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Microwave Absorption Spectrum of the CO^+ Ion*

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The $K = 0 \rightarrow 1$ pure rotational spectrum of CO^+ ($X^2\Sigma, v = 0$) has been detected in a direct absorption experiment, in which microwave radiation is passed through a $3\frac{1}{2}$-m-long dc glow discharge in carbon monoxide or a helium–carbon-monoxide mixture. The discharge tube is cooled with liquid nitrogen, and the signal is detected with source modulation and computer-controlled signal averaging. The measured frequencies are 117 692.55 MHz ($J = \frac{1}{2} \rightarrow \frac{1}{2}$) and 118 101.99 MHz ($J = \frac{1}{2} \rightarrow \frac{3}{2}$).

Although the microwave rotational spectra of molecular ions potentially contain the same sort of precision quantitative information on molecular structure, chemical bonding, and molecular dynamics as those of neutral molecules, the only nonoptical spectrum of an ion so far reported is that of H_2^+, for which Jefferts[1] has observed several magnetic dipole transitions within the spin and hyperfine multiplets using an indirect method. (The efficiency of photodissociation of the H_2^+ contained in an ion trap, and thus the ratio H_2^+/H^+, is changed when the rf radiation is resonant with the hyperfine intervals.) The more obvious technique of observing the absorption of the microwave radiation directly has not been previously employed because of the difficulties encountered in producing a sufficient quantity of ions in a manner which does not interfere with the transmission of microwaves or the sensitive detection system of the spectrometer. The microwave spectrometer[2] which we have used to observe several transient and stable neutral species seemed to us to provide a solution to these difficulties. Its sample region was the plasma of a dc glow discharge, which certainly contained ions, and the presence of the discharge had been shown not to interfere unduly with the spectrometer signal. The only question was whether the sensitivity would be adequate for the rather low ion density, and detailed considerations led us to believe that it would be in favorable cases. In this Letter we wish to report that this belief has been confirmed with a successful observation of the two components of the $K = 0 \rightarrow 1$ transition of CO^+. The latter was a particularly advantageous ion because of its large dipole moment (~2.5 D[3]), its chemical suitability, its lack of nuclear spin splittings, and the availability of rather precise values of its molecular constants from previous optical work.

With the possible exception of X-ogen,[4] which has been tentatively identified[5] as HCO^+, ions have not been observed in the interstellar medium by radio astronomical techniques, in part because of their low abundance relative to neutral molecules, but also because of the lack of laboratory measurements of the frequencies of their microwave transitions. If these difficulties could be overcome, however, observations of the radio spectra of ions in the interstellar clouds would certainly be of great interest, because ions and ion-molecule reactions play a prominent role in

recent theories of the formation and chemistry of molecules in space.[6-10] The present measurements should greatly facilitate astronomical searching for CO^+ and permit positive identification of any spectrum that may be found. Although CO is one of the most abundant molecules in the interstellar clouds, CO^+ is expected to be rare compared to other ions because it is efficiently removed by reaction with hydrogen.[10,11] Whether interstellar sources exist with sufficient column densities of CO^+ for it to be detectable with currently available sensitivity is not clear. Another possibility, however, for astronomical observation of this ion's rotational spectrum lies in the ionic tails of comets, where CO^+ is thought to be the predominant molecular species.[12-14]

The basic apparatus, in which microwave radiation is passed down a 15-cm×3½-m discharge tube, is exactly as it has been described previously.[2] An OKI 120V10 klystron was the radiation source, and a Baytron 1N-5 crystal holder with a 1N-5/X diode was used as the detector. A Raytheon 704 computer system was used to digitize, store, and average the spectrum. The klystron frequency was swept repetitively and data points were taken at uniform time intervals. The difference frequency between the klystron and the fourth harmonic of a 30-GHz, phase-locked, computer-controlled, digital source[15] (backward-wave oscillator) was passed through an i.f. amplifier and a 57-MHz FM discriminator. The latter's output was monitored by the computer to generate markers for synchronizing the beginning of data taking on a given sweep and for measuring the frequency of the absorption line. When an initial search at room temperature using the Zeeman modulation system of Woods[16] proved unsuccessful, we substituted an identical glass discharge tube equipped for liquid-nitrogen cooling but lacking the magnet coils. Cooling was accomplished with several hundred feet of ¼-in. gum-rubber tubing coiled closely around the pipe, covered with 2 in. of Fiberfrax insulation (No. 4 density, Carborundum Corporation), and fed by a continuous flow from a pressure vessel. A 30-kHz source-modulation (FM) scheme was employed with a square wave form which went positive and then negative on alternate excursions from zero[17]. This technique minimizes the spurious baseline shift normally associated with source modulation.

