favored over the one observed. The calculation predicts that the $|2^+\frac{7}{2},\frac{7}{2}\rangle$ state will decay only to the $|2^+\frac{5}{2},\frac{9}{2}\rangle$ state. Since the 1686 state has this decay pattern and the energy predicted by the calculation, it is identified as the $|2^+\frac{7}{2},\frac{7}{2}\rangle$ state.

The shape of the calculated curves in Fig. 2 is governed by the effect of the Coriolis interaction, which reduces the energy of the states in proportion to the alignment of the total angular momentum, I, and the particle angular momentum, j.[9] I and j are aligned when R and j are aligned, or antialigned. An arch curve is expected when the Fermi surface is near the low-lying states of given parentage. A flatter curve is expected when the Fermi surface is near the higher states of a given parentage, as less alignment is possible. These are the same conditions which produce $\Delta I = 2$ or $\Delta I = 1$ yrast bands. In ^{99}Ru the Fermi surface satisfies the former condition for the $g_{7/2}$ and $h_{11/2}$ multiplets and the latter condition for the $d_{5/2}$ multiplet as shown in Fig. 2.

In addition to the $R \simeq 2$ multiplets, states from the 4^+ and second 2^+ multiplets are expected. States having the energies and transition properties calculated for $R \simeq 4$ multiplets have been observed. Unfortunately, the spins of many states at higher excitation energies could not be determined in the present work because of poor statistics. Thus, no reliable measure of completeness for $R \simeq 4$ multiplets has been attempted. Other states are observed which do not fit into the pattern of the particle-rotor model. Thus the reaction may be more complete than has been demonstrated for the $R \simeq 2$ multiplets.

As evidenced by the presented results, the (^{3}He, $2n\gamma$) reaction is a powerful tool for populating nonyrast states in a wide range of angular momenta. In fact, three complete particle-core multiplets have been observed experimentally and successfully interpreted with a particle-rotor model. The empirical results are actually more complete than the model. This completeness allows a more rigorous test of various models than has previously been possible.

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Velocity-Modulated Infrared Laser Spectroscopy of Molecular Ions: The ν_1 Band of HCO^+

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The first observation of vibration-rotation transitions in HCO^+ is reported. The ν_1 absorption band was measured with a color-center laser by modulating the drift velocity of the ion in an ac discharge and detecting the Doppler-shifted absorptions with lock-in techniques. The ν_1 frequency is determined as 3088.727 ± 0.003 cm^{-1}.

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Vibration-rotation spectroscopy of charged molecules has become experimentally realizable only within the last decade, principally through the pioneering efforts of Wing and co-workers[1] and Oka[2]. Wing and co-workers have observed vibrational spectra of HD^+, HeH^+, and D_3^+ in fast ion beams by monitoring the changes in charge-transfer cross sections that result when vibration-rotation transitions of these ions are velocity tuned into coincidence with a CO laser.

In this approach kinematic compression of the random velocity components of the ion produces a resolution ≅ 10 times higher than that limited by the infrared Doppler width, and mass selectivity of the ion beams allows unambiguous identification of the spectral carriers. The highly excited vibrational distributions of ions and inherently small signals obtained, as well as the incomplete spectral coverage provided by line-tunable CO lasers, generally constitute serious difficulties with this otherwise powerful and elegant experiment. However, the high vibrational excitation of HD^+, HeH^+, CH^+, and H_3^+ produced in such ion beams has recently been exploited by Carrington and co-workers[3] to study states of these ions near their dissociation limits in a fast-ion-beam double-resonance method. In 1980, Oka[2] employed a frequency-modulated tunable difference-frequency laser and lock-in detection to observe directly the ν_2 vibrational absorption spectrum of H_3^+ ions which were generated in a dc blow discharge contained in a multiple-reflection cell. This same method has been used recently to study HeH^+ and NeH^+.[4] The principal difficulty encountered with this direct-absorption approach results because ions normally constitute only a few parts per million of the total gas density, and their absorption spectra are therefore very likely to be obscured by even very weak absorption features of neutral species present in the discharge. The observation of infrared emission spectra[5] of ArH^+, ArD^+, and KrH^+, generated in dc discharges, with the use of Fourier transform techniques has now been reported. Although this method is potentially a powerful approach to ion spectroscopy, it suffers from loss of the high spatial and frequency resolution inherent to laser experiments and is also subject to the same problems encountered in laser absorption spectroscopy. In this Letter we report the development of a new general technique for studying infrared absorption spectra of charged molecules which overcomes the limitations discussed above, and the implementation of this technique to measure the ν_1 vibration-rotation spectrum of the formyl ion (HCO^+).

