

Laser-Induced Temporal and Wavelength Resolved Spectroscopy of the $^2\Sigma^- - ^2\Pi$ and $^2\Delta - ^2\Pi$ Systems of CH and CD Isolated in Rare Gas Matrices

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The relaxation dynamics of matrix isolated CH and CD have been studied using laser-induced time and wavelength resolved spectroscopy. Vibrationally relaxed $B(0'-0'')$ fluorescence occurs following laser excitation both above and below the gas phase dissociation limit. The vibrational relaxation rate in the B state of CH is found to be $4.6 \times 10^6 \text{ sec}^{-1}$ while the corresponding rate in CD is $5.7 \times 10^6 \text{ sec}^{-1}$. The primary accepting mode in the relaxation process is consistent with rotation.

INTRODUCTION

Radiationless relaxation processes in diatomic molecules isolated in rare gas matrices have been the subject of many recent studies (1, 5). These molecules cannot relax unimolecularly, and the host lattices, which provide fully quantized sinks, have been shown to convert guest vibrational quanta into a large number of host lattice phonons. In some studies (4, 5), the effect of the host lattice on dissociative states has been investigated, wherein "extra" vibrational states were created and double minima in the dissociative states inferred.

In this manuscript, we present the results of wavelength and time resolved spectroscopic studies of the radiative and nonradiative relaxation processes resulting from laser excitation of the $A^2\Delta$ and $B^2\Sigma^-$ states of matrix isolated CH and CD. Besides the long-standing historical interests in CH (6, 7), it offers the possibility of studying both the A and B states (including the gas phase dissociative continuum of B) using various commercially available laser sources.

The combination of ground state $C(^3P)$ and $H(^2S)$ correlates with three states of CH: the ground $X^2\Pi$, the weakly bound $B^2\Sigma^-$, and the as yet unobserved $a^4\Sigma^-$. The combination of $C(^1D)$ and $H(^2S)$ atoms correlates with the bound $A^2\Delta$ state and various nonbound states at higher energies. The $A^2\Delta$ state lies only $\sim 3000 \text{ cm}^{-1}$ lower than the $B^2\Sigma^-$ state (Fig. 1), and such approximately iso-energetic vibrational levels may be expected to interact.

The lifetimes of these states have been studied in the gas phase with a view toward determining the mechanism of interstellar formation of CH. Values for the lifetimes obtained from examining unresolved rotational envelopes (8) have been reinvestigated as a function of rotational quantum number (9, 10) and as a function of total pressure (11). These lifetime measurements indicate that the $B^2\Sigma^-$

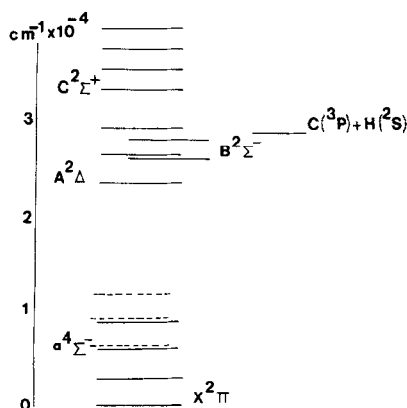


FIG. 1. Gas phase energy level diagram of CH (7). The data for the $a^4\Sigma^-$ state is taken from J. Hinze, G. Lie, and B. Liu, *Astrophys. J.* **196**, 621-631 (1975).

state of CH is rotationally predissociated with a barrier to dissociation ≥ 500 cm^{-1} (9). Since the origin of $A^2\Delta$ state lies approximately one vibrational interval lower than the origin of the B state, a possible crossing to this state from the B state presents an interesting subject for investigation through matrix isolation. The effect of the matrix environment on the different electronic states of CH can be determined by comparison with the well-known gas phase potential constants.

