Radiative lifetime of the B $^2\Sigma^-$ state of CH

Richard A. Anderson
Missouri University of Science and Technology

Jerry Peacher
Missouri University of Science and Technology, peacher@mst.edu

David M. Wilcox

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Richard A. Anderson, Jerry Peacher, and David M. Wilcox

Department of Physics, University of Missouri-Rolla, Rolla, Missouri 65401
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The radiative lifetimes of the $N'=3$ to 15 rotational states of the $v'=0$ level of the $B\,^2\Sigma^-$ state of CH were measured. Emission lines were observed to $N'=15$, but no lines above this rotational state were observed. This result agrees with previous studies. The lifetimes of all rotational states were between 300 and 400 ns. Previous measurements have indicated that the $N'=15$ level might have a lifetime as short as 100 ns.

INTRODUCTION

Experimental and theoretical studies have shown that the $B\,^2\Sigma^-$ state of CH has a potential maximum.[1–5] Experimentally the emission spectrum[1] from the $v'=0$ level of this state breaks off at $N'=16$ and the broadening of absorption lines[2] occurs at $N'=18$. Johns and Herzberg[2] predicted a maximum in the potential curve of the state from limiting curves of dissociation and the form of this potential maxium has been theoretically studied.[3–5]

Initial lifetime studies[6–9] only measure band head lifetime with instruments of low dispersion. Brooks and Smith[10] performed the first extensive study on this state. The lifetimes of the rotational levels to $N'=15$ for $v'=0$ and the $N'=6$ for $v'=1$ were observed.

Three theoretical studies[11–13] to predict the lifetime of the $B\,^2\Sigma^-$ state have been performed. In all of these studies only state lifetimes were calculated and not lifetimes for individual rotational levels.

The present experiment is similar to that of Brooks and Smith,[10] except that a different experimental technique was used. The delayed coincidence technique was employed so that actual decay curves of the excited levels could be observed. Many lines at shorter wavelengths could be described by single exponential decays and those at longer wavelengths exhibited two exponential decays. In the discussion of our paper this distinction will be important.

EXPERIMENTAL METHOD

The delayed coincidence method of single photon counting was used in conjunction with a pulsed rf discharge at 70 MHz with an electrical cutoff of 15 ns. The spectral lines were isolated by a Spex 1500 $\frac{3}{4}$ m monochromator with a 1500 lines/mm grating. The spectral lines were detected with an EMI 6256S photomultiplier. For the isolation of most spectral lines, a bandwidth of less than 0.3 Å was used. The output pulse of the photomultiplier was amplitude discriminated by an EG&G T200/N fast trigger and was timed by an Ortec 437 time to pulse height converter (TPHC). This output was stored in a Nuclear Data 1100 multichannel analyzer. The data were converted to paper tape and cards and read directly into an IBM 370 computer for analysis.

The methane (CH_4) used in the experiment was Matheson ultrahigh purity grade. The gas was flowed continuously through the discharge region. The pressure was controlled with a stainless steel needle valve and measured with a CVC thermocouple gauge calibrated against a Stokes mercury manometer.

For the time calibration of the TPHC and the multichannel analyzer two methods were used. In one case, a pulse was sent to the start of the TPHC and also through a cable of accurately known delay to the stop of the TPHC. Several different cables were used and counts were accumulated in the memory of the multichannel analyzer depending upon the time delay. In the second case, a start pulse from a HP 222 A pulse generator was used to start the TPHC and drive a Dumont 792 A pulse generator which had a variable delay. This delayed pulse stopped the TPHC. The delay times set on the pulse generator were measured on a HP 1710A oscilloscope which was time calibrated with a Tektronix 180-S1 time mark generator.

RESULTS AND DISCUSSION

A spectrum of the emission taken at high pressure is shown in Fig. 1. The long wavelength region of the spectrum was overlapped by a short lifetime component. This component is strongly quenched so that at high CH_4 pressures the spectrum is mainly that of CH. At low pressures the intensity of the short lived component can become equal to or slightly greater in intensity than the long lived components for some lines. These are the 3953, 3962, 3972, 3983, 3995, 4008, and 4021 Å lines.

