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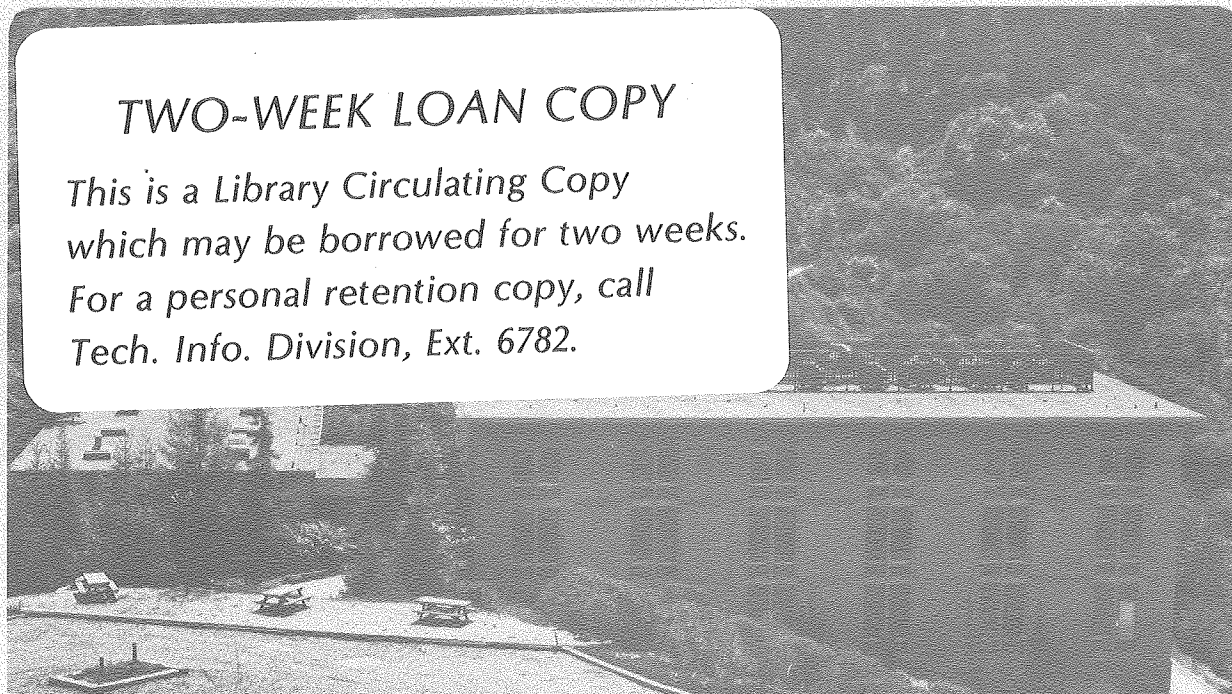
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Fred J. Grieman, Bruce H. Mahan, and Anthony O'Keefe

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THE LASER INDUCED FLUORESCENCE
SPECTRUM OF TRAPPED CD^+

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In the last few years great interest has centered around the study of molecular ions by means of electronic spectroscopy. This interest has led to the development of several new techniques aimed at overcoming the problems associated with the production and manipulation of sufficient numbers of ions.^{1,2} While advances have been made, it is evident that the class of ions presenting the greatest challenge to the spectroscopist is that of fragment ions, many of which are of interest in atmospheric and astrophysical processes.

We present here what we believe to be the first electronic absorption spectrum of a molecular fragment ion, CD^+ . While the light isotope analog, CH^+ , has been the subject of several emission studies,³⁻⁵ CD^+ has not been studied under resolution great enough to resolve rotations. Isotope shifts are particularly useful for hydrogen containing diatomics.⁶ For these reasons we undertook the study of CD^+ and present here preliminary results on the 0,0 vibrational band of the A-X electronic transition.