Two closely analogous hydrides, OH and NH, have previously been studied in low temperature matrices (2, 3). The observed phonon structure of the transitions implied slightly perturbed free rotation. Emission and absorption spectra of matrix isolated CH have also been studied (12). In this paper, we obtain higher resolution spectra which support the suggestion that rotation also plays a role in the relaxation processes of CH. Lifetimes of the various vibrational levels involved in the transitions have been measured and the rate of vibrational relaxation in the $B^2\Sigma^-$ state of CH and CD are reported.

EXPERIMENTAL DETAILS

Methane or acetylene:rare gas mixtures (1:1000-1:20 000) were prepared by standard manometric techniques. Methane (Matheson, 99.97%), argon (Matheson grade), and krypton (Airco, 99.995%) were used without further purification. Acetylene (Airco, Commercial grade) was used after passing through several freeze-pump-thaw cycles.

C_2D_2 was prepared by base catalyzed exchange of C_2H_2 with D_2O . The mixtures were deposited onto a LiF window maintained at approximately 13K by an Air Products Displex refrigerator. To prepare the matrices, mixtures of CH_4 or C_2H_2 and a selected rare gas were subjected to a microwave discharge as the mixture was flowed through a quartz tube terminating approximately 10 cm from the cold substrate. Generally, 5-8 mmoles of the mixture were deposited over a period of 1 h.

Two excitation sources were used. A Molelectron UV 400/DL 200 nitrogen pumped dye laser was used for wavelength and time resolved excitation in the range 4405–3700 Å. This laser was subject to the following specifications: bandwidth, 0.4 cm^{-1} ; pulse width, 10 nsec; and peak power, $\sim 50\text{ kW}$. The 3371 Å line of the nitrogen laser was also used in examining emissions with origins above 3500 Å. Continuous wave (cw) emission spectra were obtained using the UV lines of a Coherent Radiation CR 18 argon ion laser. An external cavity prism was used to disperse the UV output into three wavelength resolved components at 3638, 3511–3514, and 3336 Å. Typical power levels were: 3638 Å $\sim 200\text{ mW}$, 3511–14 Å $\sim 200\text{ mW}$, and 3336 Å $\sim 50\text{ mW}$.

Luminescence was wavelength resolved with a 1.0-m spectrometer (McPherson 225) equipped with a grating blazed at 2000 Å and a HTV R928 photomultiplier tube. A maximum resolution of $\sim 7\text{ cm}^{-1}$ was achievable in the spectral region of interest under ideal conditions. Signals received by the photomultiplier tube were conducted to an electrometer–strip chart recorder combination for wavelength resolved spectra or a Biomation 8100 transient recorder for time resolution. Signal averaging was carried out for typically 512 laser pulses using a Nicolet 1070 signal averager and processed by a minicomputer. The time resolution was limited by the 40 nsec rise time of the Biomation. Also, the laser scatter from the matrix was much stronger than the luminescence signal and could not be eliminated completely by using cutoff filters. This severely affected the rise of the luminescence signal and hence no direct measurements of the rise of population of the various vibrational levels were possible.

RESULTS AND DISCUSSION

Spectra

Keyser (12) reported the absorption spectrum of CH in Ar matrix and assigned the observed absorption bands to $A(0'-0'')$, $B(0'-0'')$, and $B(1'-0'')$. In the present study, we observed weak absorptions due to $A(0'-0'')$ and $B(0'-0'')$ only. Pulsed dye laser excitation of the $A(0'-0'')$ transition between 4320 and 3920 Å gave

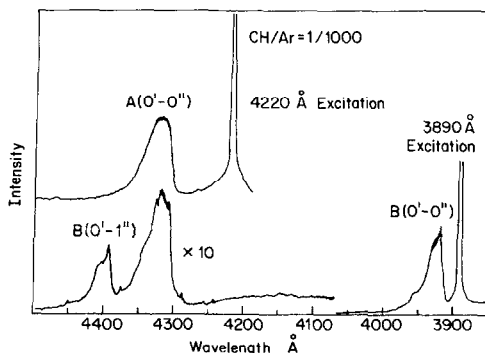


FIG. 2. Top: Emission of the $A(0'-0'')$ transition of CH in Argon with excitation into the absorption of $A(0'-0'')$ at 4220 Å. Bottom: Emission of $B(0'-0'')$, $A(0'-0'')$ and $B(0'-1'')$ with excitation into the absorption of $B(0'-0'')$ at 3890 Å.

