

## New Vibrational Bands of CH<sub>2</sub> ( $\tilde{b}^1B_1$ )

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Singlet methylene has been produced in its lowest rotational states by photolysis of jet-cooled ketene at photolysis wavelengths near threshold, and the laser-induced fluorescence excitation spectrum has been recorded from 16 170 to 18 250 cm<sup>-1</sup>. The spectral simplification obtained has allowed identification of several previously unknown vibrational bands in the upper state. Three of the new bands are assigned as combination bands involving the  $\nu_1$  vibration of the  $\tilde{b}$  state; they should allow a more accurate determination of this mode's frequency and anharmonic constants. The variations in intensity with photolysis wavelength and the photolysis energy thresholds determined by photofragment excitation spectra for selected transitions permit unambiguous assignments of the lower states. The techniques presented here provide important tools for dealing with this congested and highly perturbed spectrum. © 1989 Academic Press, Inc.

### INTRODUCTION

The spectroscopy of the methylene radical has long been the subject of intense study for a variety of theoretical reasons and practical applications (1-3). Methylene has recently become the probe of choice in fundamental studies of photofragmentation dynamics in this and other laboratories (4-8), leading to revived interest in assigning its spectra.

The most accessible region of the methylene spectrum is the visible  $\tilde{b}^1B_1$ - $\tilde{a}^1A_1$  system. The original work on this system, as on many other small molecules, was done by Herzberg and co-workers (9, 10). In 1966, Herzberg and Johns reported about 1000 lines over the range 11 000-19 000 cm<sup>-1</sup> and assigned two vibrational levels of the  $\tilde{a}$  state and 25  $\tilde{b}$  state vibrational levels. In a dispersed fluorescence study, Feldmann *et al.* were able to identify 5 more  $\tilde{a}$  vibrational levels, but gave only incomplete rotational assignments (11). Stimulated Emission Pumping (SEP) experiments by Dai and coworkers, and blue-shifted "hot-band" fluorescence from some of these low-lying vibrational levels, measured in this laboratory, have recently allowed more complete assignments of these  $\tilde{a}$  levels (12). In 1984 Petek *et al.* (13) measured  $\approx 10^4$  transitions in the range 15 600-18 650 cm<sup>-1</sup>. They were able to assign only 486 of the observed transitions to vibrational bands reported by Herzberg and Johns

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100

100

100

100

(3, 13). The origin of 95% of the transitions—about 3 lines/cm<sup>-1</sup>—in the spectrum left an unanswered question in their study. Magnetic rotation spectra showed that more than half of the singlet methylene states were significantly perturbed by the interactions among the three low-lying electronic states (13). Petek and coworkers were also able to measure the CH stretching fundamentals of the *a* state in the infrared at high resolution (14). Their analysis of the visible system was limited by the very large number of observed lines and their lack of a model for predicting the *b* state rovibrational term values with any accuracy, or even of estimating how many upper state vibrational bands are intermingled in any region of the spectrum. These problems were complicated by the singlet-triplet and rovibrational perturbations, which affect the *a* state.

Duxbury and Jungen have fit many of the experimental results to theoretical potential energy surfaces, allowing more definitive vibrational numbering of the *b* state, and identifying *a* state vibrational levels which are apparently strongly coupled with the *b* state (15, 16). This theoretical work gives reason to hope that the highly perturbed *b* state may be much more completely analyzed in the near future.

Particular mention should also be made of the recent experimental work by Dai and coworkers on SEP spectroscopy of the higher vibrational states of the *a* state (12, 17). Because of the extreme spectral congestion, it seems likely that making substantial progress on the higher rotational and vibrational levels of the *a* state will require double-resonance techniques of this type.

In the present work photolysis is carried out just above the singlet CH<sub>2</sub> formation threshold, so that only the lowest methylene rotational states are produced. This allows relatively straightforward identification of several *b* state vibrational bands whose spectra overlap the vibrational bands previously assigned (13). Many other new transitions are also observed, adding to the already too-numerous unassigned lines in this spectrum. However, the techniques developed in the present study show considerable promise for attacking this formidable spectroscopic problem for low-*J* transitions.

#### EXPERIMENTAL DETAILS

The laser-induced fluorescence (LIF) excitation spectrum of singlet methylene produced by variable wavelength photolysis of jet-cooled ketene was measured using the apparatus described previously (4-7). The spectra were measured at intervals over the course of several years under slightly different conditions; the general procedure is given here. Helium carrier gas ( $\approx 1$  atm) was flowed over or through liquid ketene, typically maintained at dry ice temperature where its vapor pressure is 150 Torr, and the mixture sent through a pulsed valve into a vacuum chamber. The ketene, cooled to about 10 K by the expansion, was photolyzed by a frequency-doubled, Nd:YAG-pumped dye laser, yielding a few mJ/pulse of narrow-band ( $<0.5$  cm<sup>-1</sup>) ultraviolet light at wavelengths ranging from 325 to 331 nm. (The appearance threshold of singlet methylene is at 332 nm (5, 6).) The singlet methylene produced was excited with a second pulsed dye laser, of 0.4- or 0.2-cm<sup>-1</sup> bandwidth, pumped either by a second Nd:YAG or by a XeCl excimer, and its fluorescence detected with a red-sensitive photomultiplier through longpass filters (Schott RG 630, RG 610, or OG 590) which

block the scattered laser light. The LIF excitation spectra were measured at several photolysis wavelengths over the range 16 170 to 18 250  $\text{cm}^{-1}$ , excluding 16 405 to 16 525  $\text{cm}^{-1}$ . In regions of the spectra where many strong lines were observed more photolysis wavelengths were employed than in the sparser regions. The frequency was calibrated using singlet methylene transitions known from the previous high-resolution study (13, 14) as markers; the uncertainty in the line centers is  $\pm 0.2 \text{ cm}^{-1}$ . Nonlinearities in the dye-laser scanning were found to be larger than expected, so a more reliable frequency-calibration procedure using simultaneously measured  $0.66\text{-cm}^{-1}$  FSR etalon fringes and Ne atomic reference lines, described in Ref. (5), was used in the later experiments. This method increased the precision to better than  $\pm 0.1 \text{ cm}^{-1}$ . Although the methylene spectra are measured at considerably lower resolution than in the absorption study of Petek *et al.* (3, 13), the reduction in spectral complexity from using jet-cooled ketene and longer photolysis wavelengths more than makes up for the loss of resolution, at least for relatively low  $J, K$  transitions. At short photolysis wavelengths, where a large number of singlet methylene rotational states can be produced, higher resolution than achieved here would be necessary to resolve the very congested spectrum (4). Some improvement is possible by the use of a narrow-bandwidth laser system, but significant improvements will require reduction of the Doppler width of the methylene photofragment.

Working near the photochemical threshold with a variety of photolysis wavelengths greatly simplifies the spectral assignments. At the longest photolysis wavelengths only a very few singlet methylene rotational states can be produced, yielding an ultra-simple spectrum. In some scans lower seeding ratios of ketene in helium cooled the ketene to  $\approx 3 \text{ K}$ , reducing the number of lines still further. Higher sensitivity for the low- $J$  states is achieved than in the room-temperature measurements of Petek *et al.* (13); thus many new lines have been observed. As the photolysis photon energy is increased various spectral lines grow in, while others decline in intensity. The thresholds and intensity variations give good clues to the identity of the lower state of the spectral transitions. Only a manageable number of spectral lines are produced, allowing straightforward assignment by combination differences. When necessary, cold-beam PHOFEX scans of an unassigned transition yield the lower state's threshold with  $\pm 0.5 \text{ cm}^{-1}$  precision (5-7).