Our approach involves confining ions to a small (1-2 cc) region of space within a cylindrical R. F. Trap of the type described by Langmuir.⁷ The Trap consists of three electrodes; a central hollow cylindrical electrode, and two cap electrodes which are positioned at each open end of the cylinder. A voltage of fixed frequency and variable amplitude is applied to the center electrode which is maintained at some variable bias voltage with respect to the end caps. The RF amplitude determines a range of charge to mass ratios for which stable

ion trajectories within the trap exist. The biasing of the RF with respect to the end caps narrows this range of charge to mass ratios. This arrangement allowed us to operate with a mass resolution of ± 1 a.m.u. in the present experiment. Ions were created from CD_4 by a 2 msec pulse of 150 volt electrons and were stored for a period of several milliseconds at a neutral background pressure of 10^{-6} to 10^{-5} torr. A 10 nsec laser pulse from a nitrogen laser pumped dye laser was then directed through the center of the ion cloud 200 μsec after the electron pulse. The total fluorescence was collected using gated photon counting methods.

The laser used in the study had a bandwidth of approximately 1.0 cm^{-1} as determined by an optogalvanic measurement of Ne^* absorptions which was also utilized as a wavelength calibration. A laser bandwidth significantly less than this value was determined to be inappropriate due to the relatively large Doppler width of the ions within the trap.⁸ Nevertheless, rotational resolution is obtainable for many ions. The experiment was controlled by a PDP8F computer which is responsible for the storage and display of data. This arrangement allowed us to collect fluorescence signal, optogalvanic signal, a measurement of the laser power and a signal proportional to the ion density after each laser pulse. Typically the signal was averaged over several thousand laser pulses before the excitation wavelength was incremented by 0.1 \AA . The resulting spectrum was normalized to the variations in laser power and ion density during the scan.

The band system studied here was the 0-0 ($A \ ^1\Pi \leftarrow X \ ^1\Sigma^+$) band of CD^+ , calculated⁵ to be the strongest band in the transition.

The experimentally measured radiative lifetime for this transition in CH^+ ranges over a factor of 6, from 70 to 420 nsec.⁹ Radiative lifetimes in this range are ideally suited to our detection electronics in which the fluorescence detection gate is variable between tens of nsecs and tens of μs ecs.

We present in Figure 1 a portion of the normalized spectrum of this band in which the first 15 components of the R branch are identified. Molecular constants calculated with these data are given in Table I. The number of rotational levels observed here and in CH^+ spectra¹⁰ (not reproduced here) indicate the increased sensitivity of our method over earlier emission studies³ where, for example, the highest R branch transition observed in the 0,0 band was R_8 . There are several factors working in our favor. We have an appreciable ion density (estimated to be $10^6 - 10^7$ ions/cc) within the trap and interfering fluorescence from other fragments is avoided by the mass selectivity of our system. The nearly collision free environment of the trap preserves the initial internal state distribution giving greater spectral detail. Examination of the spectra already obtained for CD^+ indicates a rotational temperature of $\sim 2500^\circ\text{K}$. The uncertainty in this value arises from the overlap of lines within this band and from overlap with components of the (2+1) band. Several components of this band can be seen in the spectrum, e.g., at $4202 \overset{\circ}{\text{A}}$ and $4209 \overset{\circ}{\text{A}}$.