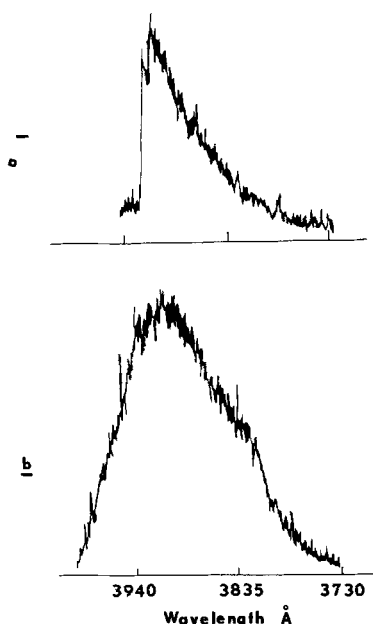


FIG. 3. Excitation spectrum of CH in Argon at 13K near the $A(1'-0'')$ and $B(0'-0'')$ absorptions. (a) monitoring 4395 Å, $B(0'-1'')$ (b) monitoring $A(0'-0'')$.

rise to $A(0'-0)$ and extremely weak $A(0'-1'')$ emissions, Fig. 2, with origins at 4310 and 4884 Å, respectively. Excitation between 3920 and 3700 Å which involves absorption primarily in to $B(0'-0'')$ produces a progression in $B(0'-v'')$ from $v'' = 0$ to $v'' = 2$, in addition to $A(0'-0'')$ emission which is shown in Fig. 2. The appearance of $A(0'-0'')$ emission for excitation in the $B(0'-0'')$ state poses the question about the mechanisms involved in populating $v' = 0$ of the A state. There are three possibilities; (1) that there is cross over from the B state to the A state, (2) the $A(0'-0'')$ absorption extends several thousand wavenumbers to the blue of the origin or, (3) the $A(1'-0'')$ absorption overlaps the region of $B(0'-0'')$ absorption. The $A(0'-0'')$ emission is much weaker than the $B(0'-0'')$ emission for excitation in the $B(0'-0'')$ manifold and also the Frank-Condon factor for $A(1'-0'')$ is $\sim 7 \times 10^{-3}$ smaller than that of $A(0'-0'')$ (13) suggesting that the direct excitation of $A(1'-0'')$ is unlikely. Therefore, an attempt was made to determine the source of the A state excitation by recording the excitation spectra of $A(0'-0'')$ and $B(0'-1'')$ in the region of $B(0'-0'')$ absorption. Excitation spectrum of $B(0'-1'')$ emission, Fig. 3a, showed a distinct onset of the $B(0'-0'')$ absorption of 3920 Å while the excitation spectrum of $A(0'-0'')$ was basically featureless and showed a continuous absorption. The $A(0'-0'')$ excitation spectrum essentially reflects the gain profile of the dye laser. The absence of any origin in the $A(0'-0'')$ excitation spectrum suggests that there is no crossover from the B state to the A state, but the $A(0'-0'')$ absorption does extend several thousand wavenumbers to the blue of its origin. The broad $A(0'-0'')$ absorption must contribute to a great extent in populating $v' = 0$ of the A state.