The formyl ion has been of central importance both in establishing the significance of molecular ions in interstellar chemistry and in the development of laboratory techniques for the study of charged molecules. Pure rotational transitions of HCO^+ were initially detected by radio astronomy,[6] and somewhat later by laboratory microwave spectroscopy of glow discharges.[7] Subsequently, its rotational spectrum has been further investigated in both fields.[8] Most recently, laboratory rotational spectra of the stable isotopic forms of HCO^+ have been measured in both ground[9] and excited vibrational states[10] and in high rotational levels.[11] In extensive microwave studies by Woods and co-workers[9, 10, 12] it was clearly demonstrated that spectra of ions and neutrals in discharges can be distinguished by exploitation of the charge on the ion. In cases where collisional broadening determines the spectral linewidth ($\bar{\nu}/p \lesssim 10^3$ cm^{-1}/Torr), the monopole-induced dipole interaction, which dominates ion-neutral collisions, results in the spectral profiles of ions being several times broader than those of similar neutral species.[10, 12] In addition, positive-ion absorption profiles exhibit a Doppler shift because of their net drift velocity in the direction of the cathode of a discharge.[9, 10] The magnitude of the drift velocity varies with the nature of the ionic species, the background neutral gas, and the discharge parameters, but is typically 300 m/sec for HCO^+ in hydrogen at 1 Torr. This corresponds to a Doppler shift of several parts per million in the absorption frequency—about the same magnitude as the Doppler linewidth. At infrared wavelengths the large value of $\bar{\nu}/p$ (4×10^3) makes collisional broadening effects difficult to observe, but the Doppler-shift effect still serves as a definitive indicator for absorptions that are due to a charged species. In our experiment, the polarity of a glow discharge is reversed at several kilohertz, thus alternately red- and blue-shifting ion absorption frequencies at this rate, or equivalently, frequency modulating the laser in the ion frame of reference. Lock-in detection thus yields the infrared spectrum of charged molecules with very little interference from the overwhelmingly more abundant neutral species.

The experimental arrangement is shown in Fig. 1. A color-center laser system (Burleigh FCL-20), operating on a F_A(II)-type RbCl:Li crystal pumped with a krypton-ion laser (Spectra Physics 171) that is amplitude stabilized by a Coherent Radiation "Noise Eater," produces 0.1–1.0 mW of narrow-band (1 MHz) cw radiation continuously tunable over the range 3600–3100 cm^{-1}. The infrared radiation is directed through a liquid-nitrogen-cooled discharge cell (0.9 cm × 100 cm) and detected with an InSb photodetector (Santa Barbara Research Center Model No. C322). A 1–8-kHz discharge is sustained in the cell by a symmetric bipolar square-wave voltage originating in

