

LABORATORY MEASUREMENT OF THE PURE ROTATIONAL SPECTRUM OF VIBRATIONALLY EXCITED HCO^+ ($\nu_2 = 1$) BY FAR-INFRARED LASER SIDEBAND SPECTROSCOPY

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ABSTRACT

Laboratory observations of the pure rotational spectrum of HCO^+ in its lowest excited bending state $(\nu_1, \nu_2', \nu_3) = (0, 1^1, 0)$ are reported. Because of their severe excitation requirements, such vibrational satellites and the high- J ground-state lines also measured here sample only hot, dense regions of matter in active molecular cloud cores and circumstellar envelopes. As the HCO^+ abundance is tied directly to the gas fractional ionization, it is probable that the vibrationally excited formyl ion transitions will provide high-contrast observations of *shocked* molecular material, rather than the more quiescent, radiatively heated gas surrounding stellar sources detected with the few vibrationally excited neutral species observed to date.

Subject headings: interstellar: molecules — laboratory spectra

I. INTRODUCTION

The tremendous energy released by intense radiation fields and shocks from young, embedded stars and stellar winds can produce regions with very high densities and temperatures in active molecular cloud cores. Recently, several molecules (HC_3N , CH_3CN , CH_3OH , HCN , and perhaps SO_2 ; Goldsmith *et al.* 1983; Hollis *et al.* 1984; Ziurys and Turner 1986) have been detected in such regions by means of their pure rotational spectra in their first excited vibrational (torsional) state, primarily in the Orion molecular cloud (OMC-1) and in the circumstellar envelope surrounding IRC +10216. The predominantly cyano-containing species observed to date, however, commonly have their highest abundance in the warm, neutral gas heated radiatively by the central stellar source. Only vibrationally excited H_2 emission near $3.8 \mu\text{m}$ has been shown to arise from directly shocked material (Beckwith *et al.* 1978).

In addition to providing much of the “backbone” of interstellar chemistry in cold clouds, ion-molecule reaction networks are also prevalent in shocked regions. Indeed, both Elitzur (1983) and Vogel *et al.* (1984) have reported increased ionization fractions in shocked gas surrounding supernovae remnants and young stellar objects. We have therefore performed laboratory measurements of the rotational spectrum of HCO^+ in the $(\nu_1, \nu_2', \nu_3) = (0, 1^1, 0)$ first excited bending state in the hope of providing a specific shock tracer of dense molecular gas. The first excited bending state should be much easier to observe in interstellar molecular clouds than the corresponding stretching vibrations because it appears at much lower energy. These results were guided by the predictions from previous high-resolution infrared spectroscopy (Davies and Rothwell 1984; Kawaguchi *et al.* 1985), and provide the necessary laboratory measurements of the pure rotational

spectrum of HCO^+ in the excited $\nu_2 = 1$ state to begin interstellar searches for these transitions. We also present accurate laboratory measurements of several high- J rotational lines of HCO^+ in its vibrational ground state which may prove useful as another tracer of dense, shocked material.

II. EXPERIMENTAL

The $(\nu_1, \nu_2', \nu_3) = (0, 0, 0)$ and $(0, 1^1, 0)$ measurements of HCO^+ were performed with a recently constructed tunable far-infrared (FIR) laser sideband spectrometer at UC Berkeley. A detailed description of the instrument will appear elsewhere (Blake *et al.* 1987). As with other systems, the current spectrometer places continuously tunable sidebands onto line-tunable FIR gas lasers by mixing the laser output with microwave radiation in a nonlinear element. Here, the mixing is performed by a GaAs Schottky-barrier diode (R. Mattauch, University of Virginia, no. 1E11) mounted in a tunable rooftop structure, which serves to optically couple the laser radiation onto the diode and to reradiate the laser sidebands via a longwire antenna (Sauter and Schultz 1977). An instantaneous mixing bandwidth of 40 GHz is provided by coupling 2–26 GHz radiation (HP synthesizer 8673B) coaxially, and 26–40 GHz radiation through waveguide after harmonic generation and amplification. In order to both couple arbitrary laser polarization onto the diode and to isolate the tunable sidebands from the overwhelmingly more intense carrier, a polarizing Michelson interferometer is inserted between the laser and the corner reflector (Martin and Pulpert 1970). Reduction of optical coupling between the mixer mount and the laser cavity is accomplished by an adjustable mesh Fabry-Perot cavity (finesse = 10) adjacent to the FIR laser output coupler.