An attempt was made to observe methylene fluorescence by exciting the molecule between 390 and 406 nm. If sufficiently strong LIF spectra were observed in this region, it might allow the SEP spectra measured by Dai and co-workers (17, 18) to be easily extended to much higher  $\tilde{a}$  state energies. The ketene was photolyzed with 5 mJ/pulse of 325-nm UV light; the probe power was about 7 mJ/pulse, generated using the new dye, Excalite 398 (Exciton), pumped by the third harmonic of a Nd:YAG laser. The measurement was made using longpass filters with a cutoff at 470 nm (Schott KV470 and GG475), using the optimal fluorescence collection geometry (7). The fluorescence observed was very weak. Only six very weak lines were observed, with fluorescence lifetimes of about 100 ns, much shorter than the 4- $\mu\text{s}$  lifetime characteristic of the methylene fluorescence at longer excitation wavelengths. It seems likely that the observed lines are not due to  $\text{CH}_2(\tilde{a}^1A_1)$  at all, but rather to  $\text{CH}(X^2\Pi)$  produced by some multiphoton process; in any case the fluorescence is probably too weak to be useful in SEP spectroscopy.

## RESULTS

*Assigning the Spectra*

The spectra reported here were assigned by the following procedure. First, the line positions were tabulated and all the differences between line positions were compared with the known differences among the  $\tilde{a}$  (0, 0, 0) state term values. The matches found were then examined for coincidences where a single transition was involved in more than one match, and the differences corresponded to lower states allowed by the optical selection rules ( $\Delta J = 0, \pm 1$ ;  $\Delta K_a = \pm 1, 3$ ;  $\Delta K_c = \text{even}$ ). The unpublished survey spectra measured by Petek *et al.* (19) were also checked for predicted transitions to these new states, providing more accurate line positions than in the lower-resolution beam studies and also providing hot-band transitions which were enormously helpful in assigning some of the new vibronic bands. The recently measured LIF spectra of  $\tilde{a}$  (0, 2, 0) and (1, 0, 0) also proved helpful by providing additional transitions to some of the same upper states (12). Tentative assignments of the new upper states found by the combination difference procedure were then checked by looking for all of the predicted transitions and by examining the changes in intensity of the transitions with photolysis wavelength. Combination differences are more useful than spectral simulations for making methylene assignments because of the extensive singlet-triplet and rovibrational perturbations in both the lower and upper states. Petek *et al.* (13) also used combination differences, but the procedure was greatly complicated by the more than 10 000 transitions originating from a large number of mostly unidentified lower states. Because of this complexity, fewer than 5% of their observed lines could be assigned. The advantages of cooling the methylene state distribution are illustrated in Fig. 1.

Five new upper state vibrational bands are reported in Table I; two  $\Sigma$ , two II, and one  $\Delta$ . Most transitions were observed in several scans; the most precisely measured frequency available is listed in the tables. For most of the assigned transitions this is a value taken from Petek, Nesbitt, Darwin, and Moore's unpublished survey spectra (19), which has an estimated uncertainty of  $0.02 \text{ cm}^{-1}$ . If the line is observed in the jet-cooled LIF spectra, the longest photolysis wavelength which yielded the line is noted. Linear molecule numbering ( $v_1, v_2^1, v_3$ ) like that used by Herzberg and Johns (10) and by Petek *et al.* (13) is used for the  $\tilde{b}$  state vibrational bands, though the bent-molecule notation employed by Duxbury and Jungen (15) has some advantages, particularly as some of the upper states observed here may be due to highly excited vibrations of the  $\tilde{a}$  state, which is decidedly bent at low energy. (High  $\tilde{a}$  state levels can steal intensity from the  $\tilde{b}$  state via Renner-Teller coupling.) The new states were fit to the standard form  $E = \nu_0 + BJ(J+1) - DJ^2(J+1)^2$ . The upper state term values and spectroscopic constants are summarized in Table II. As was found in earlier studies (9), the  $\Sigma$  bands can be fit well to this conventional Hamiltonian, but there are numerous perturbations which distort the  $l \neq 0$  bands.

*Labeling the Vibrational Bands*

The observed vibronic levels in the region of interest are illustrated in Fig. 2, along with some theoretical predictions. Because of the lack of data and the extensive Renner-

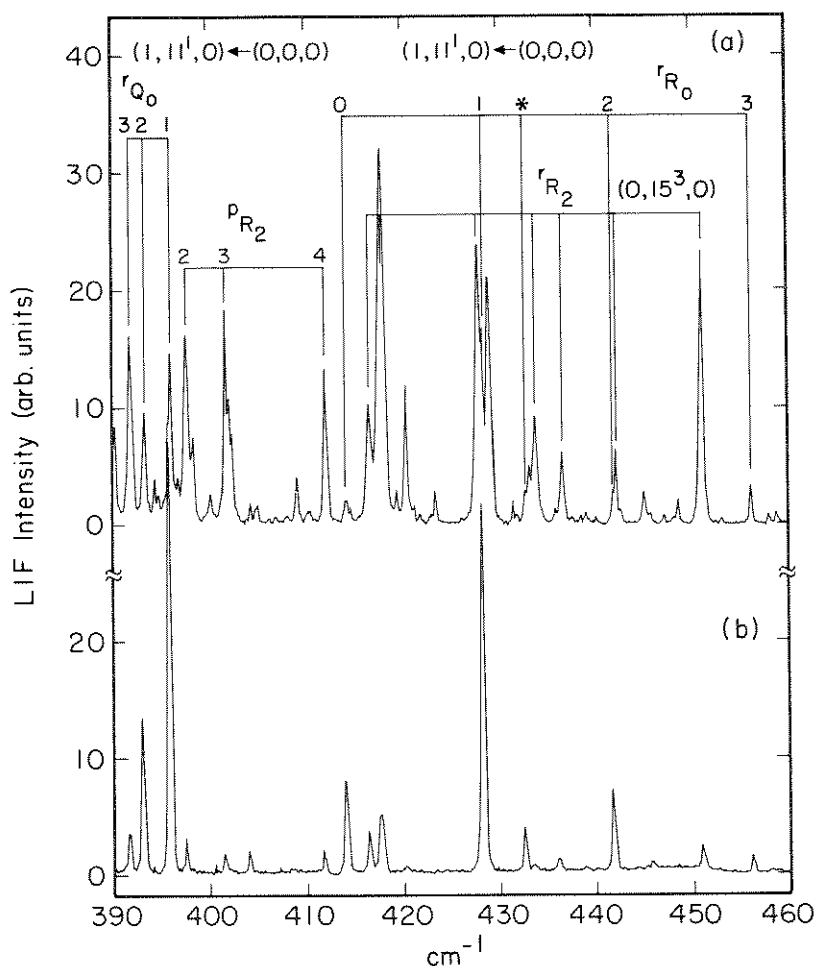


FIG. 1. The LIF excitation spectra of  $\bar{b}(1, 11^1, 0) \leftarrow \bar{a}(0, 0, 0)$  and  $\bar{b}(0, 15^3, 0) \leftarrow \bar{a}(0, 0, 0)$  of  $\text{CH}_2$  using 30 Torr rather than the usual 150 Torr ketene for cooling to about 3 K. Ketene is photolyzed (a) at 325 nm and (b) at 331 nm. \* denotes transition due to a perturbation with the  $(1, 11^1, 0) 2_{11}$  state. Note: The abscissa scale gives Wavenumber minus 17 000  $\text{cm}^{-1}$ .