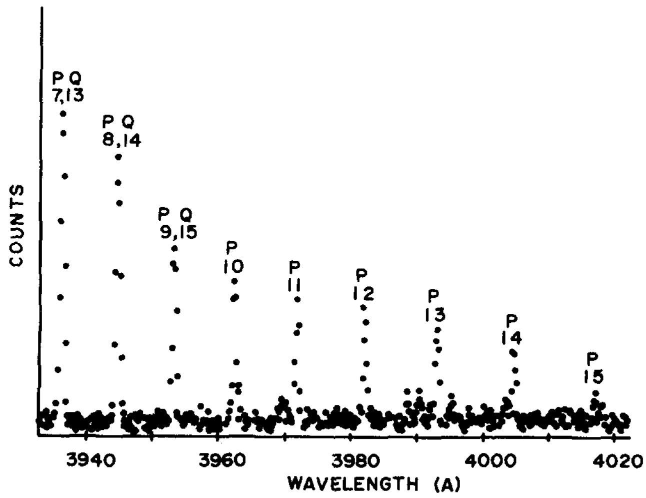

FIG. 1. A portion of the CH spectrum taken at high CH_4 pressures.

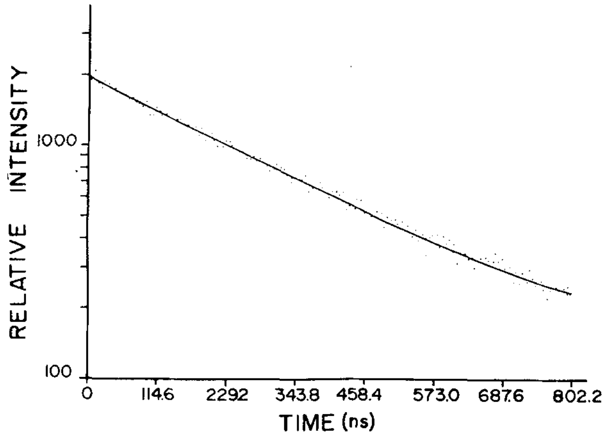

FIG. 2. The decay curve of the 3902 Å line at 30 mtorr and the computer fit.

TABLE I. Radiation lifetime of rotational states of the $v'=0$ level of the $B\,^2\Sigma^-$ state of CH.

Upper state N'	Lifetime ns	Wavelength of transition Å
3	381 ± 18	3891
4	352 ± 24	3893
5	335 ± 10	3895
7	345 ± 23	3902
8	349 ± 8	3906
9	395 ± 21 (364 ± 24*)	3910 (3953*)$P(9)Q(15)$
10	345 ± 16	3916
11	368 ± 20	3972
12	405 ± 26	3983
13	399 ± 29	3995
14	430 ± 18	4008
15	416 ± 53 (364 ± 24*)	4021 (3953*)$P(9)Q(15)$

A typical decay curve for the 3902 Å line at 30 mtorr CH_4 pressure is shown in Fig. 2. The solid line is the computer fit to the curve. Data on all lines were taken at four or more CH_4 pressures. The 3902 Å line is nearly a single exponential decay. Most CH lines, which are not overlapped by the short lived component, are nearly pressure independent. CH lines overlapped by the strongly pressure dependent short lived component are more pressure dependent. This dependence is mainly caused by the fact that the computer cannot yield an entirely unique solution to an equation of the form $I = A\,\exp(-t/\tau_1) + B\exp(-t/\tau_2) + C$.

Lifetimes of the long decay component are shown in Fig. 3. These lifetimes were measured by examining lines where there was no overlap of other CH lines. Since the line arising from the $N'=15$ level was weak, the overlapped $P(9)\,Q(15)$ line at 3953 Å was also examined. The lifetime (asterisk) for the 3953 Å line is shown opposite the nonoverlapped lifetimes for the $N'=9$ and 15 levels. Table I shows the same results in tabular form.

The CH spectral lines were identified from the papers by Moore and Broida[14] and Bass and Broida.[15] In these papers the levels are designated by lower state rotational quantum numbers. Brooks and Smith[10] identified these as upper state quantum numbers. If only Q lines are examined, this makes no difference, but if P and R branch lines are included in their figures, the rotational quantum numbers may be mislabeled. The recent work by Botterud, Lofthus, and Veseth[16] on the term values of CH indicate that Moore and Broida[14] used lower state rotational quantum numbers.

