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PROBABILITIES FOR RADIATION AND PREDISSOCIATION

II. THE EXCITED STATES OF CH, CD, AND CH^+, AND SOME ASTROPHYSICAL IMPLICATIONS*

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ABSTRACT

Decay rates determined from data on absolute phase shift versus frequency are presented for the $A\ ^2\Delta$, $B\ ^2\Sigma^-$, and $C\ ^2\Sigma^+$ states of CH, as well as for the $B\ ^1\Delta$ state of CH^+. The spectra were produced by electron-beam excitation of low-pressure CH_4 and CD_4 gases. Our results for the radiative lifetimes of the A and B states of CH support the recent findings of Fink and Welge. For the $C\ ^2\Sigma^+$–$X\ ^2\Pi$ transition of CH and CD, the phase data are shown to represent quantitative measures of predissociation probabilities. Higher-resolution spectrograms are used to specify a simple model for the observed phase shifts in which the F_1 spin components predissociate about 3 times faster than the F_2 spin components. Since, as shown by our new data, nearly every photon absorbed in a line terminating in $C\ ^2\Sigma^+$ results in the photodestruction of CH, the formation rates of CH in interstellar space must be significantly increased to account for the observed intensities. It is also pointed out that the lack of agreement between calculations of the solar G-band intensity and equivalent-width measurements is not due to uncertainties in the molecular constants.

I. INTRODUCTION

In a preliminary report (Hesser and Lutz 1968*a*) we presented quantitative evidence for a nonradiative decay mode in the $C\ ^2\Sigma^+$ states of CH and CD as determined from measurements of the absolute phase shifts of the $C\ ^2\Sigma^+$–$X\ ^2\Pi$ emissions, and we indicated how the phase-shift measurements could be interpreted in terms of predissociation probabilities. Our results substantiated the conclusions concerning the existence of this perturbation affecting the C state of CH that were reached by Herzberg (1967) from qualitative spectral-intensity information. In this paper we present the detailed measurements of the absolute phase shifts of the C–X 0–0 band, and we report new data on the variation of the absolute phase shifts with wavelength within the P- and R-branches of the C–X transition. In addition, because of the discrepancy between the measurements of Bennett and Dalby (1960) and of Fink and Welge (1967) on the lifetime of the CH $B\ ^2\Sigma^-$ state, we have remeasured the lifetimes of the $A\ ^2\Delta$ and $B\ ^2\Sigma^-$ states. We also report phase-shift data for an emission system in the electron-beam-excited spectra of CH_4 and CD_4 gases, which only recently has been identified by Carre (1969) to be the CH^+ $B\ ^1\Delta$–$A\ ^1\Pi$ transition. Some immediate implications of these results for astrophysical problems in the interstellar medium and in solar and stellar atmospheres are discussed.

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II. EXPERIMENTAL PROCEDURE

The phase-shift apparatus and its typical operating conditions are adequately described elsewhere by Lawrence (1965) and others (Lawrence and Savage 1966; Savage and Lawrence 1966; Hesser 1968). The emission spectra were produced by the impact of a radiofrequency-modulated beam of 100- or 200-V electrons upon CH_4 and CD_4 gases of high chemical and isotopic purity.[1] We recorded the spectra with a 0.5-m Seya-Namioka vacuum monochromator and a thermoelectrically cooled EMI 6256A photomultiplier. Standard filters were used to prevent second-order interference. Typical bandwidths were between 5 and 8 Å. The Ne II 1908–1935 Å multiplet was our absolute phase reference (Savage and Lawrence 1966), although for some of the measurements the C I 1657 Å transition was used as a secondary phase reference after careful calibration against the Ne II multiplet. The phase measurements exhibited no dependence on electron energy or on gas pressure over the ranges of 90–200 V and about 1–11 μ Hg, respectively, in the excitation region. For a single exponential decay, the absolute phase shift ϕ is related to the lifetime τ of the excited state by

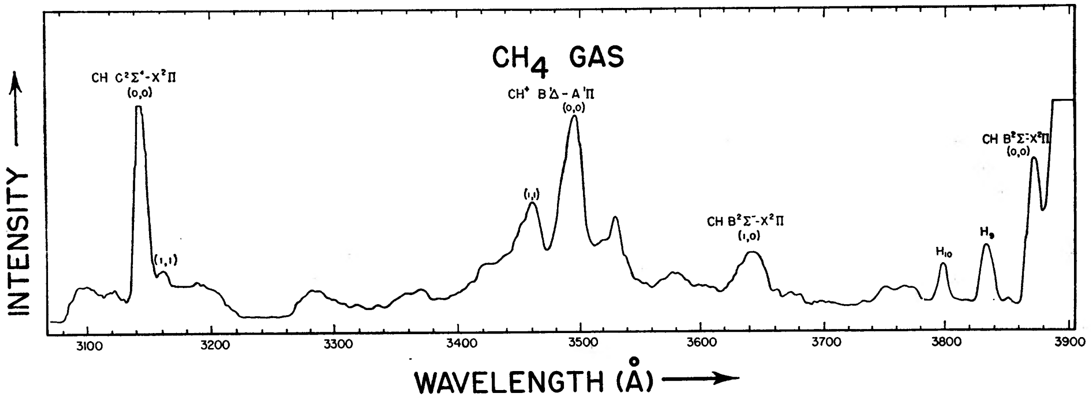

FIG. 1.—Emission spectrum of CH_4 gas produced by low-energy electron excitation in low-pressure methane. The transitions $C\ ^2\Sigma^+-X\ ^2\Pi$ and $B\ ^2\Sigma^--X\ ^2\Pi$ in CH are shown, as well as the CH^+ $B\ ^1\Delta-A\ ^1\Pi$ system centered at ~3500 Å. This spectrum was made by using 100-V electrons with about 4 μ Hg of CH_4 in the excitation region and was recorded at a modulation frequency of 0.54 Mc/s. Filters were used to eliminate second-order interference at wavelengths greater than 3080 Å.

$$\tau = \omega^{-1} \tan \phi , \tag{1}$$

where $\omega = 2\pi f$, and f is the modulation frequency. The intensity of the recorded emission is also a function of the modulation frequency and the radiative lifetime, i.e.,

$$I(\omega,\tau) \propto (1 + \omega^2\tau^2)^{-1} . \tag{2}$$

To obtain the C–X emissions of CH and CD at high resolution, we photographed the spectra of simple electrodeless discharges through high-purity CH_4 and CD_4, respectively, mixed with helium. The spectrograms were taken in the second order of a 10.6-m concave-grating spectrograph which was fitted with a grating of 1200 lines mm^{-1} blazed at 6000 Å.