Teller and Fermi perturbations it is difficult to definitively assign vibrational (or even electronic) quantum numbers to some of the observed bands, but reasonable guesses are possible. Herzberg and Johns (9) give an approximate formula for the vibronic band origins  $T_{\text{ev}}(0, v_2^1, 0)$  which matches most of the assigned vibrational bands above 15 000  $\text{cm}^{-1}$  within 100  $\text{cm}^{-1}$ . Neglecting the anharmonic interactions between  $\nu_1$  and  $\nu_2$ , one can write  $T_{\text{ev}}(v_1, v_2^1, 0) = T_{\text{ev}}(0, v_2^1, 0) + (\omega_e - \omega_e x_e) v_1 - \omega_e x_e v_1^2$ . The harmonic and anharmonic constants for  $\nu_1$  are not known experimentally, but all of Herzberg and Johns' assigned combination bands can be fit reasonably well by setting  $\omega_e = 3100 \text{ cm}^{-1}$  and  $\omega_e x_e = 60 \text{ cm}^{-1}$ . This formula predicts that the  $(1, 12^0, 0)$  and  $(1, 11^1, 0)$  band origins should lie at 18 230 and 17 389  $\text{cm}^{-1}$ , respectively. Duxbury

TABLE I  
Transitions to Newly Assigned Vibrational Bands

Assignment <sup>a</sup>	$\nu$ (cm <sup>-1</sup> )	$\lambda_{\max}$ <sup>b</sup> (nm)	Assignment <sup>a</sup>	$\nu$ (cm <sup>-1</sup> )	$\lambda_{\max}$ (nm) <sup>b</sup>
	(1,10 <sup>0</sup> ,0)			(1,12 <sup>0</sup> ,0)	
0 <sub>00</sub> <sup>+1</sup> <sub>10</sub>	16 710.569	331		18 161.01	331
1 <sub>01</sub> <sup>-1</sup> <sub>11</sub>	16 729.83 <sup>c</sup>	331		18 180.55 <sup>d</sup>	331
	-2 <sub>11</sub>	330		18 135.69	331
2 <sub>02</sub> <sup>-1</sup> <sub>10</sub>	16 755.8 <sup>d</sup>	331		18 206.93 <sup>c</sup>	331
	+2 <sub>12</sub>	331		18 178.72	331
	+3 <sub>12</sub>	330		18 106.29	331
	-3 <sub>30<sub>f</sub></sub>	e		18 029.5 <sup>d</sup>	328
	-3 <sub>12</sub>	-		16 751.20	-
3 <sub>03</sub> <sup>-2</sup> <sub>11</sub>	16 760.41	330		18 212.41	331
	-3 <sub>13</sub>	330		18 176.89	331
	-4 <sub>13</sub>	325		18 074.24	330
	-4 <sub>31<sub>f</sub></sub>	-		17 999.98	328
	-3 <sub>13</sub>	-		16 823.273	-
4 <sub>04</sub> <sup>+3</sup> <sub>12</sub>	16 760.884	330		18 215.16	331
	+4 <sub>14</sub>	330		18 176.70	e
	-5 <sub>14</sub>	325		18 042.70	e
	+5 <sub>32<sub>f</sub></sub>	-		17 965.48	325
	-5 <sub>14<sub>f</sub></sub>	-		16 685.93	-
	-5 <sub>32</sub>	-		16 598.77	-
5 <sub>05</sub> <sup>-4</sup> <sub>13</sub>	16 758.889	325		18 213.51	328
	-5 <sub>15</sub>	325		18 175.69	e
	+6 <sub>15</sub>	-		18 010.70	-
	+5 <sub>33</sub>	e		-	-
6 <sub>06</sub> <sup>-5</sup> <sub>14</sub>				18 211.54	325
	-6 <sub>16</sub>			18 176.29	e
	+7 <sub>16</sub>			17 983.44	e
				17 976.99	328
	+5 <sub>32<sub>f</sub></sub>			18 134.26	e
	-5 <sub>14<sub>f</sub></sub>			16 854.715 <sup>g</sup>	-
	+6 <sub>16<sub>f</sub></sub>			16 824.184	-
	-7 <sub>16</sub>			16 622.20	-

<sup>a</sup> The coldest jet conditions (T ≈ 3K) were used for photolysis at 331 nm; for other wavelengths T ≈ 10K. Unless noted, the lower vibronic state is  $\bar{a}^1A_1(0,0,0)$ .

<sup>b</sup> Longest photolysis wavelength for which the transition was observed in the jet-cooled LIF spectra.

<sup>c</sup> Overlapped in spectra of Ref. (19).

<sup>d</sup> Not observed in high resolution absorption spectra using 308 nm photolysis and room temperature ketene (Ref. (19)).

<sup>e</sup> Overlapped in jet-cooled LIF spectra.

<sup>f</sup> Denotes transition from  $\bar{a}(0,1,0)$  level.

<sup>g</sup> Uncertain assignment.

TABLE I—Continued

Assignment <sup>a</sup>	$\nu$ (cm <sup>-1</sup> )	$\lambda_{\max}^b$ (nm)	Assignment <sup>a</sup>	$\nu$ (cm <sup>-1</sup> )	$\lambda_{\max}^b$ (nm)
New $\Lambda$ band					
$2_{20}^{-1}1_0$	16 820.714	331	$2_{21}^{-1}1_1$	16 825.17	331
$+2_{12}$	16 792.422	331	$+2_{11}$	16 780.40	330
$-3_{12}$	16 719.95 <sup>d</sup>	330	$+3_{31}$	16 643.80	325
$+3_{30}$	16 643.23	330			
$3_{22}^{-2}1_2$	16 845.913	331	$3_{21}^{-2}1_1$	16 831.678	330
$+3_{12}$	16 773.52 <sup>d</sup>	330	$+3_{13}$	16 796.133	330
$+3_{30}$	16 696.726	325	$-3_{31}$	16 695.09	325
$+4_{14}$	16 735.15 <sup>d</sup>	330	$+4_{13}$	16 693.50	-
$+4_{32}$	16 622.00 <sup>d</sup>	325	$+4_{31}$	16 619.26 <sup>d</sup>	325
				16 616.63 <sup>d</sup>	325
$4_{22}^{-3}1_2$	16 840.173	330	$4_{23}^{-3}1_3$	16 852.90 <sup>d</sup>	330
$+3_{30}$	16 763.34 <sup>d</sup>	325	$-3_{31}$	16 751.84 <sup>d</sup>	325
$+4_{14}$	16 801.721	330	$-4_{13}$	16 750.323	330
$+4_{32}$	16 688.68	325	$-4_{31}$	16 676.03 <sup>d</sup>	325
$+5_{14}$	16 667.70	-	$+5_{33}$	16 583.66	325
$+5_{32}$	16 590.46	325			
$5_{24}^{-4}1_4$	16 877.60 <sup>d</sup>	330			
$+5_{14}$	16 743.581	325			
$+6_{16}$	16 708.35 <sup>d</sup>	325			
$+4_{32}$	16 764.556	325			
$+5_{32}$	16 666.34	325			
$+6_{34}$	16 559.88	-			
	(1, 11 <sup>1</sup> , 0)			(0, 15 <sup>1</sup> , 0)*	
$1_{11}^{-1}0_1$	17 396.28	331		17 689.59	331
$+2_{21}^f$	17 316.04	330		17 618.32	331
$-1_{01}^f$	16 043.82	-		16 346.118	316.5
$+2_{21}^f$	15 956.84	-		16 259.13	-
$-(0, 2, 0)1_{01}$	-	-		15 031.42 <sup>d</sup>	303.5
$-(1, 0, 0)1_{01}$	-	-		14 892.7 <sup>d</sup>	302.5

