



New observations on the B state of the CH radical from UV multiphoton dissociation of ketene

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Abstract

In multiphoton dissociation experiments on ketene (CH_2CO) using a UV dye laser emission spectra were observed in the 360–370 nm range. The spectra were seen only with a focused laser beam and consist of lines attributable to emission from rotational levels in the $v' = 1$ vibrational state of the $\text{B}^2\Sigma^-$ electronic state of the methylidyne (CH) radical. In these spectra rotational transitions to the $N' = 7$ level of the B state from the ground (X) state, $v'' = 0$, were observed. Time-resolved fluorescence measurements on the $N' = 1, 2, 3, 4, 5$ and 6 levels yielded lifetime data contributing to the existing values in the literature. Based on line broadening a lifetime estimate is given for the strongly predissociated $N' = 7$ level.

1. Introduction

The CH molecule has been the subject of intense study over many decades. Already the first spectroscopic papers on this radical emphasized the strong predissociation taking place in the second electronically excited ($\text{B}^2\Sigma^-$) state [1–3]. Although all rotational levels in methylidyne above the ground state dissociation threshold ($D_0^0(\text{CH}) = 27920(80) \text{ cm}^{-1}$ [4]) are predissociated to various degree, the predissociation in the $v' = 1$ rotational stack of the B state is a specially strong rotational effect, due to the

shallow potential functions and the small centrifugal exit barriers belonging to the successive N' rotational states [5,6]. No transitions have ever been reported to $v' = 2$ and higher vibrational states in B.

While in absorption such a predissociation shows up in broadening of the transitions ending on high rotational levels in the $v' = 1$ state (Ref. [3], and see Fig. 49 in Ref. [7], where, e.g. the P series can be followed up to $N' = 11$), in emission observations reported so far for the 1–0 vibrational band [1,3] the rotational structure between 362 and 370 nm ends abruptly at transitions to the $N' = 6$ level. In the latest works on the B state accurate spectral data were given for the 0–0 band [8], and for the 0–0, 1–0 and 1–1 vibrational bands [9]. Transitions listed there for the 1–0 band also end at $N' = 6$ or below this rotational state. The latest ground state parameters for CH are found in Ref. [10].

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Lifetimes for the various vibration–rotation levels in the B state have already been measured and theoretically estimated. An experimental radiative lifetime is given in Ref. [11] for the $v' = 0$ vibrational level, later more accurate measurements were reported [4] for individual rotational levels for both $v' = 0$ and $v' = 1$ using high resolution electron beam deflection experiments. Theoretical estimates for non-radiative lifetimes from quasi-bound level calculations based on an 'ab initio' potential function are available [12] updating earlier estimates [13]. Experimental radiative lifetimes for the $v' = 1$ state are around 400 ns for $N' = 3$ –6 [4], while predissociation lifetimes were calculated to lie between 66 and 5 ps from $N' = 1$ –6 [12].

In our emission spectra for the 1–0 band of the B state all long-lived rotational features are strong making it possible to estimate radiative lifetimes for the corresponding upper rotational levels using conventional time-resolved fluorescence technique. In addition we observed broad spin doublets due to P(8), Q(7) and R(6) transitions ending on the strongly predissociated $N' = 7$ level. The width of these features allowed us to obtain an approximate value for the $N' = 7$ lifetime in the B state. To our knowledge

our result constitutes the first experimental estimate for this short-lived level of the CH molecule in emission.

2. Experimental

Ketene, the precursor to methylidyne, was produced by pyrolyzing acetic acid anhydride in a quartz oven at 600°C. The ketene sample was distilled from a dry ice/acetone trap to a liquid nitrogen trap to remove undecomposed anhydride, acetic acid and other products of the pyrolysis, mainly CO₂. Ketene samples were photolysed by a dye laser (FL 3002, Lambda Physik GmbH), pumped by an excimer laser (LPX 100, Lambda Physik GmbH), using a direct UV dye (LC 3590 DMQ). Scattered laser light was removed with two low-pass filters cutting around 380 and 390 nm. The dye laser was operated at 10 Hz with pulse power between 3 and 6 mJ.

