values of the rotational constants B'_0 and C'_0 available in the literature were estimated by Loo et al. [37]. The value of $B'_0=9.55\text{ cm}^{-1}$ is in agreement with our result while the value of $C'_0=4.9\text{ cm}^{-1}$ is too large. The constants B'_0 and C'_0 determined in this work nearly fulfill the relation $C=\frac{1}{2}B$, valid for a planar symmetric top. The deviation from the relation is a result of the inertia defect, $A'_0\approx 2I_b(\frac{1}{2}B'_0-C'_0)/C'_0$, which is not significantly greater than the value in the electronic ground state [38]. The momentum of inertia itself, $I_b^{(0)}=h/(8\pi^2cB'_0)$, is only slightly greater than that of the ground state [31]. This means that the C–H bond lengthens less than 0.5% following the excitation from the $2p\ a_2''$ electron orbital in the ground state into the $3p\ a_2''$ orbital in the excited state. The quite similar values for the equivalent states of CD_3 [21,39,40] underline the non-bonding character of the $2p\ a_2''$ and $3p\ a_2''$ orbitals. Calculations [41] indicate that the electron den-

sity of these orbitals is located mostly above and below the plane of the molecule, concentrated at the symmetry axis.

The observed predissociation of the $3p_z$ state consists of a homogeneous and a heterogeneous part. The values for both parts of the predissociation, $\Delta\nu_0$ and $s=c\Delta\nu_0$ respectively, are in good agreement with the values of Chandler et al. [23], 4 and 0.2 cm^{-1} , respectively. The equivalent $3p_z$ state of the deuterated molecule CD_3 possesses substantially lower predissociation rates. Chandler et al. [42] gave the values $\Delta\nu_0=0.75\text{ cm}^{-1}$ and $s=0.015\text{ cm}^{-1}$ for the $3p_z$ state of CD_3 .

Symmetry considerations may help to identify electron–vibronic states responsible for the predissociation. The heterogeneous predissociation caused by the Coriolis interaction is proportional to the square of the rotational angular momentum perpendicular to the symmetry axis, which transforms in the D_{3h} point group as the representation E'' . Thus, the Coriolis interaction can couple the $3p_z\ ^2A_2''$ state to a vibronic state of $E'=A_2''\otimes E''$ symmetry which dissociates or quickly predissociates. A possible candidate is the $3p_{x,y}\ ^2E'$ Rydberg state which is predicted to be located about 2000 cm^{-1} below the $3p_z$ state [43]. To date, this state has been observed neither for CH_3 nor for CD_3 [21]. Another, perhaps more likely set of heavily predissociating levels are provided by the \tilde{B}^2A_1' electronic state. The potential energy minimum of the \tilde{B} state lies 16000 cm^{-1} below the $3p_z$ state [44]. Excitation of the vibrations $\nu_3(e')$ or $\nu_4(e')$ in the \tilde{B} state will give rise to vibronic levels of E' symmetry. The homogeneous predissociation of the $3p_z\ ^2A_2''$ state requires an interaction with other vibronic levels of A_2'' symmetry. Again the \tilde{B}^2A_1' state provides vibronic levels of required symmetry if the vibration $\nu_2(a_2'')$ is excited. In addition, the lifetime of the \tilde{B} state is much shorter for CH_3 than for CD_3 [44–46]. This can explain the strong predissociation of the $\text{CH}_3\ 3p_z$ state.

In the second part of the discussion the implications for quantitative CH_3 detection are examined. In particular, the temperature dependence of this REMPI transition requires a careful interpretation of the signals in terms of relative concentrations. The influence of the heterogeneous predissociation on the REMPI spectrum gives rise to two interesting aspects for quantitative CH_3 detection. First, the spectral po-

sition of the Q branch maximum is temperature insensitive. Between 700 K and 2000 K the frequency shift of the peak is less than 1 cm^{-1} . Thus, within this temperature range the CH_3 Q branch maximum can be excited, to a good approximation, at one properly chosen laser frequency.

The other aspect which should be considered, is the REMPI intensity loss which increases with increasing temperature. The losses which are caused by increasing predissociation of the $3p_z$ state and depopulation of the vibrational ground state cannot trivially be deduced from the REMPI spectra. To quantify these effects, the spectra were simulated in the same way as described above. Additionally, the relative population of the vibrational ground state was determined from the vibrational partition function using the known frequencies of the four modes and their degeneracies [47]. Therefore, the energy levels of the mode ν_1 , ν_3 and ν_4 were calculated in the harmonic oscillator approximation, while for the strong anharmonic mode ν_2 a third-order polynomial was used [31]. For further discussion it is convenient to introduce a *temperature scaling factor* (TSF) which is defined as the REMPI peak intensity of the dominant Q branch at a reference temperature of 300 K normalized to the equivalent value at the temperature of interest. By this definition the CH_3 REMPI peak intensities measured at different temperatures can be converted to relative concentrations simply by multiplying with the respective TSFs. For temperatures up to 2300 K the TSFs are shown in Fig. 4. A linewidth of the exciting laser which is of similar magnitude or broader than the homogeneous CH_3 linewidth would lead to a slightly smaller increase of the TSFs with increasing temperature.