III. RESULTS

a) Spectra and Radiative Lifetime Measurements

The emission spectrum of CH_4 gas from about 3100 to 4400 Å, as observed with the 0.5-m monochromator, is presented in Figures 1 and 2. Figure 1, which was recorded

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[1] The mass spectroscopic analysis of the 99.95-percent-pure CH_4 provided by the Matheson Company was: $CO_2 < 10$ ppm, $O_2 = 13$ ppm, $N_2 = 45$ ppm, $C_2H_6 = 12$ ppm, and $C_3H_8 < 5$ ppm. The isotopic purity of the CD_4 provided by Merck, Sharp, and Dohme was 99.13 percent, while chemical impurities due to air were less than 0.1 percent. Further purification of either gas was not attempted.

at a modulation frequency of 0.54 Mc/s with about 4 μ Hg of CH_4 in the excitation region, shows two CH transitions, C–X and B–X, and the CH^+ transition, $B\ ^1\Delta$–$A\ ^1\Pi$, near 3500 Å. Figure 2, which was also recorded by using a modulation frequency of 0.54 Mc/s, shows the detailed spectrum of the A–X and B–X emissions in CH under slightly higher resolution. The pressure of CH_4 for Figure 2 was reduced to about 2 μ Hg.

Measurements of absolute phase shifts made at two modulation frequencies, 0.54 and 0.96 Mc/s, on the A–X and B–X transitions provide a useful comparison with the results of previous workers, as indicated in Table 1. The large uncertainties ascribed to our results in Table 1 reflect the fact that the measurements were made near the long-lifetime limit of our apparatus. Because of the long lifetimes encountered, it was not possible to extend the measurements to frequencies greater than 0.96 Mc/s (cf. eq. [2]).

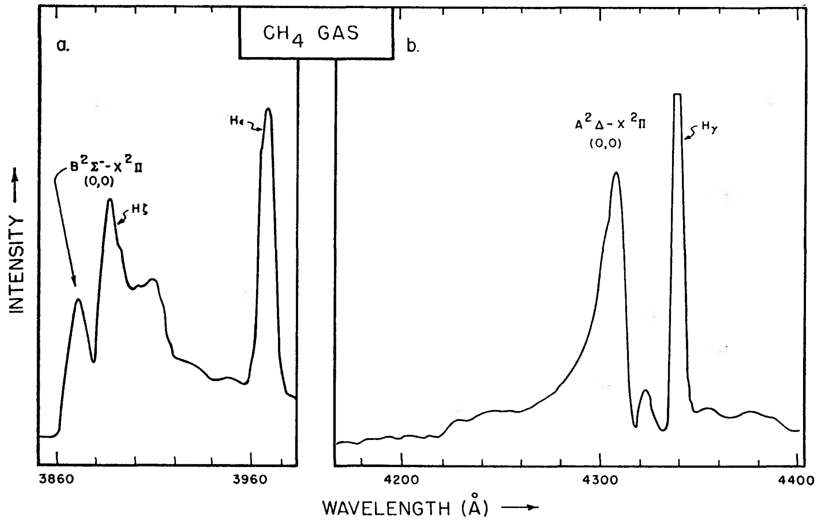

Fig. 2.—Detailed spectra of the $B\ ^2\Sigma^-$–$X\ ^2\Pi$ and $A\ ^2\Delta$–$X\ ^2\Pi$ transitions in CH. These spectra were recorded with the pressure in the excitation region reduced to about 2 μ Hg of CH_4 and with the exit slit narrowed.

TABLE 1

RADIATIVE LIFETIMES OF THE A AND B STATES OF CH

Lifetime (nsec)		
A State	*B* State	Reference
470±75	345± 50	This work
560±60	1000±400	Bennett and Dalby (1960)
300±30	. . .	Jeunehomme and Duncan (1964)
540±40	400± 60	Fink and Welge (1967)
. . .	355± 95	Linevsky (1967)*
200	95	Hurley (1959)†
775	415	Huo (1968)‡

Note.—The first five references are experimental; the last two are theoretical.

* Linevsky's $f(A$–$X)/f(B$–$X)$ relative *absorption* measurement has been placed on an absolute scale by using Fink and Welge's (1967) lifetime for the A state.

† Hurley's "intra-atomic, correlation-correction" results for the absorption f-values were adopted for use in Table 1; no error estimates were given for these early and highly approximate estimates of the CH f-values.

‡ Huo used the "active-electron, dipole-length" approximation in her calculations of the absorption oscillator strengths, and they are stated by her to be of order-of-magnitude accuracy only, based upon comparisons with the results of various approximate forms of the matrix elements of the dipole transition moment.

However, the close agreement between the lifetimes derived from the phase data at the two usable frequencies (agreement to within 7 percent for the A state and to within 2 percent for the B state) indicates that the decays are very probably exponential. Furthermore, no detectable difference was found in the phase shifts measured at 0.54 Mc/s between the A–X transitions of CH and those of CD. The B–X emission of CH was measured at two wavelengths, 3871 and 3903 Å, to insure that the phase data were not contaminated by the *possible* impurity emission, N_2^+ $B\ ^2\Sigma_u^+$–$X\ ^2\Sigma_g^+$ 0–0. No trace of this impurity or of its effects was found. Because of a slight amount of N_2 impurity in the CD_4, it was not possible to determine the absolute phase shifts of the B–X emission of CD.[2] The agreement between our results for the A- and B-state lifetimes and those of Fink and Welge (1967) substantiates the conclusion that some problem existed in Bennett and Dalby's (1960) original, preliminary measurement of the B-state lifetime, as well as in Jeunehomme and Duncan's (1964) measurement of the A-state lifetime. Unfortunately, theoretical calculations of the oscillator strengths of CH using modern SCF approximations are able to reproduce only the order of magnitude of the observed values (Huo 1968).