The cw Ar⁺ laser line at 3638 Å corresponds to $B(1'-0'')$ excitation, if blue shading of $B(1' = 0'')$ is allowed. As shown in Fig. 4, $B(0'-0'')$ is the strongest emission with 3638 Å implying that vibrational relaxation in the B state is competitive with radiative decay. A progression in $B(1'-v'')$ with $v'' = 0$ to 3 is also observed (not shown in Fig. 4). In addition to B state emission, 3638 Å (cw) excitation produces emission in the region of $A(0'-0'')$ and $A(1'-1'')$ but no $A(1'-0'')$ emission could be detected, Fig. 4. The $A(1'-0'')$ emission is expected to be much weaker than the $A(0'-0'')$ or $A(1'-1'')$ and lie close to the strong $B(0'-0'')$ emission which makes it difficult to detect. Since the 3638 Å line lies $\sim 1533\text{ cm}^{-1}$ to the blue of the expected $A(1'-0'')$ origin, the $v' = 1$ level of the A state could be populated either by direct absorption or by crossover from the B state. The weak Frank-Condon factor for $A(1'-0'')$ will make the direct population of $v' = 1$ of the A state less likely but excitation spectrum of $A(1'-1'')$ in the region of $A(1'-0'')$ absorption could not be recorded since it lies very close to $A(0'-0'')$. It is possible that both these processes are responsible for populating $v' = 1$ level of the A state. Direct excitation in the blue wing of $A(0'-0'')$ is also a possibility since the $A(0'-0'')$ absorption is shown to extend several thousand wavenumbers to the blue of its origin.

With N₂ laser (3371 Å) excitation, both A and B state progressions were observed as indicated in Fig. 5. A weak $A(1'-0'')$ emission appears at 3871 Å which was not observed with 3638 Å excitation. It is possible that the relatively higher peak power available at 3371 Å as compared to 3638 Å enables the $A(1'-0'')$ transition to be observed. The nitrogen laser excites above the dissociation limit measured in the gas phase for the $B^2\Sigma^- \leftarrow X^2\Pi$ transition, and it is thus interesting to note that the relaxed $B(0'-0'')$ emission is strongest with this excitation. This observation suggests that the guest CH undergoes large displacements at this energy, exciting local modes and enhancing nonradiative energy transfer to the matrix.

In the case of 3511–3514 Å cw excitation, which is $\sim 10\text{ cm}^{-1}$ below the $A(2'-0'')$ origin, the emissions produced are equivalent (in frequency) to those excited by 3638 Å (Fig. 4). However, $B(1'-v'')$ is considerably decreased in intensity

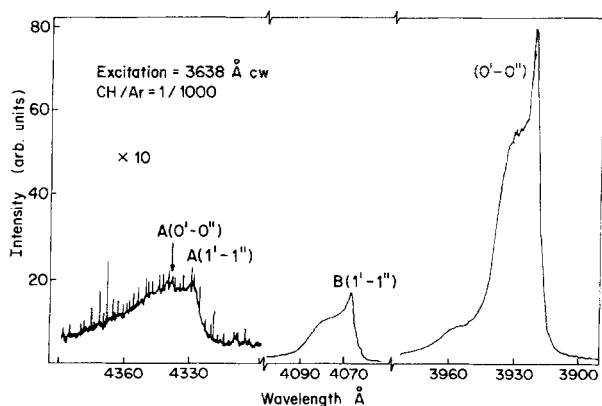


FIG. 4. Emission spectrum of CH in Argon with 3638 Å cw excitation. A $B(1'-v'')$ progression is also observed from $B(1'-1'')$ through $B(1'-3'')$.

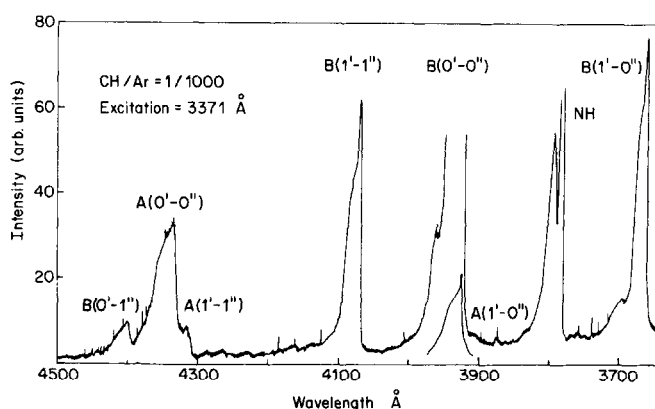


FIG. 5. Emission spectrum of CH in Argon at 13K with pulsed N_2 laser (3371 Å) excitation. Emission due to NH appears near 3800 Å.