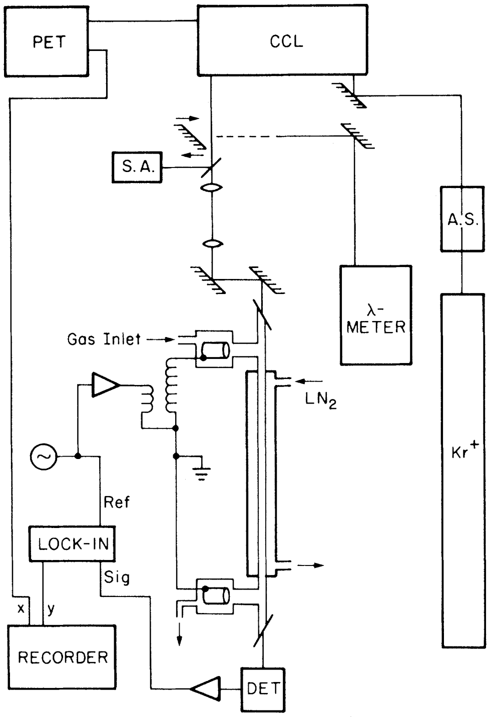

FIG. 1. Schematic of the velocity modulation spectrometer. A.S., amplitude stabilizer; S.A., spectrum analyzer; CCL, color-center laser.

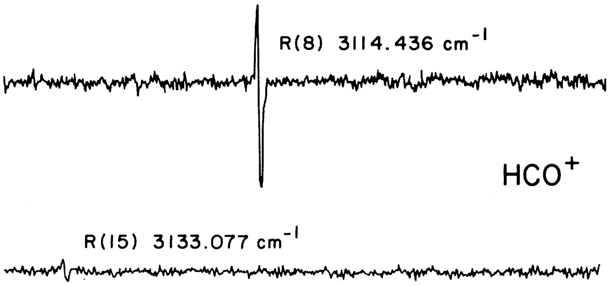

FIG. 2. The $R(8)$ and $R(15)$ transitions of HCO$^+$. These are approximately the strongest and the weakest and were observed with a 40-msec time constant.

a signal generator, amplified by a 700-W power booster (Phase Linear Model 700), and stepped up to 1–5 kV with a series of signal transformers. This configuration typically produces currents of 30–100 mA rms in the 0.65-cm^2 cross-section discharge cell operated with mixtures of H_2 and CO at total pressures near 1 Torr. The color-center laser is scanned by ramping the voltage on an intracavity etalon (~ 20 GHz free spectral range) while keeping the cavity length fixed and continuously adjusting the grating for optimum overlap of the grating tuning curve with the etalon mode being scanned. This produces tuning in 300-MHz cavity mode-hop increments over a range of ~50 GHz. Single-mode operation of the laser is insured by monitoring the laser output with a 7.5-GHz spectrum analyzer (Burleigh FCL-975). The laser wavelength is measured with an absolute accuracy of ± 0.003 cm^{-1} with a wavemeter (Burleigh WA-20) modified for low laser input power. The output of the InSb detector is routed to a lock-in amplifier (Ithaco 393), demodulated, and displayed on an XY recorder. The velocity-modulated absorption spectra of molecular ions then appear with approximately first-derivative line shapes as shown in Fig. 2. With the ν_1 frequency of HCO$^+$ predicted by Hennig, Kraemer, and Diercksen[13] (3058 cm^{-1}) as a guide, the region from 3300 cm to 3100 cm^{-1} (presently the end of our tuning range) was searched in a discharge through a 10/1 mixture of H_2 and CO at a total pressure of 800 mTorr. These discharge conditions were chosen to provide a satisfactory compromise between HCO$^+$ production and ion mobility[10]; at maximum discharge current (100 mA rms) they were subsequently found to be optimal. A total of nineteen lines, all in the R branch, were observed and measured with the wavemeter. These are given in Table I, where the frequency listed is the average of the red- and blue-shifted components. The precision of individual measurements is presently limited by the cavity mode-hop increment to ± 300 MHz; the uncertainty in wavemeter readings is ± 100 MHz at these frequencies.

The assignment of this spectrum to the ν_1 band of HCO$^+$ is based simply upon the observed chem-

TABLE I. Observed spectral lines of the ν_1 band of HCO$^+$.