The emission features near 3500 Å in electron-excited CH_4 ascribed in Figure 1 to the $B\ ^1\Delta$–$A\ ^1\Pi$ transition of CH^+ are also observed with comparable intensities in CD_4 gas. Carre (1969) has recently identified this system along with the $b\ ^3\Sigma^-$–$a\ ^3\Pi$ transition of CH^+ in the spectra of low-pressure hydrocarbons bombarded by high-energy protons (30–150 keV). Both systems have also been seen under high resolution in a hollow-cathode discharge through methane (Douglas and Lutz 1969). Measurements of absolute phase shifts made at 0.54, 0.96, and 1.71 Mc/s on the peaks of the 0–0 and 1–1 bands of $B\ ^1\Delta$–$A\ ^1\Pi$ at about 3500 and 3470 Å, respectively, yielded cascade-free lifetimes of 210 ± 25 nsec and 192 ± 25 nsec for the $v' = 0$ and $v' = 1$ levels of $B\ ^1\Delta$ of CH^+. The triplet emissions, which are extremely weak in the discharge spectra, do not overlap the 1–1 band. Consequently, the agreement of the lifetimes of the $v' = 0$ and $v' = 1$ levels indicate that the phase-shift measurements do not appear to be affected by the triplet system.

b) Experimental Studies of the C–X Emission

i) *The Q-Branch of the* 0–0 *Band*

Data on absolute phase shifts have been obtained for the Q-branch of the CH and CD C–X 0–0 bands at 3144 and 3139 Å, respectively. This band, as it appears in our source, is shown in Figure 1 and, in much greater detail, in Figure 5, below. The measured absolute phase shifts are listed in Tables 2 and 3 and plotted in Figure 3 for both the CH and CD transitions.

As previously pointed out, the data on absolute phase shifts for the C–X 0–0 bands cannot be represented by a single exponential decay (Hesser and Lutz 1968*a*). In principle the curves could be interpreted in terms of unique C-state lifetimes combined with radiative cascading from longer-lived, higher-lying states. However, despite careful searches, no higher-lying states terminating in $C\ ^2\Sigma^+$ have ever been observed. Other arguments, to be discussed in § IV*a*, also lead us to believe that our observations are the result of the blending within our spectral bandpass of many rotational lines representing a wide range of lifetimes.

In an effort to analyze our phase data quantitatively, we have employed an analytical model with the simplifying assumption of only two distinct lifetimes. In this model, the total phase shift Φ is given by

$$\Phi = \tan^{-1}\left[\frac{(I_1/I_2)\sin\phi_1 + \sin\phi_2}{(I_1/I_2)\cos\phi_1 + \cos\phi_2}\right], \tag{3}$$

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[2] The impurity emission, the N_2^+ B–X 0–0 band, was slightly less intense than the weak CD B–X emission; careful tests using only pure N_2 gas in the electron beam indicated that *no* other emission measurements made by using CD_4 gas were affected by N_2 or N_2^+ emisssion.

TABLE 2

OBSERVED AND CALCULATED ABSOLUTE PHASE SHIFTS FOR THE CH $C\,^2\Sigma^+$–$X\,^2\Pi$ TRANSITION

λ (Å)	CALCULATED			ABSOLUTE PHASE SHIFTS, ϕ (millicycles)*; MODULATION FREQUENCY, f (Mc/s)								N'†	COMMENTS†
	τ_1 (nsec)	τ_2 (nsec)	I_2^0/I_1^0	0.54	0.96	1.71	3.04	5.40	9.60	17.1	30.4	($v'=0$)	
3095±8													
Observed......	...	...	...	43±1	...	56±1	73±2	92±1	128±1	...	...	16–27	0–0 $R(J)$
Calculated.....	18	160	1.2	43	58	61	68	93	134	175	205	...	
3110±8													
Observed......	...	...	...	46±1	...	49±1	52±2	65±2	99±2	...	...	10–16	0–0 $R(J)$
Calculated.....	12	160	1.2	41	54	53	52	68	102	146	185	...	
3144±5													
Observed......	...	...	...	11±4	13±2	28±2	44±4	68±3	94±5	117±2	145±3	0–27	0–0 $Q(J)$
Calculated.....	5	18	3.0	8	14	25	43	69	98	121	145	...	
3158±5													
Observed......	...	...	...	21±1	...	22±1	23±1	36±1	55±1	...	...	2–6	0–0 $P(J)$
Calculated.....	6	160	0.4	21	25	23	24	34	56	91	136	...	1–1 $Q(J)$
3185±8													
Observed......	...	...	...	29±1	...	39±1	42±1	59±1	88±1	...	...	11–17	0–0 $P(J)$
Calculated.....	10	160	0.8	33	42	40	41	56	88	131	173	...	1–1 $P(J)$
3206±8													
Observed......	...	...	...	35±1	...	57±1	69±1	91±1	115±2	...	...	19–25	0–0 $P(J)$
Calculated.....	18	140	1.0	37	52	60	68	94	134	175	205	...	1–1 $P(J)$

* The error limits represent the standard deviations for the set of phase-difference measurements at each frequency.

† Assignments listed under N' and *Comments* are approximate and are meant to serve only as a guide.

TABLE 3

OBSERVED AND CALCULATED ABSOLUTE PHASE SHIFTS FOR THE CD $C\,^2\Sigma^+ – X\,^2\Pi$ TRANSITION

	CALCULATED			ABSOLUTE PHASE SHIFTS, ϕ (millicycles)*; MODULATION FREQUENCY, f (Mc/s)									
λ (Å)	τ_1 (nsec)	τ_2 (nsec)	I_2^0/I_1^0	0.54	0.96	1.71	3.04	5.40	9.60	17.1	30.4	N'† ($v'=0$)	COMMENTS†
3100±8													
Observed	...	...	...	43±3	...	99±3	129±3	156±3	...	...	...	26–39	0–0 $R(J)$
Calculated	36	110	2	43	69	97	125	157	190	214	229	...	
3120±8													
Observed	...	...	...	31±1	...	67±1	94±2	125±1	...	...	...	11–21	0–0 $R(J)$
Calculated	26	100	1	30	48	68	90	124	164	198	220	...	1–1 $R(J)$
3139±5													
Observed	...	...	...	24±3	42±2	68±3	98±2	126±1	155±2	...	...	1–20	0–0 $Q(J)$
Calculated	20	55	2.5	23	40	65	95	125	158	191	215	...	1–1 $R(J)$
3150±5													
Observed	...	...	...	22±4	...	49±2	76±5	100±3	140±1	...	...	0–6	0–0 $P(J)$
Calculated	20	100	0.5	24	37	52	70	101	142	182	210	...	1–1 $Q(J)$
3165±6													
Observed	...	...	...	21±4	...	48±4	76±3	101±2	...	...	...	10–17	0–0 $P(J)$
Calculated	20	100	0.5	24	37	52	70	101	142	182	210	...	1–1 $P(J)$
3180±8													
Observed	...	...	...	39±1	...	79±2	99±3	119±3	...	...	...	19–29	0–0 $P(J)$
Calculated	22	100	2	38	60	83	100	122	157	191	215	...	1–1 $P(J)$

* The error limits represent the standard deviations for the set of phase difference measurements at each frequency.