Ten laser shots were averaged by a boxcar averager (Stanford Research Systems, model SRS 280). A gate of ≈ 130 ns width was used, placed over the main fluorescence signal. The laser beam was focused by a 32 cm focal length quartz lens into the

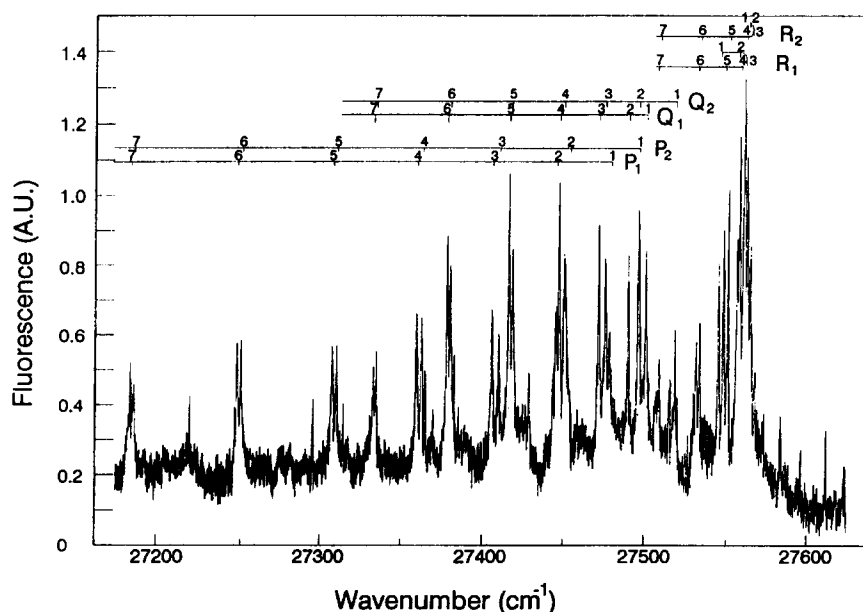


Fig. 1. A low resolution scan of the rotational features in the spectra of CH in the region 27624–27174 cm⁻¹, due to excitation from X to B, $v'' = 0$ – $v' = 1$.

fluorescence cell. No emission signals were detected between 362 and 370 nm with an unfocused beam. Both flowing and static ketene samples were photolysed, but most of the work reported here was done on static ketene samples of pressure between 500 and 100 mTorr. In addition to neat ketene, we have used mixtures with helium or argon to thermalize the CH product, thereby improving the strength and signal-to-noise ratio of the emission signal.

For lifetime measurements the decay of the fluorescence signal was measured using a LeCroy 9450A dual 300 MHz oscilloscope. Each profile was averaged over 2000 laser shots.

3. Results

3.1. Spectral features

The emission spectra were observed both by mechanical scanning of the dye laser grating and using an intracavity étalon in the dye laser. Using the Q(2) doublets an estimate for the laser linewidth was obtained as 0.898 cm^{-1} . An overall low resolution scan is given in Fig. 1 between 27624 and 27174 cm^{-1} .

The line positions in our spectra of the 1–0 vibrational transition correspond closely to the high precision values in Ref. [9]. Rough calibration was done using a Fourier-transform spectrometer in emission mode, by checking the dye-laser wavenumber at several different points in the spectrum. This resulted in a wavenumber accuracy of about 0.5 cm^{-1} . Using the highly precise wavenumbers in Ref. [9] as secondary standards calibration could be improved.

A good general agreement between the line intensities in our spectra and the theoretical formulas in Table 3.7 of Ref. [14] is obtained when in the rotational Boltzmann factor an effective temperature of 1000 K is used. However the relative intensities within a given branch and between different branches depend somewhat on the pressure of the sample, and are greatly altered when a buffer gas, such as argon, is added to the ketene sample. The intensity of the spin doubling components is expected to be the same on purely spectroscopic grounds (see e.g. formulas in Ref. [14]). However there is a marked F_1 over F_2 propensity throughout the spectra.