After isolation by the Michelson interferometer, the sideband radiation is then passed through a flowing discharge cell and detected by a liquid helium cooled InSb hot-electron bolometer (Cochise Instruments). Spectra have been recorded

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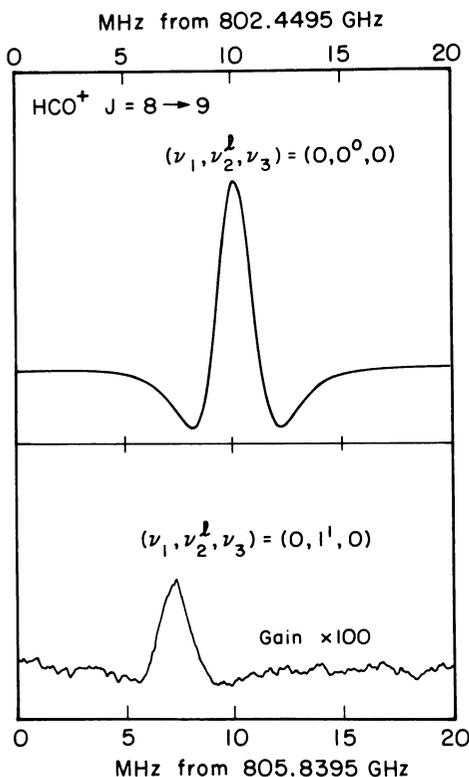


FIG. 1.—Sample spectra of the ground- and excited-state $J = 8 \rightarrow 9$ HCO^+ transitions taken with the 787 GHz DCOOD laser.

using frequency modulation of the microwave source. Specifically, a 51 kHz sine wave is applied to the FM port of the HP 8673B, and lock-in detection occurs at the second harmonic. Absorption signals therefore appear as second derivatives.

HCO^+ ions were produced in a liquid nitrogen cooled, magnetically confined DC discharge similar to that introduced by De Lucia *et al.* (1983). In the current configuration, the cell walls and magnet may be cooled independently. Decreasing the cell diameter from the minimum reported value of 1.5'' (De Lucia *et al.* 1983) to 0.7 increased the ion signals dramatically. An equimolar mixture of H_2 and CO at a total pressure of about 40 mtorr, a discharge current of 30–50 mA, and a longitudinal field strength of 300 G was found to optimize the vibrationally excited signals. Figure 1 displays sample spectra of the ground-state and excited-state HCO^+ transitions taken with the 787 GHz DCOOD laser. From the observed intensities, an effective vibrational temperature of $200 < T_{\text{vib}} < 250$ is derived. We note that this temperature is considerably cooler than that found for positive column discharges also used to study excited vibrational states of HCO^+ and other simple ions [$T_{\text{vib}}(\text{HCO}^+) \approx 1000$ K; Gudeman 1982; Gruebele, Polak, and Saykally 1986].

III. RESULTS

The ν_2 vibration-rotation band of HCO^+ near 830 cm^{-1} has been studied previously by both Davies and Rothwell (1984) and Kawaguchi *et al.* (1985) using diode laser spectroscopy, but their results are not accurate enough to unambiguously identify vibrationally excited HCO^+ lines in the

TABLE 1

MEASURED TRANSITION FREQUENCIES

l_{upper}	Frequency (MHz) ^a	Parity
$\nu_1\nu_2^l\nu_3 = (0, 0^0, 0)$		
8	713342.090(200)	...
9	802458.329(200)	...
$\nu_1\nu_2^l\nu_3 = (0, 1^1, 0)$		
7	623882.997(200)	1c
	626845.406(200)	1d
8	712969.206(200)	1c
	716354.689(200)	1d
9	802039.079(200)	1c
	805845.788(200)	1d

^a 2σ uncertainties in parentheses (kHz).

biguously identify vibrationally excited HCO^+ lines in the dense millimeter wave spectrum of molecular clouds (Sutton *et al.* 1984). Table 1 presents a listing of the lines measured in this work. Calibration of the laser frequency has been performed with CO and OCS as reference gases. The overall accuracy is estimated to be ± 200 kHz (2σ), but the individual l -type doubling splittings are known better as they are measured on the same FIR laser line in rapid succession. Rotational constants for the two states have been determined by fitting the center of gravity of the l -type doublets with the standard equation for a linear rotor in an excited bending state:

$$\nu = 2B_{\nu_1\nu_2\nu_3}(J+1) - 4D_{\nu_1\nu_2\nu_3}(J+1)[(J+1)^2 - l^2], \quad (1)$$