† Assignments listed under N' and *Comments* are approximate and are meant to serve only as a guide.

where ϕ_1 and ϕ_2 are the phase shifts of the two states with lifetimes τ_1 and τ_2, respectively. The modulated intensity ratio I_1/I_2 is

$$\frac{I_1}{I_2} = \left(\frac{I_1^0}{I_2^0}\right)\left(\frac{1 + \omega^2\tau_2^2}{1 + \omega^2\tau_1^2}\right). \tag{4}$$

Here I_1^0/I_2^0 is the unmodulated intensity ratio of two spectral lines. This method of decomposing the observed phase shift into its component phase shifts has been used previously for two overlapping atomic lines (Hesser and Lutz 1968*b*). In the present case, however, where there are more than two overlapping lines within our bandpass, I_1^0/I_2^0 is not the simple intensity ratio of two lines, but rather represents a weighted average of two groups of lines with average lifetimes τ_1 and τ_2. The finally adopted values of the fitting parameters which give the best representation of the observed data under these simplifying conditions are given in Tables 2 and 3 for comparison with the observed absolute phase shifts and will be discussed in greater detail in § IV.

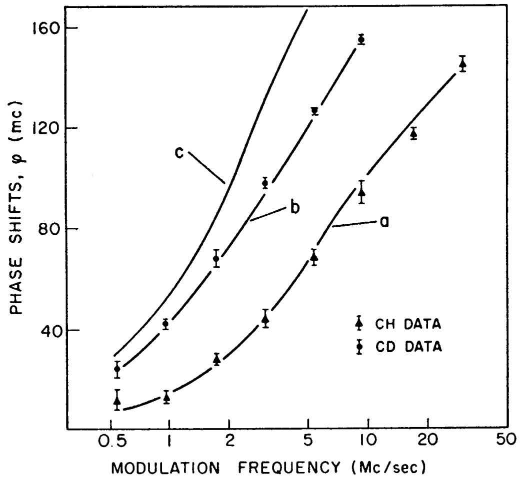

FIG. 3.—Data on phase shift versus frequency for the decay of $C^2\Sigma^+$, $v' = 0$, in CH and CD. Curve *a* is the fit obtained from the theoretical model for two unresolved emissions in which the parameters are $\tau_1 = 5$ nsec and $\tau_2 = 18$ nsec, with an unmodulated intensity ratio of $I_2^0/I_1^0 = 3.0$. Curve *b*, for CD, assumes $\tau_1 = 20$ nsec, $\tau_2 = 55$ nsec, and $I_2^0/I_1^0 = 2.5$. From comparison with the curve plotted for an exponential decay of 55 nsec (curve *c*) we can see that the mean lives of $C\ ^2\Sigma^+$ in both CH and CD are short and that there is a significant change in mean life between CH and CD.

Additional information now available from high-resolution spectrograms of the *Q*-branch of the *C*–*X* 0–0 band in CH and CD lends credence to the simple model originally adopted to explain the observed phase-shift data (Hesser and Lutz 1968*a*). For instance, our high-resolution spectrogram of a simple discharge through CH_4, selected portions of which are shown in Figure 4, shows that for $4 < N' < 12$ the lines originating from the F_1 levels are about 2–3 times weaker than those from the F_2 levels. This is consistent with our lifetime data. For $11 < N' < 17$ the doublets are not resolved and hence a comparison cannot be made. However, for $N' = 17$, the doublet splitting is just resolved and the line from F_1 is 3 times weaker than that from F_2. At higher values of N', where the spin-doublet separation would be readily resolved, the F_2 components can be seen as moderately strong lines but the F_1 components are completely absent from the spectrum. For $N' \leq 4$, the intensity difference, though clearly observable, becomes smaller as N' decreases. The difference in intensity observed is unlikely to be the result of an anomalous population of one spin component, since the spin splitting (Gerö 1941) of $C\ ^2\Sigma^+$ is quite small, typically ~ 0.5 cm^{-1} (γ, the splitting constant, is about 0.048 cm^{-1}).

In our spectrograms of the *C*–*X* emission in CD, as in CH, for $N' \leq 4$, there is little

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intensity difference between spin components. For $4 < N' < 11$ the components are unresolved. For $N' \geq 11$, where we should be able to resolve the doublets, the intensity is so weak that we cannot make any quantitative statements about the intensity distribution, although it appears that the F_1 components are missing.

ii) *Variation of Absolute Intensities within the C–X Bands*

An important question to be investigated is whether there exist variations of the absolute intensities with wavelength within the P- and R-branches of the $C \rightarrow X$ systems of CH and CD. Evidence of such variations would give additional quantitative information on the variation of predissociation probability with rotational (or vibrational) quantum number. Two experiments bearing upon this question can be made with the present experimental apparatus. The first makes use of the implications of equation (2) and involves simply recording the emission spectra by using narrow bandpasses and widely spaced modulation frequencies. In this way, as ω increases, there will be a decrease in the contribution of longer-lived upper states to the intensity of the resultant emission. The results of this experiment are illustrated in Figure 5, where data are given for CH taken at 0.54 and 17 Mc/s and for CD taken at 0.54 and 5.4 Mc/s.

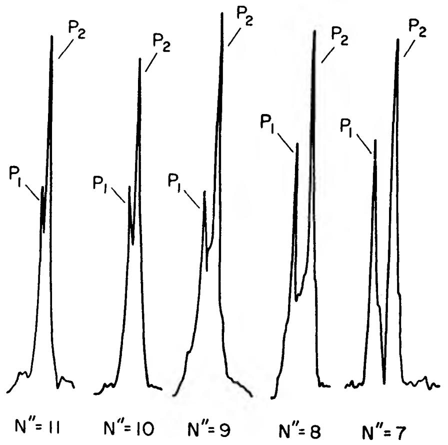

FIG. 4.—Doublet emissions in the P-branch of $C\ ^2\Sigma^+–X\ ^2\Pi$ 0–0 in CH as traced by a densitometer from selected regions of a spectrogram obtained from a simple discharge through CH_4 using the 10.6-m grating spectrograph. Note that the lines originating from F_1 levels are considerably weaker that the lines from F_2 levels. This phenomenon is attributed to predissociation in the C state, as are the results of Fig. 3.

The spectra for Figure 5 were obtained by slowly scanning the region with a 5Å bandpass three times at each modulation frequency. The resultant spectra were smoothed, averaged, and then normalized to the peak intensity at the Q-branch of the 0–0 band. Data taken at 30 Mc/s for CH and 9.6 Mc/s for CD, although much noisier (cf. eq. [2]) than those obtained at the highest frequencies used in Figure 5, strongly confirm the trends evident in the figure. We notice that the 1–1 Q-branch appears to exhibit relatively shorter characteristic decay times than the 0–0 Q-branch and that the isotopic molecule closely mimics the behavior of the normal molecule in its apparent variations in $I(\omega, \lambda)$.