The stronger $J=\frac{1}{2}\rightarrow\frac{3}{2}$ transition was originally detected in a pure-carbon-monoxide discharge, but it was found that a 90% He–10% CO mixture, which was conveniently available and was the only mixture tried, worked substantially better. The signal also improved after several hours of continuous running as visible deposits of CO_2 accumulated on the tube surface. Similar enhancement could also be achieved by distilling some dry ice into the cell directly, before starting the discharge. The color of the discharge and the wave form of its anode voltage were found to be strongly correlated with the optimum production of the signal. In particular the presence of air seemed to irreversibly spoil the CO^+ signal and characteristically change the color and anode wave form on a given cooling cycle. The optimum pressure reading on the thermocouple gauge on the cathode was about 35 mTorr. Figure 1 shows the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ line after about 1 h of averaging under optimum conditions. As predicted earlier[2,16] the presence of the discharge affects the spectrometer substantially less at these millimeter wave frequencies (almost negligibly) than in previous experiments below 40 GHz. By comparison with the signal strength of the molecular oxygen signal at 118 750 MHz in (low pressure) air, the absorption coefficient γ, under the conditions of Fig. 1, is estimated to be very approximately 2×10^{-7} cm^{-1}. The pressure-broadening linewidth cannot be estimated accurately for many reasons: incomplete modulation, nonflat baseline, Zeeman broadening, source instability, questionable pressure measurement, etc. Nevertheless, as can be seen in Fig. 1, the apparent linewidth $\Delta\nu$ is a few tenths of a MHz, and thus not grossly different from those of similar neutral molecules. That the signal was indeed that of an ion was indicated by the fact that its intensity was roughly

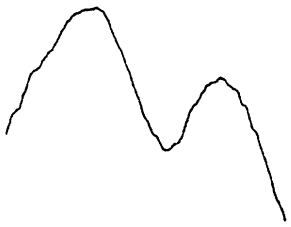

FIG. 1. The $J=\frac{1}{2}\rightarrow\frac{3}{2}$ transition of CO^+ after an average of 200 scans at a time constant of 100 msec. Each scan contained 1000 individual points and required about 15 sec. The width of the region shown is approximately 5 MHz. The discharge current was 395 mA in 32 mTorr of 90% He–10% CO with liquid-nitrogen cooling. The absorption line is the central depression which lies near a maximum in the baseline curve. The baseline pattern (but not the absorption line) may be completely changed by slight movement of the microwave horns.

proportional to current up to the maximum available, 450 mA, unlike that of previously observed neutral radicals like OH or SO. The assignment as CO^+ was also strongly supported by volatility considerations, the agreement of the frequencies with those predicted from the optical molecular constants, approximate agreement of the intensity ratio of the two lines with the expected 2/1 value, and especially, the Zeeman effect. The relation of Earth's magnetic field to the polarization of the microwave radiation was such that $\Delta M = \pm 1$ selection rules were expected. In agreement with the theory for a $^2\Sigma$ state, the weaker $J = \frac{1}{2} \rightarrow \frac{1}{2}$ transition was much more seriously broadened by Earth's field than the $J = \frac{1}{2} \rightarrow \frac{3}{2}$. In fact the former line was just barely detectable until we built a pair of coils for approximately canceling the $\frac{1}{2}$-G prevailing field, and this compensation in turn very noticeably improved the $J = \frac{1}{2} \rightarrow \frac{1}{2}$ line shape and intensity. Further evidence was obtained by reversing the current and looking at the $J = \frac{1}{2} \rightarrow \frac{3}{2}$ transition in a field of about 1 G. The latter line in this circumstance gave indication of breaking up into the theoretically expected symmetrical 1-6-1 triplet. We also observed that the $J = \frac{1}{2} \rightarrow \frac{3}{2}$ line was somewhat stronger with Earth's field canceled than without.

The measured frequencies are $117\,692.55 \pm 0.1$ MHz for the $J = \frac{1}{2} \rightarrow \frac{1}{2}$ transition and $118\,101.99 \pm 0.05$ MHz for the $J = \frac{1}{2} \rightarrow \frac{3}{2}$, where the error limits are somewhat wider than usual because of the weak signal and the nature of the measurement method. The theoretical expressions for these two frequencies are $2B_0 - 4D_0 - \gamma_0$ and $2B_0 - 4D_0 + \frac{1}{2}\gamma_0$,[18] respectively, where γ_0 is the spin-rotation coupling constant for the ground vibrational state. Using the optical value of D_0[18] for the small centrifugal distortion term, we obtain $B_0 = 58\,983.13$ MHz and $\gamma_0 = 272.96$ MHz. These are in excellent agreement with the values reported years ago from optical spectroscopy. Rao[18] gave a value of 1.9677_3 cm^{-1} (58 991 MHz) for B_0 based on an analysis of the first negative bands, and Woods determined γ_0 to be $+0.0102$ cm^{-1} ($+306$ MHz) from data on the comet-tail system.[19] In the absence of a precision microwave measurement of the vibration-rotation interaction constant α, the optical values[18] of B_e and r_e (1.1150_6 Å) cannot be improved significantly from our value of B_0, although they are certainly confirmed by it. Earlier this year other workers reported precision values of the spin-rotation constant of two other $^2\Sigma$ molecules, KAr[20] and CN.[21] The latter is isoelectronic with CO^+, and its γ value (217.1 ± 0.5 MHz) and that of CO^+ should provide an interesting pair of data points for comparison with the results of any theoretical calculations of the spin-rotation constant.

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