The pronounced temperature dependence of the TSFs is mainly caused by the depopulation of the vibrational ground state. However, the broadening of the rotational structure and the increasing predissociation contribute roughly by the same amount. Thus, at any temperature the three contributions must be included. The logarithmic scale of Fig. 4 underlines the fact that the quantitative interpretation of CH_3 REMPI spectra requires the accurate knowledge of the local gas temperature. Although the CH_3 spectrum itself contains the temperature information, an independent temperature determination is desirable.

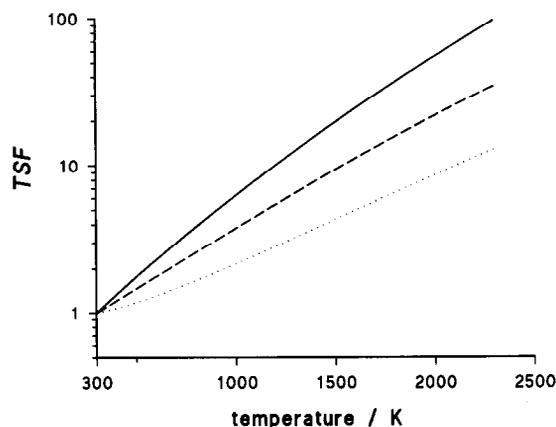


Fig. 4. The temperature scaling factor (TSF) for the REMPI peak intensities of the $\text{CH}_3 3p_z \leftarrow \bar{X} 0_0^0$ band for temperatures up to 2300 K. The total scaling factor (—) is the product of contributions caused by depopulation of the vibrational ground state (\cdots), by broadening of the rotational structure (---) and by intensity loss due to heterogeneous predissociation of the $3p_z$ state.

5. Summary

For different temperatures from 295 to 1700 K, CH_3 (2+1) REMPI spectra at 333 nm have been measured. The rotational constants B'_0 and C'_0 and the homogeneous and heterogeneous predissociation rates of the vibrationless $3p_z {}^2A'_2$ state have been determined and discussed. The simulation of the REMPI spectra has led to a temperature scaling factor of the CH_3 REMPI peak intensity which enables a straightforward conversion of the REMPI signals to relative CH_3 concentrations, if the local gas temperature is known.

Acknowledgement

We would like to thank Alexander O. Vyrodov for his help in using his temperature fit routines. Dr. Ulrich Meier is gratefully acknowledged for stimulating discussions and valuable suggestions. We would like to thank Dr. Maurice H.M. Janssen for his comments on the manuscript. This research has been financially supported by the German Ministry of Research and Technology (BMFT).