and Jungen's more sophisticated treatment of the bending mode predicts that these states will lie at 18 208 and 17 389 cm<sup>-1</sup>, respectively (15). Both predictions are in good agreement with the observations of a  $\Sigma$  band with  $\nu_0 = 18 192.2$  cm<sup>-1</sup> and a  $\Pi$  band with  $\nu_0 = 17 399.8$  cm<sup>-1</sup>. Unfortunately, the other assignments are not so clear. The  $\hat{b}(1, 10^0, 0)$  and  $(2, 6^0, 0)$  band origins are predicted by Herzberg and Johns's formula to lie at 16 670 cm<sup>-1</sup> and 16 650 cm<sup>-1</sup>, respectively, compared with the 16 741.9 cm<sup>-1</sup> band origin of a newly assigned  $\Sigma$  band. None of Duxbury and Jungen's predicted  $\Sigma$  bands lie closer to the observed band origin. The prediction for  $(2, 6^0, 0)$  is particularly uncertain, since it depends to a greater extent on the assumed CH stretching frequency and anharmonicity. The  $(1, 10^0, 0)$  band is expected to be more intense, so the observed band is assigned that way in the Tables although its relatively small  $B$  value might suggest its assignment as  $(2, 6^0, 0)$  or  $(0, 6^0, 2)$ . No vibronic

TABLE I—Continued

Assignment <sup>a</sup>	$\nu$ (cm <sup>-1</sup> )	$\lambda_{\max}^b$ (nm)	Assignment <sup>a</sup>	$\nu$ (cm <sup>-1</sup> )	$\lambda_{\max}^b$ (nm)
	(1, 11 <sup>1</sup> , 0)			(0, 15 <sup>1</sup> , 0)*	
1 <sub>10</sub> <sup>-</sup> 0 <sub>00</sub>	17 414.45 <sup>d</sup>	331		17 713.05	331
+2 <sub>02</sub>	17 360.87	331		17 659.45 <sup>c</sup>	330
+2 <sub>20</sub> <sub>f</sub>	17 314.87 <sup>d</sup>	327		17 613.38	330
+0 <sub>00</sub> <sub>f</sub>	16 062.10 <sup>g</sup>	-		16 360.5 <sup>d</sup>	e
+2 <sub>02</sub> <sub>f</sub>	16 008.35	-		-	-
-2 <sub>20</sub> <sub>f</sub>	15 955.60 <sup>c</sup>	-		16 254.232	-
+(0, 2, 0) <sub>00</sub>	-	-		15 045.47 <sup>d</sup>	303.5
+(1, 0, 0) <sub>00</sub>	-	-		14 907.0 <sup>d</sup>	302.5
+(1, 0, 0) <sub>202</sub>	-	-		14 854.1 <sup>d</sup>	302.5
2 <sub>11</sub> <sup>+</sup> 1 <sub>01</sub>	17 428.52	331		17 724.85	e
-2 <sub>21</sub>	17 348.24	331		17 644.58	e
-3 <sub>03</sub>	17 342.48 <sup>d</sup>	331		17 638.76 <sup>d</sup>	330
+3 <sub>21</sub>	17 288.22	327		17 584.59	330
+1 <sub>01</sub> <sub>f</sub>	16 076.04	-		16 372.374	e
+2 <sub>21</sub> <sub>f</sub>	15 989.03 <sup>c</sup>	-		16 285.384	e
-3 <sub>03</sub> <sub>f</sub>	15 989.90	-		16 286.254	-
+3 <sub>21</sub> <sub>f</sub>	15 929.13	-		16 225.482	-
+(0, 2, 0) <sub>303</sub>	-	-		14 971.07 <sup>d</sup>	303.5
2 <sub>12</sub> <sup>-</sup> 2 <sub>02</sub>	17 393.59	331		17 699.70	330
-2 <sub>20</sub>	17 347.57 <sup>c</sup>	330		17 653.70	330
+3 <sub>22</sub> <sub>f</sub>	17 293.88	327		17 599.97	330
+2 <sub>02</sub> <sub>f</sub>	16 041.09	-		16 347.205	316.5
+3 <sub>22</sub> <sub>f</sub>	15 934.70	-		-	-
+(0, 2, 0) <sub>202</sub>	-	-		15 031.95 <sup>d</sup>	303.5
+(0, 2, 0) <sub>220</sub>	-	-		14 972.61 <sup>d</sup>	303.5
+(1, 0, 0) <sub>202</sub>	-	-		14 894.6 <sup>d</sup>	302.5
+(1, 0, 0) <sub>220</sub>	-	-		14 848.9 <sup>d</sup>	302.5
3 <sub>13</sub> <sup>+</sup> 3 <sub>03</sub>	17 392.19	331		17 732.86	331
+2 <sub>21</sub>	17 397.96	331		17 738.65	331
+3 <sub>21</sub>	17 338.03 <sup>d</sup>	330		17 678.67	330

quantum numbers can be assigned to the new  $\Delta$  band, which lies more than 300 cm<sup>-1</sup> above the predicted origins of the  $\tilde{b}$  (1, 10<sup>2</sup>, 0),  $\tilde{b}$  (2, 6<sup>2</sup>, 0), and  $\tilde{a}$  (1, 12, 0)  $K_a = 2$  bands. It may be another  $\tilde{b}$ -state level or a highly excited  $\tilde{a}$  state vibration which steals intensity from the high-oscillator-strength  $\tilde{b}$  (0, 14<sup>2</sup>, 0) vibration only 36 cm<sup>-1</sup> lower in energy. Similarly, the newly assigned II band interacting with (0, 15<sup>1</sup>, 0) does not lie close to any other II bands predicted by Herzberg and Johns (9) or Duxbury and Jungen (15). It is labeled (0, 15<sup>1</sup>, 0)\* in the Tables. More definitive vibrational numbering of the interacting CH<sub>2</sub>  $\tilde{b}$  and  $\tilde{a}$  states will require further theoretical work along the lines of Duxbury and Jungen's study (15), supplemented by additional spectroscopic data.

Duxbury and Jungen (15) included only the pure bending states in their recent spectral fit, though they did include some effects of the strong Fermi resonance between