relative to $B(0'-0'')$ and the zero phonon line (ZPL) of $B(0'-0'')$ is also decreased in intensity relative to the phonon wing (Fig. 6). We note here that 3511–3514 Å excitation, although above the gas phase dissociation limit of the B state, is very near the top of the barrier to predissociation observed in the B state. The spectrum regained the sharp features at higher excitation energies, (3371 Å discussed previously and 3336 Å *vide infra*). It should be noted that prolonged irradiation with excitation wavelengths above the gas phase dissociation limit did not decrease the emission intensity, suggesting that little permanent dissociation occurred.

A similar situation arose in a study of ICl in Ar (4, 5) wherein a pronounced broadening in the emission occurred as the excitation wavelength approached the region of the barrier to predissociation. The broadening was also observed in ICl/Ne matrices and the relative proportions of the broad and the narrow com-

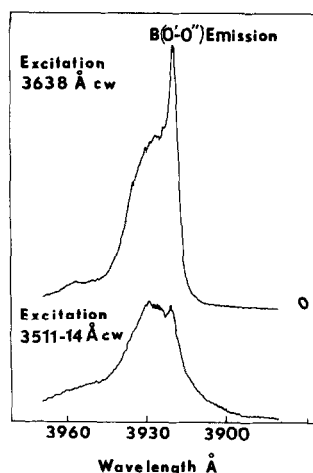


FIG. 6. Top: Emission spectrum of $B(0'-0'')$ with 3638 Å cw laser excitation; bottom: emission spectrum of $B(0'-0'')$ with 3511–3514 Å cw laser excitation.

TABLE I

Deslandres Table for the $B-X$ Transition of CH in Argon and Krypton at 10K

		v''			
		0	1	2	3
v'	0	25504 (25356)	22755	20113	
	1	27337 (27168)	24584 (24425)	21961 (21816)	19470

Note. Krypton values appear in parentheses. Wavenumbers in cm^{-1} .

ponent changed with the deposition conditions. Bondybey and Brus (5), on the basis of above observations, attribute the two band shapes to two separate and distinct maxima in the inhomogeneous line shape. The observed overall band shape is then the superposition of the two spectra. The change in band shape near the gas phase dissociation limit is due to selectively exciting vibronic transitions in molecules trapped in one particular site. Such site effects can be invoked in the case of CH/Ar to explain the observed broadening but we could not scan the inhomogeneous width of the $B(0'-0'')$ emission to confirm the presence of different sites due to the limited range of the dye laser available.

With 3336 Å excitation, emissions from $B(0'-0'')$, $B(1'-0'')$ and $B(1'-1'')$ were observed, $B(0'-0'')$ being the most intense. Emission spectra excited by 3336 Å laser line, which corresponds to a photon energy greater than the gas phase dissociation limit in the B state, were weaker than the luminescence excited by 3638 and 3511–3514 Å lines. The Deslandres table for the B state transitions is given in Table I and the spectroscopic constants calculated from this data are shown in Table II. These tables also contain the results for Kr matrices which generally paralleled those for Ar. There is insufficient data to calculate A state parameters but the spectroscopic data allows calculation of the $A(2'-0'')$ origin at 3496 Å. This can be compared with 3509 Å from gas phase data implying that ω_e of the A state has been increased somewhat by matrix perturbations, as is that of the B state.