The second experiment, a more difficult one to perform well, because of the low intensities encountered, is the direct measurement of the absolute phase shifts of the weak emissions on either side of the Q-branch of the 0–0 band. We have performed such measurements at five wavelengths bracketing the 0–0 Q-branch by using the C I λ1657 line as the phase reference for all the measurements. A large number of phase differences were determined at each frequency to insure suitable averaging over the weak signals encountered. The detailed measurements confirm the qualitative behavior of $I(\omega,\lambda)$ found in Figure 5, as may be seen in Tables 2 and 3, and present some interesting new questions as well. Using our simple two-component model, we find that the phase data which are expected to contain a significant intensity contribution from the 1–1 band (see, e.g., the *Atlas* of Bass and Broida 1961) yield approximately the same τ_1 values as the data on the 0–0 Q-branch, but that the percentage of longer-lived emissions is very significantly reduced. This reduction suggests that a dependence on vibrational quantum number exists for the predissociation. However, although the 0–0 Q-branch results are insensitive to moderate variations of the model parameters, the fits of the two-component model given in the tables are not unique for the P- and R-branch data. Nevertheless, from the numerous model fits to the P- and R-branch data that have been attempted, it does seem that the strength of the predissociation within the 0–0 band does not change rapidly with J. This conclusion is supported by our high-resolution spectrogram.

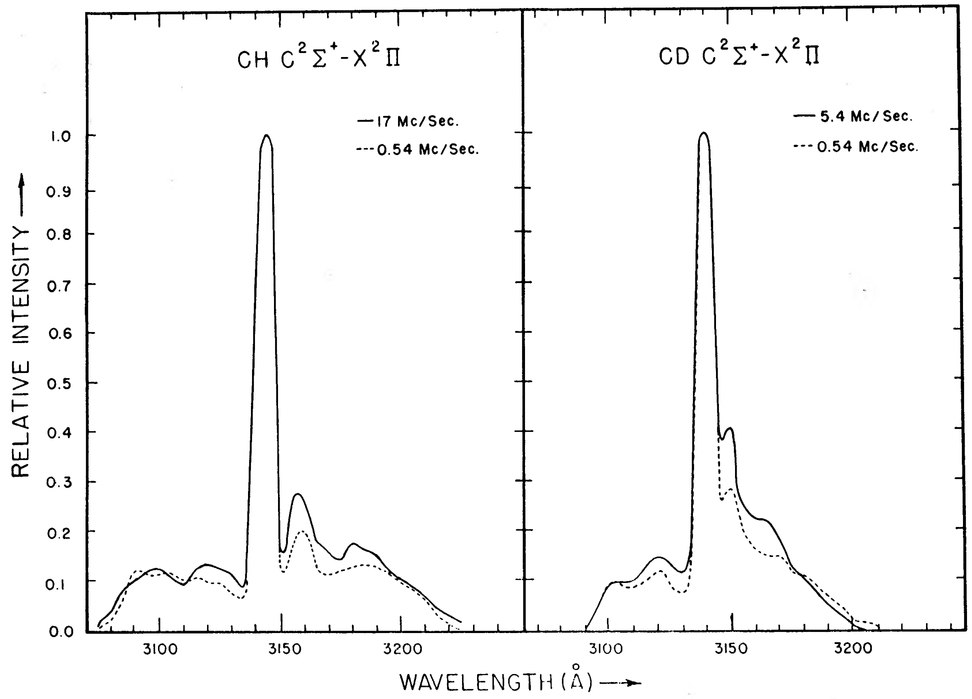

FIG. 5.—Emission intensities of the $C\ {}^2\Sigma^+$–$X\ {}^2\Pi$ transitions in CH and CD as a function of modulation frequency and wavelength. Data at each frequency are normalized to the peak intensity of the Q-branch 0–0 band, as described in the text.

Detailed interpretation of these $\Phi(\omega,\lambda)$ data for the P- and R-branches in terms of a simple two-component model, as has been done in Tables 2 and 3, is almost impossible for two reasons. First, we are dealing with a perturbation whose behavior with energy is poorly known, and hence it is difficult to know how, in detail, to unfold the effects of the overlapping transitions within our relatively wide spectral bandpass. Second, there are reasons to suspect that the entire C–X band system may be overlapped by a very weak continuum of the H_2 molecule (Coolidge 1944), ${}^3\Sigma_g{}^+ \rightarrow {}^3\Sigma_u{}^+$. Although this continuum has not been observed photoelectrically anywhere within the 1050–3300 Å interval that our spectra made with the modulated electron-beam source cover, it has been observed in spectrograms of comparable dispersion made by using an unmodulated, high-current electron source (Lutz 1969). The discrepancies in the values of τ_2 in Tables 2 and 3 between the data on the Q-branch and on the P- and R-branches may be indicative of the suspected overlap, in that without this overlapping continuum a τ_2 value more nearly like that observed for the much more intense Q-branch would be expected. The effect of the proposed continuum will be strongly dependent on the lifetime of the H_2 $^3\Sigma_g{}^+$ state, because the intensity contribution of a long-lived state in our modulated source is reduced according to equation (2) over its initial, unmodulated value.[3] Nevertheless, the weakness of the P- and R-branches in the CH and CD C–X emissions, the overlapping of the vibrational transitions, the behavior of the values of $\tau_2(\lambda)$ in Tables 2 and 3, the observations of the unmodulated electron-excitation spectrum of CH_4, and the known ease of producing H_2 in electron collisions with CH_4 (American Petroleum Institute) make it clear that a more sophisticated model will be necessary to account in detail for the phase shifts of the P- and R-branches in Tables 2 and 3. However, because of the much greater intensities observed within the C–X Q-branches in CH and CD, the interpretations of the data on the 0–0 Q-branch given in this paper are not expected to be affected appreciably by this suspected and unfortunate spectral overlap with the H_2 continuum. Furthermore, our tentative conclusions that the 1–1 Q-branch band head appears to contain proportionally more emissions that are short lived than the other wavelengths (except the CH 3185Å or CD 3165Å measurements, which contain large contributions from the 1–1 bands) is not contradicted by the presence of the H_2 continuum.