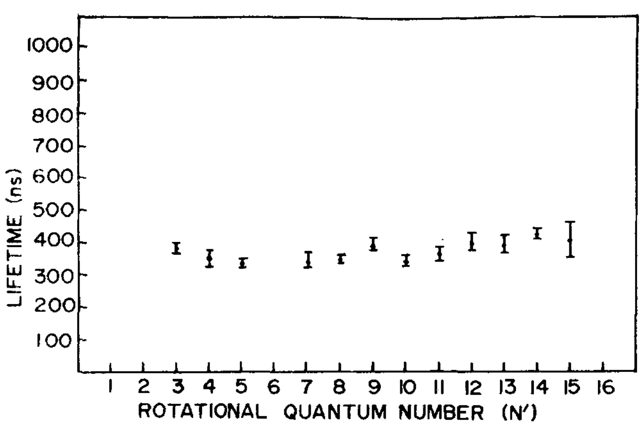

FIG. 3. The lifetimes of rotational states of the $v'=0$ level of the $B\,^2\Sigma^-$ state of CH.

The most striking difference between our results and those of Brooks and Smith[10] is that the $N'=15$ level does not shorten. The lifetime of the $N'=15$ level was measured at 4021 Å corresponding to the $P(15)$ line[16] and the 3953 Å line was also examined corresponding to the $P(9)\,Q(15)$ line.[16] At 3953 Å the short lived component became apparent and for the lines between 3953 and 4021 Å the "zero pressure" short component lifetime was between 50 and 100 ns. This may have been the lifetime measured by Brooks and Smith.[10] Since this short component lifetime was evident for all lines above 3953 Å, it could not be identified as the shortened lifetime of the $N'=15$ state. It was probably caused by a background of H, H_2, and CH^+.[10] Since the background was intense and the $P(15)$ line was weak, the error for this line is larger than for the other lines, but the lifetime value observed in our experiment is close to the lifetime of all of all other CH lines and also the $P(9)\,Q(15)$ line at 3953 Å. All lifetimes listed in Table I are nonoverlapped CH lines except for the 3953 Å line which was measured for comparison with $P(15)$ line at 4021 Å.

When the emission spectra of CH are examined, the last line observed is the $P(15)$ line with the intensity of the lines gradually decreasing from the $P(8)\,Q(14)$ line at 3943 Å. The $P(16)$ line is not present and this agrees with earlier studies.[1] From this study the $N'=16$ level of CH is the first level tunneling through the potential barrier and has a lifetime so short that it cannot be measured. Since all CH levels from $N'=3$ to 15 have the same lifetime, they are all visible but may have gradually decreasing intensities beyond $N'=8$, and the $N'=16$ level is not apparent because of its rapid tunneling through the potential barrier. This rapid tunneling also accounts for the broadening of the $N'=18$ level in absorption.[2] Since the absorption line ending on the $N'=18$ level is broadened and the true predissociation limit can best be determined by the break-off of an emission series, the $P(16)$ line first shows predissociation and the $N'=16$ level can have a lifetime 10 100, or more times less than the $N'=15$ level.

From these results the barrier height of the $B\ ^2\Sigma^-$ state must be greater than 700 cm^{-1} using the data of Herzberg and Johns[2] and Botterud, Lofthus, and Veseth.[16] This result is also in close agreement with the results of Herzberg and Johns[2] and Lee, Hinze, and Liu,[3] which are greater than 500 and 800 cm^{-1}, respectively.

CONCLUSION

In conclusion, the lifetime of all rotational states from $N'=3$ to 15 are nearly the same with a slight increase in lifetime with the rotational quantum number. The $P(16)$ line does not appear and the $N'=16$ level has a lifetime so short that the line arising from it is not seen. This result agrees with the observation of emission spectra and the broadening of the $N'=18$ level in absorption. This result combined with new determinations fo term values[16] yields a potential maximum greater than 700 cm^{-1}.

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