TABLE I—Continued

Assignment <sup>a</sup>	$\nu$ (cm <sup>-1</sup> )	$\lambda_{\max}$ <sup>b</sup> (nm)	Assignment <sup>a</sup>	$\nu$ (cm <sup>-1</sup> )	$\lambda_{\max}$ (nm) <sup>b</sup>
	(1, 11 <sup>1</sup> , 0)			(0, 15 <sup>1</sup> , 0)*	
<sup>3</sup> <sub>13</sub> <sup>-4</sup> <sub>23</sub>	17 271.08	327		17 611.76	328
- <sup>4</sup> <sub>41</sub> <sub>f</sub>	-	-		17 481.18	328
+ <sup>3</sup> <sub>03</sub> <sub>f</sub>	16 039.64 <sup>c</sup>	-		16 380.31	316.5
- <sup>2</sup> <sub>21</sub> <sub>f</sub>	16 038.79	-		16 379.5 <sup>d</sup>	316.5
- <sup>3</sup> <sub>21</sub> <sub>f</sub>	15 978.81	-		-	-
- <sup>4</sup> <sub>23</sub> <sub>f</sub>	15 911.85	-		16 252.523	-
- <sup>4</sup> <sub>41</sub>	-	-		16 103.026	-
-(0, 2, 0) <sub>3</sub> <sub>03</sub>	-	-		15 065.15 <sup>d</sup>	303.5
-(0, 2, 0) <sub>3</sub> <sub>21</sub>	-	-		14 997.85 <sup>d</sup>	302
-(0, 2, 0) <sub>4</sub> <sub>23</sub>	-	-		14 930.6 <sup>d</sup>	302.5
-(1, 0, 0) <sub>2</sub> <sub>21</sub>	-	-		14 933.8 <sup>d</sup>	302.5
+(1, 0, 0) <sub>3</sub> <sub>03</sub>	-	-		14 928.2 <sup>d</sup>	302.5
+(1, 0, 0) <sub>3</sub> <sub>21</sub>	-	-		14 874.9 <sup>d</sup>	302.5
<sup>3</sup> <sub>12</sub> <sup>-2</sup> <sub>02</sub>	17 442.18 <sup>d</sup>	331			
+ <sup>3</sup> <sub>22</sub>	17 342.48 <sup>d</sup>	e			
- <sup>4</sup> <sub>04</sub>	17 326.80	327			
- <sup>4</sup> <sub>22</sub> <sub>f</sub>	17 257.04	325			
- <sup>2</sup> <sub>20</sub> <sub>f</sub>	16 036.94	-			
- <sup>3</sup> <sub>22</sub> <sub>f</sub>	15 983.33	-			
- <sup>4</sup> <sub>04</sub> <sub>f</sub>	15 974.47 <sup>g</sup>	-			
- <sup>4</sup> <sub>22</sub>	15 897.88	-			
<sup>4</sup> <sub>13</sub> <sup>-3</sup> <sub>03</sub>	17 456.23	331			
+ <sup>3</sup> <sub>21</sub>	17 402.01 <sup>c</sup>	331			
- <sup>4</sup> <sub>23</sub>	17 335.05 <sup>d</sup>	327			
+ <sup>5</sup> <sub>05</sub>	17 313.08 <sup>d</sup>	327			
+ <sup>5</sup> <sub>23</sub> <sub>f</sub>	17 220.83	327			
+ <sup>3</sup> <sub>21</sub> <sub>f</sub>	16 042.88	-			
- <sup>4</sup> <sub>23</sub> <sub>f</sub>	15 975.96 <sup>c</sup>	-			
- <sup>5</sup> <sub>05</sub> <sub>f</sub>	15 961.05	-			
+ <sup>5</sup> <sub>23</sub>	15 861.23	-			

the symmetric stretch and the bend. The identification here of three new  $\tilde{b}$  state combination bands involving the symmetric stretch vibration should allow comprehensive fits to include this mode as well, and so determine the stretching frequency and certain anharmonic constants.

It is interesting to note that all of the newly assigned vibrational bands except (1, 12<sup>0</sup>, 0) are very nearly resonant with known high oscillator strength  $\tilde{b}$ (0,  $v_2^1$ , 0) bands with which they can interact, i.e.,  $\Delta l = 0$  or 2. This suggests that the intensity of the new bands may be due primarily to interaction with these bands, rather than to their intrinsic Franck-Condon factors. Theoretical estimates of the  $\Delta l = 2$  matrix elements would be valuable for testing whether there is significant interaction between (1, 11<sup>1</sup>, 0) and (0, 15<sup>3</sup>, 0) and between (1, 10<sup>0</sup>, 0) and (0, 14<sup>2</sup>, 0).

TABLE I—Continued

Assignment <sup>a</sup>	$\nu$ (cm <sup>-1</sup> )	$\lambda_{\max}$ <sup>b</sup> (nm)	Assignment <sup>a</sup>	$\nu$ (cm <sup>-1</sup> )	$\lambda_{\max}$ (nm) <sup>b</sup>
	(1,11 <sup>1</sup> ,0)			(0,15 <sup>1</sup> ,0)*	
4 <sub>14</sub> <sup>+4</sup> <sub>04</sub>	17 396.28 <sup>c</sup>	e			
+ <sub>3</sub> <sub>22</sub>	17 412.15 <sup>d</sup>	331			
+ <sub>4</sub> <sub>22</sub>	17 326.56	330			
+ <sub>5</sub> <sub>24</sub> <sub>f</sub>	17 251.34	e			
+ <sub>4</sub> <sub>04</sub> <sub>f</sub>	16 043.97	-			
+ <sub>3</sub> <sub>22</sub> <sub>f</sub>	16 052.80	-			
+ <sub>4</sub> <sub>22</sub> <sub>f</sub>	15 967.36	-			
+ <sub>5</sub> <sub>24</sub> <sub>f</sub>	15 892.04	-			
5 <sub>14</sub> <sup>+4</sup> <sub>04</sub>	17 466.60 <sup>d</sup>	327	17 826.47 <sup>c</sup>	330	
+ <sub>4</sub> <sub>22</sub>	17 396.79	-	17 756.72	328	
+ <sub>5</sub> <sub>24</sub>	17 321.60	327	17 681.50	328	
+ <sub>6</sub> <sub>24</sub>	17 175.79	327	17 535.66	325	
+ <sub>5</sub> <sub>42</sub>	-	-	17 545.82 <sup>d</sup>	328	
+ <sub>6</sub> <sub>42</sub> <sub>f</sub>	17 070.42	-	17 430.39	e	
+ <sub>4</sub> <sub>22</sub> <sub>f</sub>	16 037.54	-	-	-	
+ <sub>5</sub> <sub>24</sub> <sub>f</sub>	15 962.21	-	16 322.176	-	
+ <sub>6</sub> <sub>24</sub> <sub>f</sub>	15 815.39 <sup>g</sup>	-	16 175.24	-	
+ (0,2,0) <sub>4</sub> <sub>22</sub>	-	-	15 076.25 <sup>d</sup>	302	
5 <sub>15</sub> <sup>+4</sup> <sub>23</sub>	17 412.22	331	17 726.56	328	
+ <sub>5</sub> <sub>05</sub>	17 390.25	327	17 704.58	328	
+ <sub>5</sub> <sub>23</sub>	17 298.06 <sup>g</sup>	325	17 612.22 <sup>d</sup>	328	
+ <sub>6</sub> <sub>25</sub>	17 219.44 <sup>g</sup>	327	17 533.62	330	
+ <sub>6</sub> <sub>43</sub> <sub>f</sub>	-	-	17 387.96 <sup>d</sup>	328	
+ <sub>4</sub> <sub>23</sub> <sub>f</sub>	16 052.89	-	-	-	
+ <sub>5</sub> <sub>05</sub> <sub>f</sub>	16 038.19	-	16 352.432	e	
+ <sub>5</sub> <sub>23</sub> <sub>f</sub>	15 938.25	-	-	-	
+ <sub>6</sub> <sub>25</sub> <sub>f</sub>	15 859.90	-	16 174.236	-	
+ <sub>6</sub> <sub>43</sub> <sub>f</sub>	-	-	16 011.17	-	
+ (0,2,0) <sub>4</sub> <sub>23</sub>	-	-	15 045.50 <sup>d</sup>	e	
+ (0,2,0) <sub>5</sub> <sub>05</sub>	-	-	15 037.71 <sup>d</sup>	e	
+ (1,0,0) <sub>4</sub> <sub>23</sub>	-	-	14 923.7 <sup>d</sup>	302.5	
	(1,11 <sup>1</sup> ,0)			(0,15 <sup>1</sup> ,0)*	
6 <sub>15</sub> <sup>+5</sup> <sub>05</sub>	17 481.71 <sup>c</sup>	328	17 858.37	328	
+ <sub>5</sub> <sub>23</sub>	17 389.41	-	17 766.02	328	
+ <sub>7</sub> <sub>07</sub>	17 283.49	325	-	-	
+ <sub>7</sub> <sub>25</sub> <sub>f</sub>	-	-	17 508.70	-	
+ <sub>5</sub> <sub>05</sub> <sub>f</sub>	16 129.65	-	16 506.23	-	
+ <sub>5</sub> <sub>23</sub> <sub>f</sub>	16 029.79	-	16 406.395	-	
+ <sub>6</sub> <sub>25</sub> <sub>f</sub>	15 951.42	-	-	-	
+ (0,2,0) <sub>5</sub> <sub>05</sub>	-	-	15 191.4 <sup>d</sup>	302	
+ (1,0,0) <sub>7</sub> <sub>07</sub>	-	-	14 863.1 <sup>d</sup>	302.5	
"Lone States"					
2 <sub>11</sub> <sup>-1</sup> <sub>01</sub>	17 432.82	331	3 <sub>31</sub> <sup>-2</sup> <sub>21</sub>	18 134.56	330
+ <sub>3</sub> <sub>03</sub>	17 346.72	327	+ <sub>3</sub> <sub>03</sub>	18 128.78	331
+ <sub>3</sub> <sub>21</sub> <sub>f</sub>	17 292.59 <sup>d</sup>	327	+ <sub>3</sub> <sub>21</sub>	18 074.56	e
+ <sub>1</sub> <sub>01</sub> <sub>f</sub>	16 080.43	-	+ <sub>4</sub> <sub>23</sub>	18 007.71	-
+ <sub>2</sub> <sub>21</sub> <sub>f</sub>	15 993.40	-	+ <sub>4</sub> <sub>41</sub> <sub>f</sub>	17 877.10	328
+ <sub>3</sub> <sub>21</sub> <sub>f</sub>	15 933.49	-	+ <sub>3</sub> <sub>03</sub>	16 776.23	-