Development of a successful P- and R-branch model will require greater input of experimental intensity ratios between the suspected H_2 continuum and the CH emissions than currently available, an accurate lifetime for the H_2 $^3\Sigma_g{}^+$ state, and, probably, lifetime data made with higher spectral resolution. It is our hope that the data in Tables 2 and 3 and the above discussion will serve as a guide for further experimental and theoretical efforts to answer the intriguing questions put forth at the beginning of this section—especially since the wide range of wavelengths covered by this emission system, coupled with its astrophysical importance, makes it seem both amenable to, and worthy of, much closer scrutiny with spectroscopic techniques of moderate to high resolution.

IV. DISCUSSION

a) Probabilities for Radiation and Predissociation in the C $^2\Sigma^+$–$X^2\Pi$ Transitions of CH *and* CD

The phase data obtained for the C $^2\Sigma^+$–X $^2\Pi$ 0–0 bands of CH and CD can be adequately described only by the overlap of *at least* two distinct lifetimes (cf. discussion of § III*b*i). On the basis of a model consisting of overlapping transitions involving two lifetimes we expect, from the analysis of the data presented above on the phase shift of the Q-branch of the 0–0 band, that the longer-lived components are about 3 times more intense than the shorter-lived ones. Such differences in intensity have been observed between lines from F_1 and F_2 levels of CH in the higher-resolution spectrograms obtained with simple discharges. Consequently, we can plausibly assign the following characteristics to the rotational levels of C $^2\Sigma^+$, $v' = 0$, in both CH and CD. In CH, weak emissions arise from F_1 levels which have an average lifetime of $\tau_1 \simeq 5$ nsec, while strong emissions arise from F_2 levels which have an average lifetime of $\tau_2 \simeq 18$ nsec.[4] In CD, weak lines originate from F_1 levels of average lifetime $\tau_1 \simeq 20$ nsec, while strong lines originate from F_2 levels of average lifetime $\tau_2 \simeq 55$ nsec.

That the mechanism which is responsible for these effects in CH and CD must be predissociation (Herzberg 1967; Hesser and Lutz 1968*a;* Herzberg and Johns 1969) is evident from the following observations. In experiments involving the flash photolysis

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[3] If the H_2 continuum is present and our interpretations of its influence are correct, we may estimate from the values of τ_2 in Tables 2 and 3 that the $^3\Sigma_g{}^+$ state has a radiative lifetime of approximately 100–160 nsec, provided that cascading effects are unimportant.

[4] Note that for clarity we have chosen the subscripts for τ_1 and τ_2 to agree with the subscripts for F_1 and F_2, respectively.

of CH_2N_2 and CD_2N_2, Herzberg (1967) noted that, although C–X fluorescence is observed in the spectrum of the deuterated compound, it is absent or weaker by at least a factor of 5 in the normal compound. Since no emissions from the $C\ ^2\Sigma^+$ state have ever been found to terminate in a state other than $X\ ^2\Pi$, the observed difference in intensity between the two isotopes is evidence for a weak predissociation affecting the C state—a striking conclusion when it is recalled that the entire C–X emission system is regularly seen in the spectra of discharges and flames. The absolute phase shifts observed for the C state in both CH and CD are much smaller than those expected from the radiative lifetime computed from Linevsky's (1967) or Herbig's (1968) relative absorption f-values put on the absolute scale of Fink and Welge (1967). Upon further comparison with Linevsky's or Herbig's work, the phase-shift results indicate that nonradiative processes occur in the C states of both CH *and* CD, while the increase in lifetimes with the change of isotope from H to D is consistent with the observation that deuterated compounds are often more stable against predissociation.

The intensity anomaly of the spin doublets observed in our high-resolution spectrogram can be explained neither by a mixing of the C state with a close-lying state of the same symmetry properties nor by a radiative depopulation or overpopulation of the F_1 levels of $C\ ^2\Sigma^+$ relative to the F_2 levels. Since the dipole matrix elements are independent of whether the transition is one of emission or of absorption, the first of these alternatives can be ruled out by the lack of the required intensity anomalies in high-resolution absorption spectra of CH or CD (Herzberg and Johns 1969). The second alternative is also quite unlikely, since a transition between spin levels of the same N' is strictly forbidden by parity considerations. The process of F_1 levels radiating to another electronic state forbidden to F_2 levels is eliminated, since transitions to any observed or predicted lower-lying states, except $X\ ^2\Pi$, are forbidden to both F_1 and F_2. The observed range of lifetimes, about 5–55 nsec, must be characteristic of the interaction and is much too short for these forbidden radiative processes. Radiative overpopulation mechanisms are also discarded by the lack of observed emissions from any higher-lying electronic states of CH terminating in $C\ ^2\Sigma^+$.[5] The only remaining process which is consistent both with the intensity difference between the isotopes and with the intensity anomalies which are observed between the spin-doublet emission lines is a weak predissociation.

In both molecules it appears from the data presented above that the F_1 spin components predissociate about 3 times faster than the F_2 spin components, at least for $N' > 4$. In CH, both levels predissociate about 5 times faster than in CD. The absence of any CH C–X lines with $N' \leq 4$ noted in Herzberg's (1967) observations is consistent with the interpretation that even for $N' \leq 4$ the C states are predissociated. Our spectrogram shows that the doublet components with $N' \leq 4$ are about equally predissociated, but the absolute strength of predissociation remains uncertain.

From our observations of the Q-branch, the average probabilities for predissociation of F_1 and F_2 in CH are $A(F_1) \simeq 1.9 \times 10^8$ sec^{-1} and $A(F_2) \simeq 4.7 \times 10^7$ sec^{-1}, while in CD they are $A(F_1) \simeq 4.1 \times 10^7$ sec^{-1} and $A(F_2) \simeq 9 \times 10^6$ sec^{-1}, for $N' > 4$, after the radiative contribution of 9×10^6 sec^{-1} (Linevsky 1967; Fink and Welge 1967) is subtracted from the values of $1/\tau$ in the two-component model in Tables 2 and 3. The lifetimes of the levels $N' \leq 4$ will not affect these results strongly, since their integrated emission is very small compared with that for levels $N' > 4$. These extremely small predissociation probabilities, of the same order of magnitude as radiative-transition probabilities, make clear why no diffuseness of the rotational lines is observed in the absorption spectrum.

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[5] Since the cross-section for collisional excitation depends solely upon the electron-velocity distribution, it appears to be highly improbable that selective overpopulation of one of the sublevels could take place in the dissociation of the parent methane molecule in the electron-beam or discharge sources used in this work.