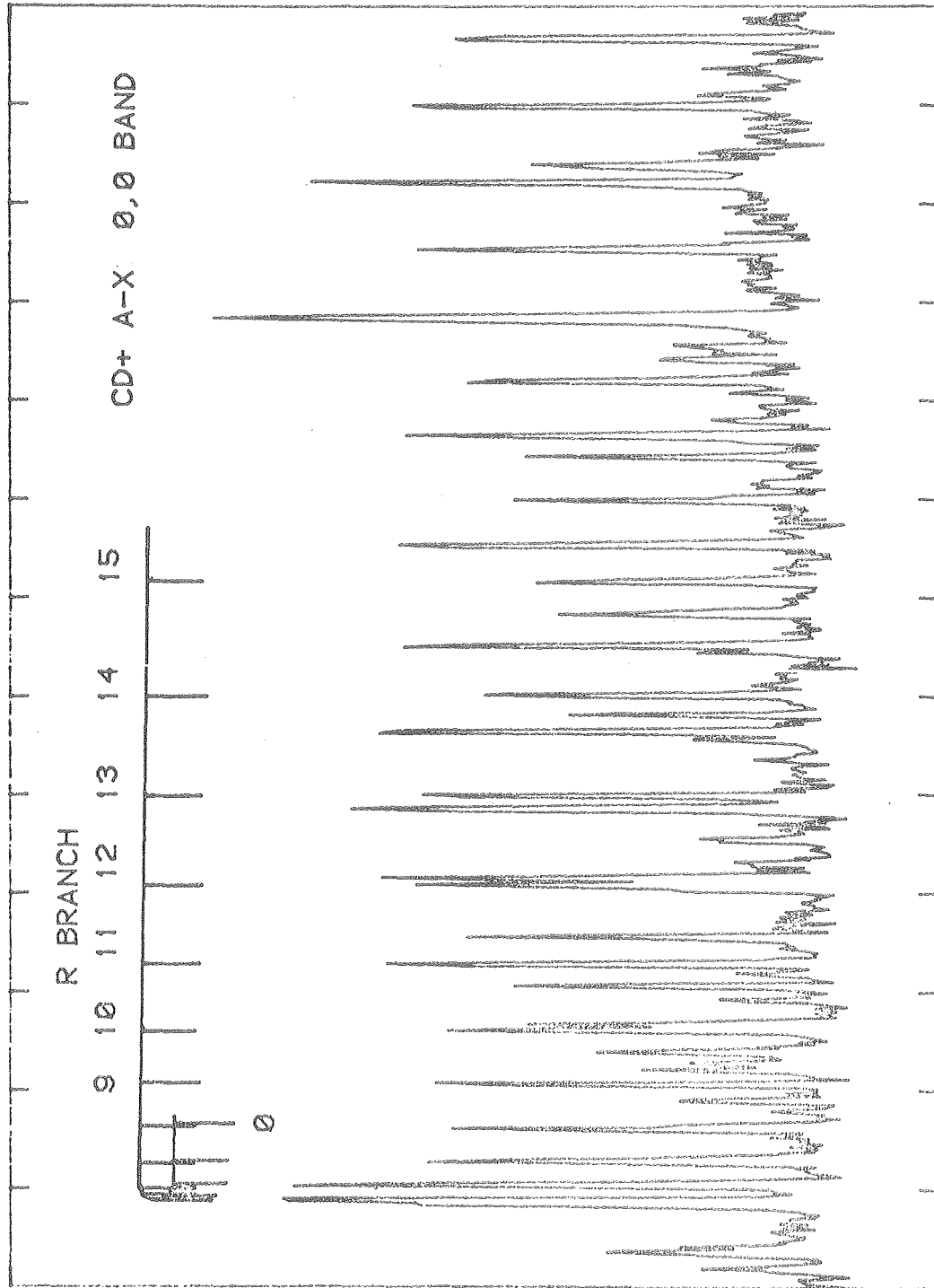
In summary, we have demonstrated a versatile method for the study of molecular fragment ions. A more complete study of the CH^+ and CD^+ ions, including measurement of radiative lifetimes, will be reported in a future article.

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Table I
Molecular Constants for CD^+

	$X \text{ } ^1\Sigma$	$A \text{ } ^1\Pi$
V_{00}	-	23747.8 cm^{-1}
B_0^{RP}	7.54 cm^{-1}	6.21 cm^{-1}
B_0^{Q}	-	6.20 cm^{-1}
D_0	$4.13 \times 10^{-4} \text{ cm}^{-1}$	$5.75 \times 10^{-4} \text{ cm}^{-1}$



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