TABLE II  
Term Values of Newly Observed CH<sub>2</sub>  $\tilde{b}$  State Levels (cm<sup>-1</sup>)

$J_{K_a K_c}$	experiment	(obs-cal)	$J_{K_a K_c}$	experiment	(obs-cal)
	(1,10 <sup>0</sup> ,0) <sup>a</sup>			(1,12 <sup>0</sup> ,0) <sup>b</sup>	
0 <sub>00</sub>	16 741.88	-0.03		18 192.32	0.10
1 <sub>01</sub>	16 756.96	0.02		18 207.66	0.01
2 <sub>02</sub>	16 787.08	0.03		18 238.27	-0.23
3 <sub>03</sub>	16 832.33	0.00		18 284.37	-0.40
4 <sub>04</sub>	16 892.87	-0.04		18 347.13	0.66
5 <sub>05</sub>	16 969.00	0.03		18 423.60	0.00
6 <sub>06</sub>				18 515.97	-0.18
	(1,11 <sup>1</sup> ,0) <sup>c</sup>			(0,15 <sup>1</sup> ,0)*	
1 <sub>10</sub>	17 414.48	-1.3		17 713.05	
1 <sub>11</sub>	17 414.57	-1.2		17 716.86	
2 <sub>11</sub>	17 446.77	-1.0		17 743.12	
2 <sub>12</sub>	17 447.21	-0.6		17 753.33	
3 <sub>12</sub>	17 495.80	0.0			
3 <sub>13</sub>	17 496.50	-0.3		17 837.185	
4 <sub>13</sub>	17 560.53	0.7		17 884.178 <sup>d</sup>	
4 <sub>14</sub>	17 565.32	6.5		17 867.910 <sup>d</sup>	
5 <sub>14</sub>	17 635.52	-4.3		17 995.44	
5 <sub>15</sub>	17 637.60	-2.2		17 951.93	
6 <sub>15</sub>	17 729.10	-6.7		18 105.72	
	New A band <sup>e</sup>				
2 <sub>20</sub>	16 852.01	-1.6	4 <sub>22</sub>	16 972.15	5.2
2 <sub>21</sub>	16 852.35	-1.2	4 <sub>23</sub>	16 960.45	-6.5
3 <sub>22</sub>	16 905.48	3.3	5 <sub>24</sub>	17 048.02	0.0
3 <sub>21</sub>	16 903.63	1.4			

<sup>a</sup>  $\nu_o=16\ 741.91$ ,  $B=7.5124$ ,  $D=-0.00188$ .

<sup>b</sup>  $\nu_o=18\ 192.22$ ,  $B=7.7125$ .

<sup>c</sup>  $\nu_o=17\ 399.8$ ,  $B=8.0$ .

<sup>d</sup> previously reported in Ref. 13.

<sup>e</sup>  $\nu_o=16\ 805.0$ ,  $B=8.1$ .

### $\Delta K_a = 3$ Transitions

A number of previously unassigned transitions are identified here as  $\Delta K_a = 3$  transitions to  $\tilde{b}$ -state levels, Fig. 3, cataloged by Petek *et al.* (13); the intensity of these branches, which are listed in Table III, and of the  $\Delta K_a = 3$  branches observed by Dai and coworkers is larger than expected. (17) This also may be due to strong  $\Delta l = 2$  couplings. Some new rotational-term values for previously identified vibronic levels have been assigned in the present work; they are listed in Table IV.

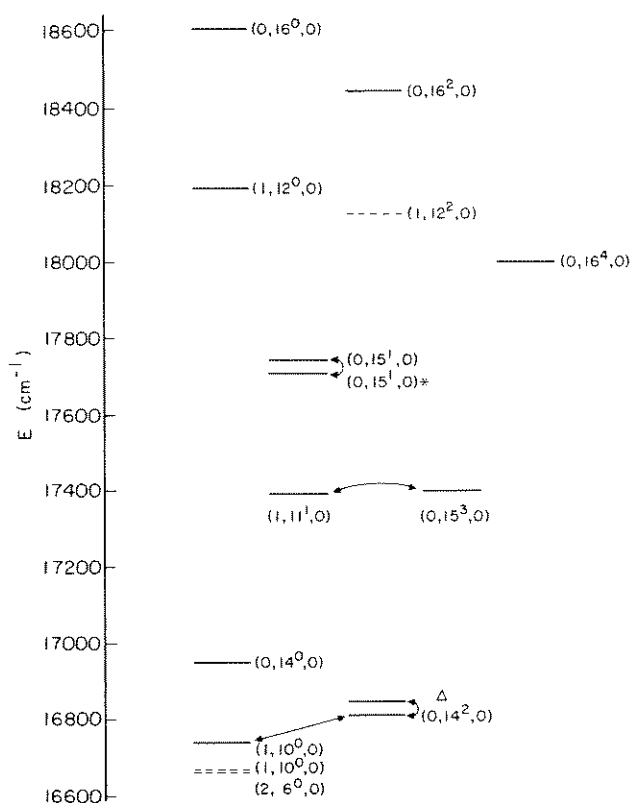


FIG. 2. Vibrational level structure of the  $\tilde{b}$  state. The dashed lines are predictions and the solid lines are experimental results. Arrows show expected strong interactions.