where $B_{\nu_1\nu_2\nu_3}$ and $D_{\nu_1\nu_2\nu_3}$ are the usual rotational and distortion constants, J is the rotational quantum number of the lower state, and l is the vibrational angular momentum quantum number, while the l -type doubling has been fitted using the difference between the individual doublets and the equation

$$\Delta\nu = 2q_{\nu_1\nu_2\nu_3}(J+1) - 4q_D(J+1)^3 \quad (2)$$

(Gordy and Cook 1984). Unlike the infrared work, the precision here is sufficient to determine not only the l -type doubling constant $q_{\nu_1\nu_2\nu_3}$ but also the centrifugal constant q_D . Seven constants, the rotational and distortion constants for the upper and lower states and the l -type doubling constants q and q_D , are therefore required to fit the observed pure rotation data.

We have performed a weighted fit of all microwave, millimeter, and FIR data available on the ground-state and $\nu_2 = 1$ state of HCO^+ , the results of which are presented in Table 2. The ground-state microwave, millimeter, and FIR data not reported here are taken from Gudeman (1982), Sastry, Herbst, and De Lucia (1981), and van den Heuvel and Dymanus (1983). A simultaneous fit including the diode laser work of Davies and Rothwell (1984) and Kawaguchi *et al.* (1985) on

TABLE 2
 DERIVED ROTATIONAL CONSTANTS OF HCO⁺

Constant	Value (MHz) ^a (0, 0 ⁰ , 0)	Value (MHz) ^a (0, 1 ¹ , 0)
$B_{\nu_1\nu_2\nu_3}$	44594.43631(72)	44676.98025(246)
$D_{\nu_1\nu_2\nu_3}$	0.0827668(96)	0.084433(180)
$H_{\nu_1\nu_2\nu_3}$	0.298(37) ^b	...
$q_{\nu_1\nu_2\nu_3}$	211.7783(56)
$q_D(\nu_1\nu_2\nu_3)$	0.001842(40)

^aError bars in parenthesis are 2 σ .

^bValue for H distortion constant in Hz.

the $\nu_2 = 1$ state yields essentially the same rotational constants for the upper state (the ground-state constants were fixed to the microwave values in the diode laser studies) because of the higher precision of the tunable FIR technique. Introducing the distortion constant q_D changes the value of q_{010} by a negligible amount. Although both Davies and Rothwell (1984) and Kawaguchi *et al.* (1985) measure a similar number of lines and report uncertainties of 0.0005–0.001 cm⁻¹, the 3 σ error bars of Kawaguchi *et al.* (1985) are considerably smaller (up to a factor of 10). The present results and the constants of Davies and Rothwell (1984) are in agreement as are our rotational constants and those of Kawaguchi *et al.* (1985), but their l -type doubling constant and that from the present work differ by nearly 9 σ . These results dramatically illustrate the need for prior *direct* laboratory measurement of pure rotational transitions in the millimeter and submillimeter regions before interstellar searches are attempted, and they demonstrate also the dangers in overinterpreting the accuracy of diode laser data for even simple reactive species.

Because of the high correlations among the constants and the limited nature of the present data set, it is necessary to include this correlation in any estimates of the uncertainties in the HCO⁺ pure rotational spectrum (cross-correlation parameter = 0.982). As an aid to future work we present in Table 3 a listing of all excited bending state transitions lying longward of the 350 μ m atmospheric window. The frequency uncertainties of these transitions translate into an approximately constant velocity window of ± 0.15 km s⁻¹ and should

 TABLE 3
 PREDICTED PURE ROTATIONAL FREQUENCIES OF HCO⁺

J_{upper}	(0, 0, 0) (MHz) (2 σ , kHz)	(0, 1 ¹ , 0) Lower (MHz) (2 σ , kHz)	(0, 1 ¹ , 0) Upper (MHz) (2 σ , kHz)
1 ...	89188.542(002)
2 ...	178375.065(006)	178282.361(094)	179129.430(094)
3 ...	267557.619(008)	267418.530(128)	268689.023(128)
4 ...	356734.288(012)	356548.686(152)	358242.470(152)
5 ...	445902.996(018)	445670.826(158)	447787.725(158)
6 ...	535061.711(024)	534782.943(147)	537322.735(147)
7 ...	624208.522(034)	623883.035(090)	626845.456(090)
8 ...	713341.416(048)	712969.127(081)	716353.808(081)
9 ...	802458.400(066)	802039.158(129)	805845.797(129)
10 ...	891557.480(092)	891091.151(175)	895319.350(175)
11 ...	980636.660(128)	980123.101(220)	984772.418(220)

easily be accurate enough to definitively identify vibrationally excited HCO⁺ emission from interstellar molecular clouds.