CD Emission Spectra

In experiments involving CD, the results generally paralleled those for CH. Very weak $A(0'-1'')$ CD emission could be detected shifted $\sim 100 \text{ cm}^{-1}$ from CH in the gas phase but it is surprising that no distinct $B(0'-0'')$ or $A(0'-0'')$ emission is observed. The 3511–3514 Å lines of the Argon ion laser are near resonant with $B(2'-0'')$ of CD and excitation at this wavelength gives rise to emission from $B(2'-1'')$, $B(1'-0'')$, $B(1'-1'')$, and $B(0'-0'')$ of CD. $A(2'-2'')$ emission also occurs with this excitation line and appears at 4345 Å.

TABLE II
Spectroscopic Constants of CH and CD

	$\nu_{00}(A-X)$	$\nu_{00}(B-X)$	$\omega_0(B)^c$	$\omega_1(B)^c$	ω_e''	$\omega_e''x_e''$
CH gas ^a	23218 ^b	25698	1795	...	2859	63
Ar emission	23200	25504	1830	...	2884	65.5
Kr emission	23111	25356	1812	...	2877	67
	$\nu_{00}(A-X)$	$\nu_{00}(B-X)$	ω_0^c	ω_1^c	ω_0	
CD gas	23255	25797	1405	1157	2046	...
Ar emission	23200 ^d	25504 ^d	1525	1204	2043	...

^aG. Herzberg and J.W.C. Johns, *Astrophys. J.*, **158**, 399 (1969).

^bUnits are cm^{-1} , estimated error 7 cm^{-1} .

^cThe potential well of the B state is too shallow for ω_e and $\omega_e x_e$ to have much physical significance.

^dOrigins independent of CH not observed.

Lifetimes

The excited state lifetimes of CH have been the subject of numerous investigations in the past decade. Spectroscopically, both the *B* state and *C* state have been observed to predissociate (8, 9) and recently Brzozowski *et al.* (10) have found evidence for predissociation in the *A* state. Lifetimes have been studied as a function of *N*, the rotational quantum number, to find the best value for the dissociation energy and to investigate the importance of radiative recombination of interstellar space. In emission, predissociation has been observed in the *B* state of $N' = 16$, $v' = 0$, and $N' = 7$, $v' = 1$ of CH. In the *B* state of CD, rotational predissociation has been observed at $N' = 25$, $v' = 0$, and $N' = 17$, $v' = 1$. The $v' = 2$ state of CD has not been observed in emission except under high pressures, where equilibrium is attained, although in absorption this state can be observed to $N' = 10$ before predissociation occurs. In the $A^2\Delta$ state, Brzozowski (10) has observed a shortening in the radiative lifetime of $v' = 1$ at $N' = 12$.

Comparison of the matrix lifetimes with the gas phase values, Table III, shows

TABLE III
Lifetimes of CH

Assignment	Gas Phase $\tau(\text{ns})$	CH:Ar Matrix $\tau(\text{ns})$	CH/CD:Ar Matrix $\tau(\text{ns})$
A(0'-0'')	497 \pm 55	372 \pm 7	306 \pm 65
B(0'-0'')	342 \pm 53	233 \pm 16	182 \pm 15
B(1'-0'')	389 \pm 28	106 \pm 3	165 \pm 30