### Other Results

A number of heavily perturbed levels have been assigned in the present work. Several "lone transitions" seen in spectra measured under the coldest beam conditions are apparently due to local resonances between assigned  $\tilde{b}$  states and unidentified rovibronic states of very low intrinsic oscillator strength. One of these intensity-stealing states is apparently a doublet with the (1, 11<sup>1</sup>, 0)  $2_{11}$  state; see Fig. 1. Another isolated rotational state is identified as  $3_{31}$  by combination differences. The assigned transitions to these states are listed at the end of Table I. A mysterious transition appears in the cold spectra at 16 830.55  $\text{cm}^{-1}$ ; it is tentatively assigned as a doublet with the transition  $\Delta 2_{20} \leftarrow 1_{10}$ , but there are no other well-resolved transitions available at this time which can confirm this assignment. A careful PHOFEX (5-7) study of this weak transition might clear up this question. As with the doublets assigned by Petek *et al.*, in most cases no other rotational states of the "dark" vibronic bands have been identified. However, in this work several members of the vibrational band which caused the doublets identified by Petek for the  $\tilde{b}$  (0, 15<sup>1</sup>, 0)  $J = 4$  states have been identified.

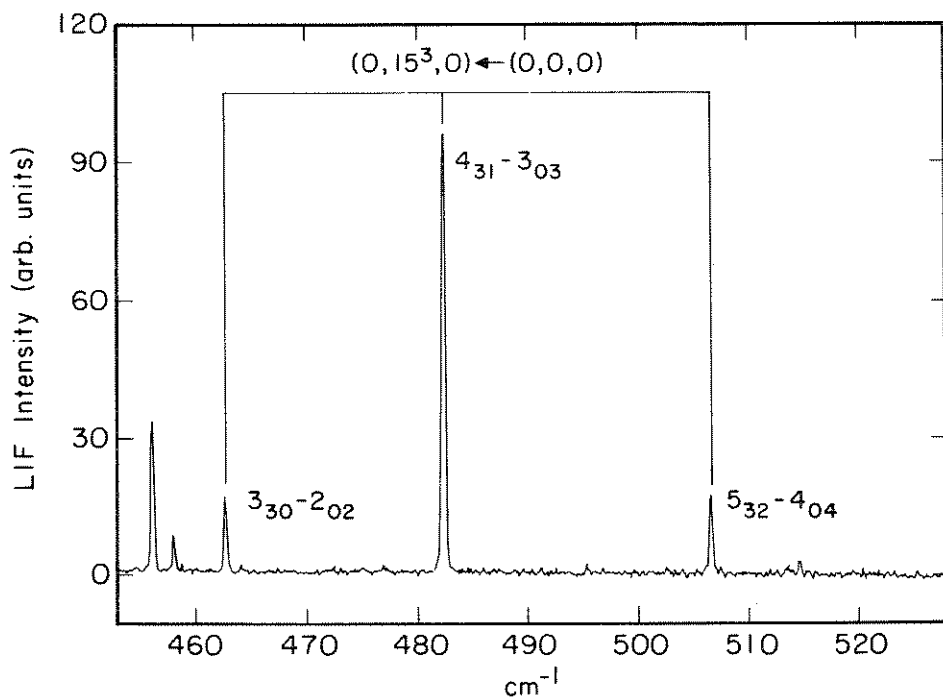


FIG. 3. The  $\Delta K_a = 3$  transitions of  $\tilde{b}(0, 15^3, 0) \leftarrow \tilde{a}(0, 0, 0)$  for photolysis at 330 nm. The lowest frequency peak is the  $\tilde{b}(1, 11^1, 0) 4_{13} \leftarrow \tilde{a}(0, 0, 0) 3_{03}$  seen in Fig. 1. Note: The abscissa scale gives Wavenumber minus  $17\,000\text{ cm}^{-1}$ .

Table II. The large number of transitions observed in the vicinity of  $\tilde{b}(0, 15^1, 0) \leftarrow \tilde{a}(0, 0, 0)$ , and the large perturbations observed suggest that a third vibronic band may be interacting with the two identified so far, though it has not been possible to conclusively identify this third band in the present study.

#### CONCLUSION

While previous work has shed much light on this challenging spectrum, it has often produced as many questions as answers. The origin of the great many lines observed by Petek *et al.* (3, 13) was particularly troublesome; by identifying the presence of many overlapped vibronic bands of comparable magnitude, and unexpectedly strong  $\Delta K_a = 3$  transitions, the present work has begun to answer that question. Even with the new assignments presented here, which represent important progress in dealing with this complex system, more than 90% of the observed transitions remain unassigned. However, the limited results reported here demonstrate the efficacy of this spectroscopic technique for identifying the upper state vibrational bands. This is difficult to do from room-temperature spectra because the high  $\tilde{b}$  vibrational state density and the large rotational constants of methylene cause the different vibrational bands to overlap, and the ubiquitous perturbations make it impossible to predict line positions

TABLE III

Observed  $\Delta K_a = 3$  Transitions to Previously Assigned  $\hat{b}$  States