Transition	Frequency (cm^{-1})	Transition	Frequency (cm^{-1})
$R(0)$	3091.679	$R(10)$	3119.882
$R(1)$	3094.612	$R(11)$	3122.573
$R(2)$	3097.515	$R(12)$	3125.232
$R(3)$	3100.395	$R(13)$	3127.871
$R(4)$	3103.251	$R(14)$	3130.481
$R(5)$	3106.084	$R(15)$	3133.077
$R(6)$	3108.886	$R(16)$	3135.636
$R(7)$	3111.674	$R(17)$	3138.178
$R(8)$	3114.436	$R(18)$	3140.7[a]
$R(9)$	3117.171		

[a] Based on a single measurement.

istry and spectroscopic porperties. Although we have not yet been able to detect the band origin and P branch of this band (because of the color-center laser frequency limit of 3100 cm^{-1}) and an unambiguous assignment of J is not possible, it is possible to determine $B_1 - B_0$ precisely from the first differences. If we neglect centrifugal distortion, the difference in rotational constants is found to be 363 ± 6 MHz, which compares very well with that measured by microwave spectroscopy[10] (353.89 ± 0.04 MHz). Furthermore, if one assumes the J assignment given in Table I and $D_1 = D_0 = 82$ kHz,[11] the sum ($B_1 + B_0 = 88\,885 \pm 100$ MHz) and a more accurate value for the difference ($B_1 - B_0 = 857.5 \pm 6$ MHz) are obtained. The microwave work has determined the sum to be $88\,834.97 \pm 0.04$ MHz. Because of its similar structure, HOC^+, the metastable isomer of HCO^+, may conceivably be the spectral carrier. Previous work[10, 14] has shown, however, that HOC^+ is not an abundant constituent in H_2/CO discharges. Also, reassigning J by one unit leaves $B_1 - B_0$ essentially unchanged and gives $B_1 + B_0 = 89\,655$ MHz. $B_1 + B_0$ for HOC^+ can be estimated to be $\sim 89\,120 \pm 50$ MHz with use of a theoretical prediction of α_1.[13] On the basis of the J assignment given in Table I, we determine the value 3088.727 ± 0.003 cm^{-1} for the observed vibrational frequency, in excellent agreement with the *ab initio* result for the ν_1 band of HCO^+ (3058 cm^{-1}).[13]

Several observations regarding the velocity modulation technique can also be made. HCN is known[10] to be abundant in H_2/CO discharges because of ubiquitous N_2 impurities. However, a search for the ν_1 band of HCN near 3311 cm^{-1} under conditions which optimize the HCO^+ spectra yielded negative results. One expects that asymmetry between the positive and negative half-cycles of the ac discharge would lead to a concentration modulation of short-lived ($\tau \leq 1/f_{\text{mod}}$) neutral species. This has indeed been observed in one case for an unidentified neutral absorber, wherein the intensity of a spectral feature (which consisted of a single lobe, not the derivative line shape shown in Fig. 2) increased with an increasing ratio of the dc to ac components of the discharge current. Moreover, lock-in detection at $2f_{\text{mod}}$ resulted in a fivefold enhancement in the strength of this neutral signal, while nearby HCO^+ lines became barely observable. It is possible that in certain cases fast neutrals created by charge-exchange reactions will be nearly as abundant as charged species. The resulting neutral absorption signals could then appear similar to those of charged absorbers, but as yet, such spectra have not been observed.

Because the strength of the HCO^+ signals depends on both the ion velocity and the ion density, we cannot separately determine both properties at this time. However, we estimate the density of HCO^+ to be near 10^{11} cm^{-3} on the basis of other work[10]; the strongest lines in the HCO^+ spectrum correspond to a fractional absorption of $\sim 3 \times 10^{-3}$, indicating a sensitivity near 10^{-5} cm^{-1} for the velocity-modulation method, which is about the same as that for the difference-frequency experiment. Hence, the velocity-modulation approach to infrared laser spectroscopy should prove useful for the study of a variety of important molecular ions. Moreover, since the ratio of the drift-velocity Doppler shift to the Doppler linewidth is independent of frequency, this same technique can be applied in a variety of spectroscopy experiments spanning frequencies from the microwave through the visible.

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