that matrix lifetimes for the $A^2\Delta$ and $B^2\Sigma^-$ states are shortened with respect to the gas phase values. A contribution to shortening of the lifetimes is expected due to the index of refraction of the matrix, but as has been previously observed for OH (2) and NH (3), calculated index of refraction effects greatly over estimate the shortening. The observed differences are similar to those found for OH (2) and NH (3) in inert matrices. Lifetimes of the $A(0'-0'')$ and $B(0'-0'')$ transitions were independent of the excitation wavelengths and matrix ratio within the experimental error. In the case of CD:Ar, a significant proportion of CH was present in the matrix due to incomplete exchange and as mentioned before no unique $A(0'-0'')$ or $B(0'-0'')$ was observed. However, as shown in Table III, a shortening of the $A(0'-0'')$ and $B(0'-0'')$ lifetimes was observed in these matrices as compared to undeuterated CH matrices. This is probably due to an energy transfer from CH to CD as a result of long-range dipole-dipole interaction. A similar effect has been observed in the case of OH and OD (2). The lifetimes of $v = 1$ of the B state of CH and CD do differ markedly. The $v = 1$ level of the B state of CD has a longer lifetime than the corresponding state of CH. The vibrational relaxation rate and the radiative rate in the $B^2\Sigma^-$ state of CH can be calculated from the measured lifetimes of $v' = 0$ and $v' = 1$ and the relative intensities of the $B(0'-0'')$ and $B(1'-1'')$ emissions, assuming that the intrinsic radiative rates of $v' = 0$ and $v' = 1$ are the same. The vibrational relaxation rate in the $B^2\Sigma^-$ state of CH in Ar matrices turns out to be $4.6 \times 10^6 \text{ sec}^{-1}$ while the radiative rate is found to be $4.8 \times 10^6 \text{ sec}^{-1}$. In the case of CD/Ar, the vibrational relaxation rate was calculated on the basis of the difference in the lifetime of $v' = 1$ and $v' = 0$ levels since the matrices contained a significant amount of CH and no separate CD, $B(0'-0'')$ emission could be detected. The vibrational relaxation rate of CD in Ar is $5.7 \times 10^5 \text{ sec}^{-1}$. As is generally observed (2, 3) these relaxation rates violate the proposed energy gap law (14) according to which the relaxation rates of different diatomics in the host should show an inverse logarithmic dependence on the energy gap.

Although we have been unable to observe rotational motions in relatively concentrated matrices ($M/A \approx 1000$), the emission spectrum for matrices with $M/A \geq 10\,000$ clearly showed the rotational fine structure, Fig. 7. If rotation is considered as the primary accepting mode, a correlation between the relaxation rate and the minimum number of rotational levels necessary to match the vibrational energy gap can be expected on the basis of a multirotational quantum transition to the ground state (15). The observed relaxation rates for CH and CD are in reasonable agreement with the hypothetical curve shown in Ref. (15) suggesting that rotation plays a role in the relaxation processes of CH and CD.

CONCLUSION

It is shown that the $A^2\Delta$ state of CH is not populated by radiationless processes following excitation in the $X^2\Pi \rightarrow B^2\Sigma^-$ transition. However, the $A(0'-0'')$ absorption extends several thousand wavenumbers to the blue of its origin and largely accounts for direct excitation of $A(0'-0'')$. The CH spectroscopy indicates little perturbation in the ground state with a slight constrictive effect in the $B^2\Sigma^-$ state.

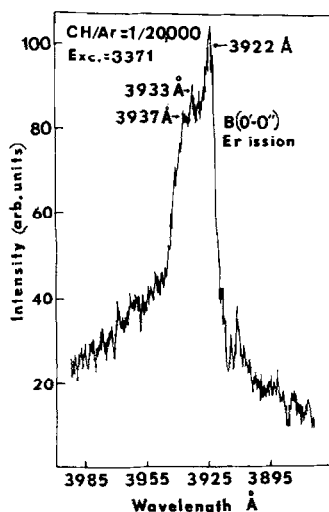


FIG. 7. Rotational structure as observed in the $B(0'-0'')$ emission of CH in Argon ($M/A = 20\,000$).

Well-resolved zero phonon lines are observed in the $B-X$ transition, while the zero phonon lines in the $A-X$ transition are not as well resolved, indicating strong coupling of the A state to the lattice modes. The rotations appear to participate as a local mode in the $B-X$ relaxation dynamics, at least in the case of very dilute matrices, supporting the results of a previous study (12). Relaxation within the $B^2\Sigma^-$ vibrational manifold is found to be faster for CH than for CD, as was found in the previously investigated examples of OH (2) and NH (3).

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