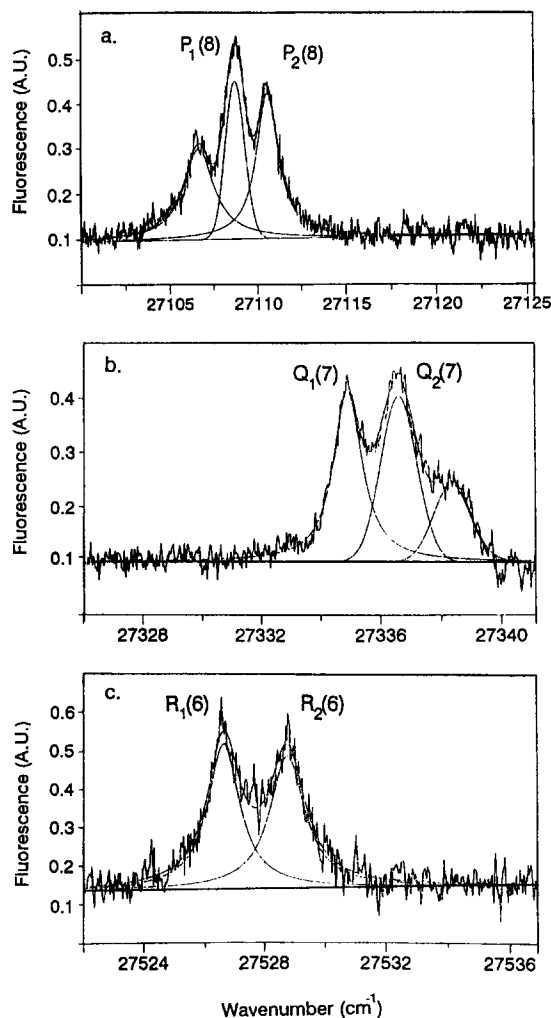


Fig. 2. Low resolution line profiles of the R(6), Q(7) and P(8) spin doublets. (a), (b) and (c) indicate the corresponding results of Voigt fits to the spin components.

The broad and weak R(6), Q(7) and P(8) doublets were recorded both at mechanical scanning of the dye laser grating and using an intracavity étalon. The corresponding low resolution spectra are shown in Fig. 2. The results of Voigt deconvolution are also shown. The R(7) and Q(8) transitions going to $N' = 8$ are weak in neat ketene, but easily detectable upon adding buffer gas, such as argon, to the sample. As the presence of a buffer gas changes lifetimes due to collisional quenching effects we do not discuss $N' = 8$ features. The étalon scans of the $N' = 7$ transitions

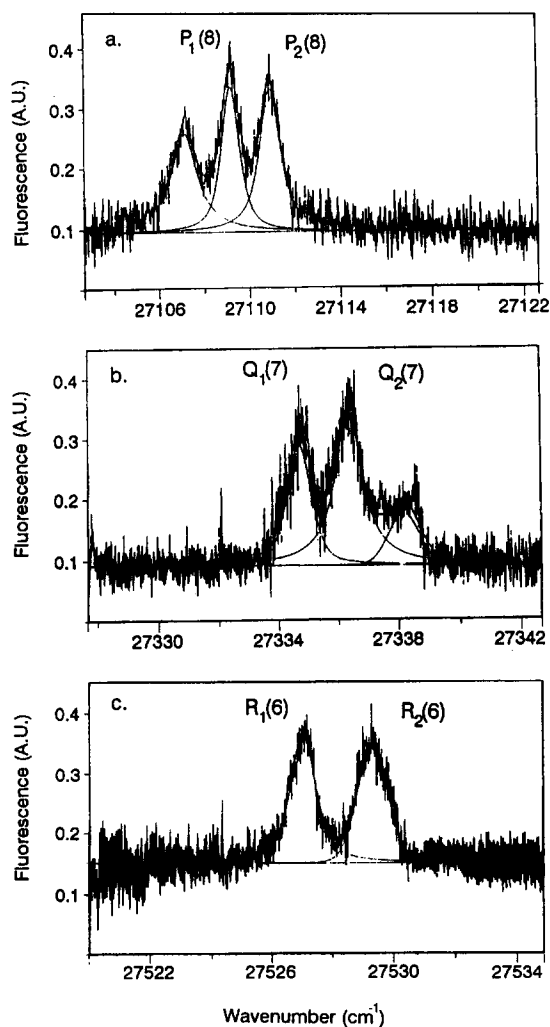


Fig. 3. High resolution étalon scans of the line profiles of R(6), Q(7) and P(8). (a), (b) and (c) indicate the corresponding results of Voigt fits to the spin components.

looked very similar to Fig. 2. The corresponding line profiles are shown in Fig. 3. The assignment of these relatively weak lines was aided by using the molecular constants for the $v = 0$ state in $X^2\Pi$ and $v = 1$ in $B^2\Sigma^-$ in Ref. [9].