Values of predissociation probabilities such as those given above are typically expected for forbidden predissociations, consistent with the fact that the only possible interacting states whose dissociation limit lies below $C\ ^2\Sigma^+$ are the observed $B\ ^2\Sigma^-$, the predicted bound state $^4\Sigma^-$, the repulsive state $^4\Pi$, and the ground state $X\ ^2\Pi$. These states are all derived from atomic C and H in their normal states, ^3P and ^2S, respectively. The ground state of CH could produce a J-dependent predissociation, but according to Kovacs's (1958) calculations the predissociating $^2\Pi$ state must be inverted to interact with the F_1 levels of $^2\Sigma^+$ more than with the F_2 levels. Since the ground state of CH is regular, it is excluded as a possibility. The manifold of states which could predissociate the $C\ ^2\Sigma^+$ state of CH and of CD is the same as that which could cause the strikingly similar predissociation of the $A\ ^2\Sigma^+$ state of OH (Gaydon and Wolfhard 1951). Arguments identical with those presented by Gaydon and Wolfhard, which establish $^2\Sigma^-$ as the predissociating state of OH, show that $B\ ^2\Sigma^-$ is most probably the state of CH and of CD which produces the observed effects. This interaction unfortunately requires a rather large variation in the vibrational overlap between the $^2\Sigma^+$ and $^2\Sigma^-$ states for a change of only two rotational quantum numbers, but this difficulty seems insufficient to eliminate $B\ ^2\Sigma^-$. Naegeli and Palmer (1967) have argued that predissociation via the repulsive $^4\Pi$ state could also produce the observed differences in intensity in $A\ ^2\Sigma^+$ of OH, and more recently (Palmer and Naegeli 1968) they have proposed $^4\Sigma^-$ as the predissociating state of OH. The calculations by Kovacs (1958) indicate that the F_1 and F_2 levels of $^2\Sigma^+$ are affected to precisely the same degree in the $^2\Sigma^+$–$^4\Pi$ interaction, as well as in the $^2\Sigma^+$–$^4\Sigma^-$ interaction. For these two interactions only a Franck-Condon effect as proposed by Gaydon and Wolfhard could account for the observed differences in intensity. Interaction with the $^4\Pi$ or $^4\Sigma^-$ states would not involve such an effect. If the data presented by Palmer and Naegeli (1968) do represent breaking-off points in the A state of OH, and if their Figure 1 is a true limiting curve, then the predissociation reported by them is probably a new one, different from that reported by Gaydon and Wolfhard.

Dressler (1969*a*) has pointed out that predissociation to the $^4\Pi$ continuum would also produce the observed differences in intensity if the $^4\Pi$ continuum contained a small admixture of an appropriate $^2\Pi$ wave function. Kovacs's (1958) matrix elements for mixing show that the F_1/F_2 intensity differential depends upon (i) the magnitudes of the spin-orbit coupling, (ii) the coupling between the electronic orbital angular momentum and the nuclear rotation, and (iii) the $^2\Sigma^+$–$^2\Pi$ energy difference. For the F_1 levels of $C\ ^2\Sigma^+$ to be affected more than the F_2 levels, as observed, the $^2\Pi$ state must be inverted. The only $^2\Pi_i$ state of CH and of CD which differs from $C\ ^2\Sigma^+$ by only one orbital in its electron configuration is $\pi^3\ D\ ^2\Pi_i$, which was recently observed in absorption (Herzberg and Johns 1969). This state has a spin-orbit coupling constant of only about -28 cm^{-1} in both CH and CD, and lies some 20000 cm^{-1} above the dissociation limit, $^2S + {}^3P$. Consequently, we feel that predissociation to the $^4\Pi$ continuum by means of a small admixture of a $^2\Pi_i$ wave function in the continuum could not be strong enough to produce even these observed weak effects in CH and CD. A definitive selection between the models proposed, however, must await a quantitative comparison of the matrix elements describing the two possible interactions, $C\ ^2\Sigma^+ \leftrightarrow B\ ^2\Sigma^-$ and $C\ ^2\Sigma^+ \leftrightarrow ({}^4\Pi + {}^2\Pi_i)$.

b) Formation Rates of CH *in the Interstellar Medium*

If the levels $N' \leq 4$ of the C state of the CH radical are predissociated to about the same extent as the rotational levels of higher N', then this predissociation has important consequences in the present theories of the formation of interstellar molecules. As also pointed out by Herzberg (1967) and by Dressler (1969*b*), nearly every photon absorbed in a line terminating in $C\ ^2\Sigma^+$ results in the photodestruction of the molecules. If we compute the Einstein absorption coefficient, B, from the absolute absorption f-value

(Linevsky 1967; Fink and Welge 1967), $f = 6.2 \times 10^{-3}$, and use the value of the radiation density at ~3000 Å in interstellar space (Bates and Spitzer 1951), $u(\nu) = 1.2 \times 10^{-28}$ erg cm^{-3} sec^{-1}, we find that CH is destroyed at a rate given by:

Destruction rate of CH by predissociation (per molecule) $= Bu(\nu) \simeq 9 \times 10^{-11}\ \text{sec}^{-1}$.

Comparing this value with the photodissociation rate of 1.5×10^{-11} sec^{-1} estimated by Bates and Spitzer (1951; see also Kramers and ter Haar 1946), we see that destruction of CH radicals by absorption in the *C–X* system and subsequent predissociation of the molecule may be about 6 times more efficient than destruction by photodissociation. Furthermore, higher-lying $D\ ^2\Pi_i$ and $E\ ^2\Pi$ states are known to be strongly predissociated at low *J*-values (Herzberg and Johns 1969), thereby making predissociation the overwhelming destruction mechanism for interstellar CH.

Stecher and Williams (1966) have asserted that if photodissociation is the fastest destruction mechanism in clouds about 10^3 pc from hot stars, then exothermic chemical exchange reactions of the form

$$\text{(graphite grain) H} + \text{C} \rightarrow \text{(graphite grain)} + \text{CH}$$

can, under certain conditions, produce densities of interstellar CH which are consistent with observations. However, with the recognition of the much more efficient photodestruction mechanism associated with the predissociation of the *C* state, the cloud model needed to produce the observed space densities becomes inconsistent with the models used to produce the observed densities of other diatomic molecules. It therefore seems likely that interstellar CH is formed by mechanisms in addition to the exchange reactions envisioned as taking place with graphite grains, perhaps by the dissociation of larger molecules such as CH_4. This relatively old approach (Bates and Spitzer 1951) to the production of CH in interstellar space, although it leaves open the question of the formation of the parent molecule(s), again appears promising in light of the recent, tentative identification of interstellar CH_4 in the infrared spectrum of α Ori (Herzberg 1968) and the identification of microwave emission from interstellar NH_3 and H_2O (Cheung *et al.* 1968, 1969) and of microwave absorption of interstellar H_2CO (Snyder *et al.* 1969). Herbig (1968) has also called attention to the fact that in at least one H I region—namely, that near ζ Oph, where $n(\text{H}) \simeq 730$ cm^{-3} instead of ~20 cm^{-3} as found by Strömgren (1948)—gas-phase, two-body recombination to form CH must again be seriously considered. In any case, the rate of generation of CH molecules in interstellar space must be significantly more rapid than previously realized, and the process of photodestruction described here for the *C–X* transition (and the even stronger one for the *D–X* and *E–X* transitions) must be considered in any modern revision of Bates and Spitzer's classic work.[6]