(0, 16, 0) ← (0, 0, 0)	← (0, 1, 0)	(0, 14, 0) ← (0, 0, 0)
<sup>3</sup> <sub>03</sub> <sup>-3</sup> <sub>31</sub> <sup>a</sup>		<sup>3</sup> <sub>03</sub> <sup>-3</sup> <sub>31</sub> <sup>b</sup>
<sup>4</sup> <sub>04</sub> <sup>-4</sup> <sub>32</sub>	<sup>4</sup> <sub>04</sub> <sup>-4</sup> <sub>32</sub>	<sup>4</sup> <sub>04</sub> <sup>-4</sup> <sub>32</sub> <sup>c</sup>
<sup>5</sup> <sub>05</sub> <sup>-5</sup> <sub>33</sub>		<sup>5</sup> <sub>05</sub> <sup>-5</sup> <sub>33</sub> <sup>b</sup>
		<sup>6</sup> <sub>06</sub> <sup>-6</sup> <sub>34</sub> <sup>a, c</sup>
		<sup>2</sup> <sub>02</sub> <sup>d-3</sup> <sub>30</sub> <sup>b</sup>
	<sup>2</sup> <sub>02</sub> <sup>-3</sup> <sub>30</sub> <sup>a</sup>	<sup>2</sup> <sub>02</sub> <sup>-3</sup> <sub>30</sub> <sup>b, e</sup>
<sup>3</sup> <sub>03</sub> <sup>-4</sup> <sub>31</sub>	<sup>3</sup> <sub>03</sub> <sup>-4</sup> <sub>31</sub> <sup>a</sup>	<sup>3</sup> <sub>03</sub> <sup>-4</sup> <sub>31</sub> <sup>c</sup>
		<sup>3</sup> <sub>03</sub> <sup>-4</sup> <sub>31</sub> <sup>d</sup>
<sup>4</sup> <sub>04</sub> <sup>-5</sup> <sub>32</sub>	<sup>4</sup> <sub>04</sub> <sup>-5</sup> <sub>32</sub>	<sup>4</sup> <sub>04</sub> <sup>-5</sup> <sub>32</sub> <sup>a, c</sup>
		<sup>4</sup> <sub>04</sub> <sup>-3</sup> <sub>30</sub> <sup>c</sup>
<sup>5</sup> <sub>05</sub> <sup>-4</sup> <sub>31</sub>	<sup>5</sup> <sub>05</sub> <sup>-4</sup> <sub>31</sub>	
<sup>5</sup> <sub>05</sub> <sup>-4</sup> <sub>31</sub> <sup>d</sup>		
<sup>6</sup> <sub>06</sub> <sup>-5</sup> <sub>32</sub>	<sup>6</sup> <sub>06</sub> <sup>-5</sup> <sub>32</sub>	<sup>6</sup> <sub>06</sub> <sup>-5</sup> <sub>32</sub>
<sup>4</sup> <sub>40</sub> <sup>-4</sup> <sub>14</sub> <sup>c</sup>		<sup>4</sup> <sub>40</sub> <sup>-4</sup> <sub>14</sub> <sup>c</sup>
<sup>4</sup> <sub>41</sub> <sup>-4</sup> <sub>13</sub> <sup>c</sup>		<sup>4</sup> <sub>41</sub> <sup>-4</sup> <sub>13</sub> <sup>c</sup>
<sup>5</sup> <sub>42</sub> <sup>-5</sup> <sub>14</sub> <sup>c</sup>	<sup>5</sup> <sub>42</sub> <sup>-5</sup> <sub>14</sub>	<sup>5</sup> <sub>42</sub> <sup>-5</sup> <sub>14</sub> <sup>c</sup>
<sup>5</sup> <sub>41</sub> <sup>-5</sup> <sub>15</sub> <sup>c</sup>		<sup>5</sup> <sub>41</sub> <sup>-5</sup> <sub>15</sub> <sup>c</sup>
	<sup>6</sup> <sub>42</sub> <sup>-6</sup> <sub>16</sub>	<sup>6</sup> <sub>43</sub> <sup>-6</sup> <sub>15</sub> <sup>c</sup>
<sup>4</sup> <sub>40</sub> <sup>-3</sup> <sub>12</sub> <sup>c</sup>		
<sup>4</sup> <sub>41</sub> <sup>-3</sup> <sub>13</sub> <sup>c</sup>		
<sup>5</sup> <sub>41</sub> <sup>-4</sup> <sub>13</sub> <sup>c</sup>	<sup>5</sup> <sub>41</sub> <sup>-4</sup> <sub>13</sub> <sup>a</sup>	<sup>5</sup> <sub>41</sub> <sup>-4</sup> <sub>13</sub>
<sup>5</sup> <sub>42</sub> <sup>-4</sup> <sub>14</sub> <sup>c</sup>	<sup>5</sup> <sub>42</sub> <sup>-4</sup> <sub>14</sub> <sup>a</sup>	<sup>5</sup> <sub>42</sub> <sup>-4</sup> <sub>14</sub>
<sup>6</sup> <sub>42</sub> <sup>-5</sup> <sub>14</sub> <sup>c</sup>	<sup>6</sup> <sub>42</sub> <sup>-5</sup> <sub>14</sub>	<sup>6</sup> <sub>42</sub> <sup>-5</sup> <sub>14</sub>
(0, 15 <sup>3</sup> , 0) ← (0, 0, 0)	← (0, 1, 0)	(0, 13 <sup>3</sup> , 0) ← (0, 0, 0)
<sup>3</sup> <sub>31</sub> <sup>-3</sup> <sub>03</sub> <sup>c</sup>	<sup>3</sup> <sub>31</sub> <sup>-3</sup> <sub>03</sub>	
<sup>4</sup> <sub>32</sub> <sup>-4</sup> <sub>04</sub> <sup>e</sup>	<sup>4</sup> <sub>32</sub> <sup>-4</sup> <sub>04</sub>	<sup>4</sup> <sub>32</sub> <sup>-4</sup> <sub>04</sub>
<sup>5</sup> <sub>33</sub> <sup>-5</sup> <sub>05</sub> <sup>c</sup>	<sup>5</sup> <sub>33</sub> <sup>-5</sup> <sub>05</sub>	
<sup>3</sup> <sub>30</sub> <sup>-2</sup> <sub>02</sub> <sup>c</sup>		
<sup>4</sup> <sub>31</sub> <sup>-3</sup> <sub>03</sub> <sup>c</sup>		<sup>4</sup> <sub>31</sub> <sup>-3</sup> <sub>03</sub> <sup>f</sup>
<sup>5</sup> <sub>32</sub> <sup>-4</sup> <sub>04</sub> <sup>c</sup>		<sup>5</sup> <sub>32</sub> <sup>-4</sup> <sub>04</sub> <sup>f</sup>
<sup>6</sup> <sub>33</sub> <sup>-5</sup> <sub>05</sub>	<sup>6</sup> <sub>33</sub> <sup>-5</sup> <sub>05</sub>	<sup>6</sup> <sub>33</sub> <sup>-5</sup> <sub>05</sub>
<sup>4</sup> <sub>31</sub> <sup>-5</sup> <sub>05</sub>		

a Overlapped in Ref. 19.

b Not observed in Ref. 19, but observed in beam spectra.

c Observed in beam spectra as well as in Ref. 19.

d Weak doublet reported in Ref. 13.

e Overlapped in beam spectra.

f Reported in Ref. 13.

TABLE IV  
Newly Assigned Rotational Transitions in Known Vibronic Bands

Assignment <sup>a</sup>	$\nu$ (cm <sup>-1</sup> )	$\lambda_{\max}$ (nm) <sup>b</sup>	Assignment <sup>a</sup>	$\nu$ (cm <sup>-1</sup> )	$\lambda_{\max}$ (nm) <sup>b</sup>
$\bar{b}(0,15,0)6_{34}$	17 784.91 <sup>h</sup>		$\bar{a}(0,0,0)6_{06}$	339.62 <sup>h</sup>	
+5 <sub>24</sub>	17 470.95	325	- $\bar{b}(0,15,0)5_{14}$	17 655.84	325
-6 <sub>24</sub>	17 325.20	327	- $\bar{b}(0,15,0)5_{14}$	17 633.91 <sup>d</sup>	328
-6 <sub>06</sub>	17 445.30	325	- $\bar{b}(1,11,0)5_{14}$	17 295.9 <sup>d</sup>	327
+5 <sub>42</sub>	17 335.30	e	- $\bar{b}(0,13,0)7_{16}$	16 181.93	327
+5 <sub>24</sub> <sup>f</sup>	16 111.64	-	- $\bar{a}(0,0,1)5_{05}$ <sup>i</sup>	2 768.60	-
-6 <sub>24</sub> <sup>f</sup>	15 964.71	-	- $\bar{a}(1,0,0)5_{15}$ <sup>i</sup>	2 709.72	-
$\bar{b}(0,13,0)6_{16}$	16 399.85 <sup>h</sup>		$\bar{a}(0,1,0)6_{06}$	1688.96 <sup>h</sup>	
-5 <sub>24</sub>	16 085.906	-	- $\bar{b}(0,15,0)5_{14}$	16 284.458	-
+6 <sub>06</sub>	16 060.227	-	- $\bar{b}(0,15,0)5_{32}$	15 986.50	-
+6 <sub>24</sub>	15 940.12	-	- $\bar{b}(0,15,0)7_{16}$	16 511.20	j
$\bar{b}(0,15,0)7_{16}$	18 200.16 <sup>h</sup>				
-6 <sub>06</sub>	17 860.54	328			

<sup>a-g</sup> See Table I notes.

<sup>h</sup> Term value.

<sup>i</sup> From Ref. 14.

<sup>j</sup> This transition used for PHOFEX, see Ref. 7. Threshold = 1689.1 ± 0.4 cm<sup>-1</sup> above the  $\bar{a}$  origin.

accurately. Cooling the methylene, as in the present work, permits unambiguous identification of the vibronic band origins and allows considerable progress to be made on this long-standing spectroscopic problem.

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