3.2. Measurement of lifetimes

The lifetimes of the corresponding upper N levels of the F_1 component of six Q(J) transitions have been obtained using standard time-resolved fluores-

cence methods. In these measurements the decay pattern was fitted to a single exponential decay model in the range of 500–50 mTorr of neat ketene pressure and extrapolation to zero ketene pressure was carried out. Our fitting model also took constant and linearly increasing backgrounds into account. At higher ketene pressures there was evidence of biexponential behaviour. Table 1 contains the results, the errors are one standard deviation figures.

The broad doublets in Figs. 2 and 3 were first deconvoluted using Voigt line profiles to obtain the individual spin component widths (Γ), then analyzed for lifetime (τ) using the relationship [15]

$$\Gamma \text{ (cm}^{-1}\text{)} = (2\pi c\tau)^{-1} = 5.3 \times 10^{-12}/\tau \text{ (s)}. \quad (1)$$

The width of each of the three transitions shown in Fig. 2 was obtained at four different ketene pressures at 300, 500, 1000 and 2000 mTorr but pressure was found to have a negligible effect on widths. An example of the R(6) line is given in Fig. 4.

The widths of the R(6), Q(7) and P(8) lines, as deconvoluted first by a Voigt line profile and then by the laser linewidth 0.898 cm^{-1} , were found to be $0.921(50)$ and $1.092(76)$, $0.823(101)$ and $1.106(116)$, $0.964(75)$ and $1.116(122) \text{ cm}^{-1}$, for the F_1 and F_2 spin components, respectively. High resolution étalon scans of the same transitions yielded Voigt widths $0.979(20)$ and $1.15(24)$, $0.965(30)$ and $1.107(30)$, $0.956(29)$ and $1.107(38) \text{ cm}^{-1}$ for F_1 and F_2 components in the above order.

In Table 2 lifetimes calculated from Eq. (1) are summarized for low and high resolution spectra. From the table the following lifetime averages are obtained for low resolution spectra: $\tau(F_1)_{av} =$

Table 1
Lifetime estimates of long-lived N' levels for the $v' = 1$ B state of CH (in ns)

Upper state N'	Lifetime from Q(F_1) lines
1	412(62)
2	432(77)
3	408(73)
4	429(48)
5	420(44)
6	411(25)

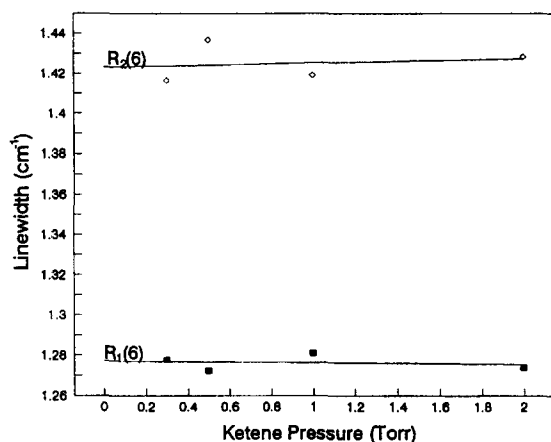


Fig. 4. Pressure dependence of the linewidth of the individual spin components for the R(6) line, in the range 0.3 to 2.0 Torr of pure ketene.

5.90(97), $\tau(F_2)_{av} = 4.80(74)$, and for the high resolution spectra $\tau(F_1)_{av} = 5.48(28)$, $\tau(F_2)_{av} = 4.73(23)$, all in ps.