References

- [1] J. Warnatz, *Ber. Bunsenges. Physik. Chem.* 87 (1983) 1008.
- [2] S.J. Harris and D.G. Goodwin, *J. Phys. Chem.* 97 (1993) 23.
- [3] C.J. Chu, M.P. D'Evelyn, R.H. Hauge and J.L. Margrave, *J. Mater. Res.* 5 (1990) 2405.
- [4] C.J. Chu, M.P. D'Evelyn, R.H. Hauge and J.L. Margrave, *J. Appl. Phys.* 70 (1991) 1695.
- [5] L.R. Martin and M.W. Hill, *J. Mater. Sci. Letters* 9 (1990) 621.
- [6] G. Herzberg and J. Shoosmith, *Can. J. Phys.* 34 (1956) 523.
- [7] G. Herzberg, *Proc. Roy. Soc. A* 262 (1961) 291.
- [8] F.G. Celii, P.E. Pehrsson, H.-t. Wang and J.E. Butler, *Appl. Phys. Letters* 52 (1988) 2043.
- [9] D.F. Davidson, A.Y. Chang, M.D. DiRosa and R.K. Hanson, *J. Quant. Spectry. Radiative Transfer* 49 (1993) 559.
- [10] K.L. Menningen, M.A. Childs, P. Chevako, H. Toyoda, L.W. Anderson and J.E. Lawler, *Chem. Phys. Letters* 204 (1993) 573.
- [11] S.J. Harris, A.M. Weiner and T.A. Perry, *Appl. Phys. Letters* 53 (1988) 1605.
- [12] S.J. Harris and A.M. Weiner, *J. Appl. Phys.* 67 (1990) 6520.
- [13] W.L. Hsu, *Appl. Phys. Letters* 59 (1991) 1427.
- [14] K.C. Smyth and P.H. Taylor, *Chem. Phys. Letters* 122 (1985) 518.
- [15] U. Meier and K. Kohse-Höinghaus, *Chem. Phys. Letters* 142 (1987) 498.
- [16] T.A. Cool, J.S. Bernstein, X.-M. Song and P.M. Goodwin, 22nd International Symposium on Combustion (Combustion Institute, Pittsburgh, 1988) p. 1421.
- [17] F.G. Celii and J.E. Butler, *Appl. Phys. Letters* 54 (1989) 1031.
- [18] F.G. Celii and J.E. Butler, *J. Appl. Phys.* 71 (1992) 2877.
- [19] E.J. Corat and D.G. Goodwin, *J. Appl. Phys.* 74 (1993) 2021.
- [20] T.G. DiGiuseppe, J.W. Hudgens and M.C. Lin, *J. Chem. Phys.* 76 (1982) 3337.
- [21] J.W. Hudgens, T.G. DiGiuseppe and M.C. Lin, *J. Chem. Phys.* 79 (1983) 571.
- [22] P. Chen, S.D. Colson, W.A. Chupka and J.A. Berson, *J. Phys. Chem.* 90 (1986) 2319.
- [23] D.W. Chandler, J.W. Thoman Jr., M.H.M. Janssen and D.H. Parker, *Chem. Phys. Letters* 156 (1989) 151.
- [24] J.F. Black and I. Powis, *J. Phys. Chem.* 89 (1988) 3986.
- [25] R. Engleman, P.E. Rouse, H.M. Peek and V.D. Baimonte, Los Alamos Laboratory Scientific Report LA 4364 (1970).
- [26] C.J. Amiot, R. Bacis and G. Guelachvilli, *Can. J. Phys.* 56 (1978) 251.
- [27] A. Timmermann and R. Wallenstein, *Opt. Commun.* 39 (1981) 239.
- [28] M.R. Levy and J.P. Simons, *J. Chem. Soc. Faraday Trans.* 1 71 (1975) 561.
- [29] D.G. Goodwin and G.G. Gavillet, *J. Appl. Phys.* 68 (1990) 6393.
- [30] K. Chen and E.S. Yeung, *J. Chem. Phys.* 69 (1978) 43.
- [31] C. Yamada, E. Hirota and K. Kawaguchi, *J. Chem. Phys.* 75 (1981) 5256.
- [32] G. Herzberg: *Electronic spectra and electronic structure of polyatomic molecules* (Van Nostrand, Princeton, 1966).
- [33] M.N.R. Ashfold, J.M. Bayley and R.N. Dixon, *Chem. Phys.* 84 (1984) 35.
- [34] M.N.R. Ashfold, R.N. Dixon and R.J. Stickland, *Chem. Phys.* 88 (1984) 463.
- [35] D.C. Jacobs, R.J. Madix and R.N. Zare, *J. Chem. Phys.* 85 (1986) 5469.
- [36] P.L. Holt, K.E. McCurdy, R.B. Weisman, J.S. Adams and P.S. Engel, *J. Chem. Phys.* 81 (1984) 3349.
- [37] R.O. Loo, H.-P. Haerri, G.E. Hall and P.L. Houston, *J. Chem. Phys.* 90 (1989) 4222.
- [38] E. Hirota and C. Yamada, *J. Mol. Spectry.* 96 (1982) 175.
- [39] F.M. Frye, T.J. Sears and D. Leitner, *J. Chem. Phys.* 88 (1988) 5300.
- [40] D.H. Parker, Z.W. Wang, M.H.M. Janssen and D.W. Chandler, *J. Chem. Phys.* (1989) 60.
- [41] J. Pacansky, *J. Phys. Chem.* 86 (1982) 485.
- [42] D.W. Chandler, M.H.M. Janssen, S. Stolte, R.N. Strickland, J.W. Thoman Jr. and D.H. Parker, *J. Phys. Chem.* 94 (1990) 4839.
- [43] H.T. Yu, A. Sevin, E. Kassab and E.M. Evleth, *J. Chem. Phys.* 80 (1984) 2049.
- [44] J. Danon, H. Zacharias, H. Rottke and K.H. Welge, *J. Chem. Phys.* 76 (1982) 2399.
- [45] S.G. Westre, P.B. Kelly, Y.P. Zhang and L.D. Ziegler, *J. Chem. Phys.* 94 (1991) 270.
- [46] S.G. Westre, T.E. Gansberg, P.B. Kelly and L.D. Ziegler, *J. Phys. Chem.* 96 (1992) 3610.
- [47] M.E. Jacox, *J. Phys. Chem. Ref. Data* 17 (1988) 269.