During the course of this work we learned of an independent series of measurements on the vibrationally excited rotational spectra of several isotopes of HCO⁺ in the laboratory of R. C. Woods (Woods 1987). These measurements extend from the rotational ground state to $J = 5$, and as such nicely complement the present observations. A fully optimized set of molecular constants would therefore involve the fitting of both data sets.

IV. DISCUSSION

The large spontaneous emission coefficients associated with the far-IR and mid-IR transitions which connect the ground-state and excited bending states of interstellar molecules (typically 1 s⁻¹) imply that densities of at least 10⁹–10¹¹ cm⁻³ are required to fully thermalize the observed pure rotational transitions from excited vibrational states. Even if large optical depths are invoked for the vibrational transitions, the required densities exceed those in all but the densest cloud cores. Thus, modeling of the vibrationally excited emission detected to date has concentrated on very dense, predominantly neutral regions immediately adjacent to intense IR and FIR sources (i.e., stars) whose radiation bathes and permeates the gas (Goldsmith *et al.* 1983). The density of the region must still be quite high (10⁶–10⁸ cm⁻³) to build up a detectable column density of molecules in the small source pumped by the IR and FIR fields, and in the limit of large optical depth trapping, such densities could conceivably compete with radiative pumping mechanisms. Only for larger molecules such as CH₃OH for which the bending or torsional modes lie at very long wavelengths have predominantly collisional excitation mechanisms been proposed, however. Even so, radiative pumping can lead to quite intense emission from highly excited states, as is evidenced by the recent detection of the $\nu_2 = 1$, $J = 3 \rightarrow 2$ HCN doublet lying nearly 1000 K above the ground rotational manifold (Ziurys and Turner 1986).

Further reinforcing the detection of such molecules in relatively quiescent regions of very dense gas is the neutral character of the observed species. High temperatures and densities combined with intense radiation fields are also present in shocks, as is best evidenced by the intense vibrational H₂ emission often associated with shock activity (Beckwith *et al.* 1978), but the column densities of hot material are small, and thus the more abundant warm material which surrounds the shock dominates the observed emission.

By virtue of its ionic character, however, HCO⁺ naturally samples different regions of interstellar gas than neutral species like HCN or CH₃OH. Most importantly, because of its charge and high abundance, HCO⁺ formation and destruction pathways are directly tied to the fractional ionization of the gas. Indeed, isotopes of HCO⁺ have been used to derive bounds on the free electron abundance in dense cloud cores (Guelin, Langer, and Wilson 1982). Simple analytical modeling and more complex numerical routines have shown that the fractional ionization in quiescent material varies roughly as $n^{-1/2}$. Thus, HCO⁺ tends to avoid the very dense, warm regions sampled by vibrationally excited neutral molecules. Early

models predicted that HCO^+ would also be destroyed rapidly in shocked material (Iglesias and Silk 1978), but more recent observational evidence and modeling suggests that, in fact, the HCO^+ abundance can be considerably enhanced by shocks. In supernova remnants this enhancement occurs via the trapping of cosmic rays to increase the gas fractional ionization (Elitzur 1983), while in molecular cloud cores the increased X-ray flux from young stars near shock fronts has been proposed as the ionization enhancement mechanism (Vogel *et al.* 1984). Further support for the presence of HCO^+ in shocked material in OMC-1 comes from the similar velocity profiles of the HCO^+ rotational lines with those of vibrationally excited H_2 . Intense IR and FIR fields will also be present in and near shock fronts in molecular clouds, and excitation of the HCO^+ ν_2 mode at 830 cm^{-1} (1200 K) should produce detectable pure rotational emission in the millimeter wave region.

To summarize, then, because the HCO^+ abundance is dramatically lowered in dense, quiescent regions the lower

column densities of material along shock fronts will not be masked by intense emission from the surrounding warm, quiescent gas. High-excitation conditions are also required for the high- J ground state transitions reported here, but because they occur in the submillimeter region of the spectrum they are much more difficult to observe. The low- J transitions of the excited bending state, however, offer the opportunity to study highly excited material in or near regions with enhanced ionization fractions such as shock fronts with good sensitivity from ground based observatories.

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