4. Discussion

There are a number of points to be discussed in connection with our emission spectra of the B state of CH. First of all we would like to point out that the observation of the $N' = 7$ level, and the estimation of its non-radiative lifetime provides a challenge for both practical applications and for further theoretical studies. A very short-lived rotational state of CH is of obvious interest for combustion diagnostics in flames and internal combustion engines. For atmospheric and higher pressure media collisional quenching renders it impossible to use laser-induced fluorescence from levels having lifetime of several hundred ns. Fluorescence from a level with a few ps lifetime is obviously not influenced by gas-kinetic collision rates and could thus provide a possibility to

extend instantaneous temperature field measurements to real life combustion environments. Crosley and co-workers [16,17] have called attention to the fact that the methylidyne radical provides complementary information to the OH radical in flame chemistry, because its distribution in the flame differs from that of hydroxyl. The possibilities for using predissociated levels in atmospheric flames were also pointed out by Andresen et al. [18].

Rotational and vibrational collisional energy transfer studies so far (e.g. Refs [16,17,19]) have not been applied to the predissociated N' levels in the $v' = 1$ state of the B electronic state of CH, therefore it is of obvious interest to extend such studies to collisional quenching effects by rare gases and nitrogen, similar to those reported by Cooper and Whitehead [19]. In the present experiments these quenching effects are minimized by the relatively low pressure of the pure ketene precursor, as we have found that the linewidth of the R(6) doublet in Fig. 4 is essentially independent of pure ketene pressure in the range 0.3–2 Torr. However since the photophysical and photochemical processes giving rise to the CH spectra reported here are quite complicated their role warrants further studies.

The lifetime measured here for $N' = 7$ is not influenced significantly by the Doppler width which is near 0.1 cm^{-1} at 300 K and about 0.17 cm^{-1} at 1000 K for the methylidyne radical around 360 nm. It contributes a few percent of error to the lifetime derived from half widths only. Additional support for our lifetime estimate comes from the comparison of linewidths in Table 2 between laser linewidth-deconvoluted half widths from low resolution to the linewidths from étalon spectra.

It would obviously be very important to obtain modern theoretical non-radiative lifetime estimates for the predissociated N' levels for $v' = 1$ in the B state using highly accurate excited state potential functions. A trend extrapolation of the non-radiative

Table 2
Lifetime estimates for the $N = 7$ level in the $v' = 1$ B state of CH (in ps)

Spin component	Low resolution			High resolution		
	R(6)	Q(7)	P(8)	R(6)	Q(7)	P(8)
F_1	5.75(33)	6.43(80)	5.50(43)	5.41(12)	5.50(18)	5.54(17)
F_2	4.85(33)	4.79(50)	4.75(43)	4.61(10)	4.79(13)	4.79(16)

lifetimes theoretically obtained in Ref. [12] to $N' = 7$ in $v' = 1$ indicates a lifetime about a factor of 2 smaller than the one reported here. On the other hand, earlier predissociation calculations by Elander et al. [13] lead to a lifetime some orders of magnitude longer than our experimental result, albeit giving quite satisfactory fit to linewidths photogrammetrically derived from absorption spectra by Herzberg and Johns [3]. Thus either the results in Ref. [13] are now seriously outdated or some other explanation should be sought for the difference between emission and absorption linewidths.

Finally the photophysical and photochemical processes that lead to an excitation of the $v' = 1$ level in the $B^2\Sigma^-$ state of CH are worthy of a study in themselves. It is well known from the photochemical literature on generating the CH_2 radical from ketene (see, e.g. Chen et al. [20]) that in the photolysis of ketene above 350 nm only triplet methylene is produced. On the other hand triplet CH_2 is known to dissociate to ground state CH [21]. Thus the spectra reported here may be due to a sequence of single photon events leading to excitation of CH from its $^2\Pi$ ground state to the $v' = 1$ level of the B state from which emission is observed. On the other hand it is possible to arrive at ground state methylidyne in a multiphoton process starting directly from the precursor ketene molecule. Ground state CH from a multiphoton dissociation of ketene has been observed by Ball et al. [22]. A careful intensity dependence study of the excitation conditions of our experiments would be necessary to decide this question.

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