c) Stellar Abundances of CH

A number of investigators have recently turned their attention to the abundance of molecules in late-type stars and in the Sun (Schadee 1964, 1968; Baschek and Holweger 1967; Withbroe 1967, 1968; Lambert 1968). However, those investigations concerned with CH have suffered to some extent from the imprecisely known *f*-value of the *G*-band $A\ ^2\Delta - X\ ^2\Pi$ 0–0. In the case of the Sun, Baschek and Holweger (1967) were

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[6] Lengthy discussion exists in Bates and Spitzer's (1951) paper concerning the *f*-value of the CH *A–X* transition and the effects its magnitude has upon the conclusions they draw. It is worth noting here that their adopted *f*-value of ~0.002, based upon very early theoretical estimates by Lyddane, Rogers, and Roach (1941), is fortuitously only a factor of 2–3 less than the modern experimental values derived from the lifetimes of Table 1, although at the time of their work a serious discrepancy appeared to exist between the preliminary experimental results due to Dunham (1940), $f \sim 0.06$, and the theoretical ones. Consequently, conclusions reached in their paper which depend upon the *A–X* *f*-value will not be as strongly affected as it was believed possible at that time.

able to estimate an f-value of $\sim 7 \times 10^{-3}$, which is within about 40 percent of the best experimental values. However, Baschek (1962), using similar procedures, found an f-value of $\sim 16 \times 10^{-3}$. The striking difference is interpreted by Baschek and Holweger as stemming primarily from the differences in the solar models used and is illustrative of the magnitude of errors that can occur in the derivation of f-values from astronomical light sources.

Schadee (1968) has recently used models with a scaled relation between solar temperature and optical depth to study the molecular abundances in G and K stars. As a method of checking his assumptions he also computed solar G-band intensities, whereupon he found that the computed values were too large by about a factor of 2; he then concluded that, since the heat of dissociation of CH is well known, Bennett and Dalby's (1960) oscillator strength is too large. Lambert (1968) independently reached the same conclusion on the basis of his more detailed solar calculations and suggested that $\tau(\mathrm{CH}\ A) \simeq 980 \pm 310$ nsec. However, as we have seen in Table 1, the recent experimental values of $\tau(A)$ support well the originally reported value of Bennett and Dalby.[7] Furthermore, the lifetime data reported by the various experimenters have been carefully checked for pressure quenching, radiative cascading, and entrapment, and no effects have been found over a very wide range of experimental conditions. Radiative cascading is not expected, since the B and C states do not connect with the A state via allowed transitions and the higher-lying states are strongly predissociated. Entrapment of resonance radiation is *highly* improbable in the case of electron excitation of diatomic species from polyatomic molecules and would, if present, make the observed lifetime appear too long, rather than too short. Furthermore, the $f(A)/f(B)$ ratio found by Fink and Welge (1967) and by ourselves is supported by Linevsky's (1967) relative absorption measurements. Although the B state is affected by a weak predissociation at *high* rotational quantum numbers, the A state does not seem to be similarly affected, as determined both from the viewpoint of spectral analysis (Shidei 1936; Herzberg 1950) and from our phase-shift measurements of CH and CD A–X. From studies of the weak predissociation in the B state, the heat of dissociation of CH has been well established, and it seems quite unlikely that the value will change by the 0.3 eV necessary to bring the solar observations into agreement with theory. From the astrophysical point of view, the great difficulties of (i) choosing a valid model to use in the computations and (ii) measuring accurate equivalent widths in this crowded region of the spectrum have been emphasized by many investigators in this field. Consequently, even though the source of the error in the solar and stellar calculations is not yet clear, Schadee's (1968) and Lambert's (1968) conclusions concerning the oscillator strength of the CH A–X system reached from the interpretation of astronomical equivalent-width measurements seems to be strongly contradicted by extensive laboratory data.

d) Future Work

Our results have shown the definite need for further work in several areas. First, it is clear that a thorough investigation of the electronic structure of the valence states of CH and CD is called for by both experimental and theoretical means. Second, new measurements at higher time and spectral resolution need to be attempted on the decay rates of the C states of CH and CD; it would be particularly interesting if individual doublet pairs could be measured. Such measurements could be used to determine positively any variation of lifetime with N' and would thus provide critical additional information about the interacting states (Mulliken 1960). Third, it would be of great astrophysical value to determine the extent of predissociation of the levels with $N' \lesssim 4$

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[7] Apparently the discordant results of Jeunehomme and Duncan (1964) listed in Table 1 may be disregarded since at least two of the lifetimes (those for the N_2 C- and NO A-states) reported by them have been substantially revised by Jeunehomme (1966*a*, *b*).

of $C\ ^2\Sigma^+$ because of their influence on the interstellar formation of CH. It is also essential for astrophysical applications that a confirmatory measurement be made of Linevsky's (1967) relative C–X absorption f-value. Finally, it may also be necessary in future work to undertake analyses of the detailed effects of the H_2 continuum upon the decay-rate measurements.

Two additional problems immediately present themselves in astrophysics. From our phase-shift data on the C–X system and Herzberg and Johns's (1969) spectral data on the other excited states, we expect that CH is much more rapidly destroyed than heretofore believed and hence that the rates of formation must be significantly larger than currently anticipated. When our work is combined with Herbig's (1968) recent observations of ζ Oph, it seems that a thorough investigation of the mechanisms of CH formation must again be performed. In this connection it will be interesting to follow the search for larger molecules in space (Townes 1955; Cheung *et al.* 1968, 1969; Snyder *et al.* 1969), since these molecules could provide the source of observed diatomic radicals as well as a possible explanation of the unidentified interstellar absorption features. Finally, the laboratory data for the G-band f-values seem sufficiently well determined that recent discussions of solar G-band intensities must turn from imprecisely known molecular constants to some other sources of error in order to account for the lack of agreement that exists between observation and theory.

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