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[17] Since the distinguishable-atom nonreactive probability $P_{00\to1}{}^N(J)$ is very similar in both energy and J dependence to $P_{00\to1}{}^R(J)$, we expect that the nonreactive integral cross section $\sigma_{00\to1}{}^N$ should also have a peak at the resonance energy. This implies that the effect of atom indistinguishability should not appreciably alter the conclusions of this analysis.

[18] The smallness of this cross section may lead to experimental detection difficulties, and other reactive systems may be more favorable candidates for experimental investigation. The point we are making is nevertheless of significant conceptual importance, namely that resonances can exist and play an important role in chemically reactive collisions for which the corresponding potential energy surface does not have an attractive well.

[19] The individual partial-wave contributions to the differential cross sections are highly oscillatory in nature, and fairly slight calculational inaccuracies in the elements of the scattering matrix element for one partial wave are usually enough to upset the delicate balance between partial waves which leads to nonoscillatory differential cross sections, thereby resulting in strong spurious oscillations. It is reasonable to expect that the presence of resonances in some of the partial waves which contribute significantly to the cross sections should have a similar effect, as is experimentally observed for inelastic electron scattering. (See H. Ehrhardt, in *Physics of the One and Two Electron Atoms*, edited by F. Bopp and H. Kleinpoppen (North-Holland, Amsterdam, 1969), p. 598.

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Laboratory Microwave Spectrum of HCO^+†

R. Claude Woods, Thomas A. Dixon, Richard J. Saykally, and Peter G. Szanto
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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The $J = 0 \to 1$ rotational transition of the HCO^+ ion has been observed with the same apparatus used earlier for detection of CO^+. A discharge in various mixtures of hydrogen and carbon monoxide cooled to near liquid-nitrogen temperature was employed in a slow-flow system. The frequency we have obtained is 89 188.545 ± 0.020 MHz, but because of the ion drift velocity in the dc discharge this exceeds, by an unknown but small amount, the true rest frequency. This observation confirms the long-standing contention that the radio astronomical *X*-ogen line is in fact due to HCO^+.

In 1970 Buhl and Snyder[1] discovered a new molecular transition at 89190 MHz in several interstellar sources. Since they could not identify with certainty the species responsible for this emission they named it *X*-ogen. Later that year Klemperer[2] postulated that this mysterious line was actually due to the molecular ion HCO^+, whose theoretically predicted rotational constant agreed very well with that corresponding to the *X*-ogen frequency and which was expected to be a fairly stable and abundant species under the conditions prevailing in the interstellar clouds. Since that time this identification of *X*-ogen as HCO^+ has become fairly generally accepted, although it has not been definitely proven. Strong support for it has come recently from Snyder *et al.*,[3] who have reported observation of an interstellar line at 86 754 MHz which they identify as $H^{13}CO^+$. More recent theories[4,5] of the processes involved in forming interstellar molecules involve ion-molecule reactions in a crucial way, and HCO^+ is a cornerstone species in this modeling of interstellar kinetics. In fact it is so important that the whole picture would be tarnished if

X-ogen were not HCO^+. In this Letter we report observation of the 89 190-MHz transition in absorption in a laboratory glow discharge in mixtures of hydrogen and carbon monoxide, confirming that it is certainly due to HCO^+.

The apparatus used here was exactly the same as that previously described[6] in connection with the observation of CO^+ in this laboratory, except that the klystron was an OKI 90V10A. Although the absorption was not detectable at room temperature in a 400-mA discharge in a mixture of roughly 10% CO in H_2, as the cell was cooled to liquid-nitrogen temperature over a period of about 2 h, it became very distinct and easily observable. Subsequent experimentation with a range of P_{CO}/P_{H_2} ratios showed that the line was considerably stronger at roughly equimolar mixtures of the two gases. It was not observed in either pure H_2 or pure CO, disappearing within 1 or 2 min after the influx of either gas was stopped. This is approximately equal to the pump-through time in the flow system. The general behavior of the transition was very similar to that of CO^+ seen earlier, but the best signal-to-noise ratio or signal-to-background ratio was several times greater with HCO^+. The HCO^+ transition could be very easily seen in a single 2-sec scan with a time constant of 10 msec. In Fig. 1 is a trace representing a computer average of 562 scans at an overall pressure of about 10 mTorr, which was about half of the pressure that gave the strongest signal. Approximately 20 min were required to accumulate the data shown in Fig. 1. Interestingly the discharges in CO-H_2 mixtures were particularly stable, and there was essentially no observable contribution of either noise or background in the spectrometer signal due to the presence of the discharge.

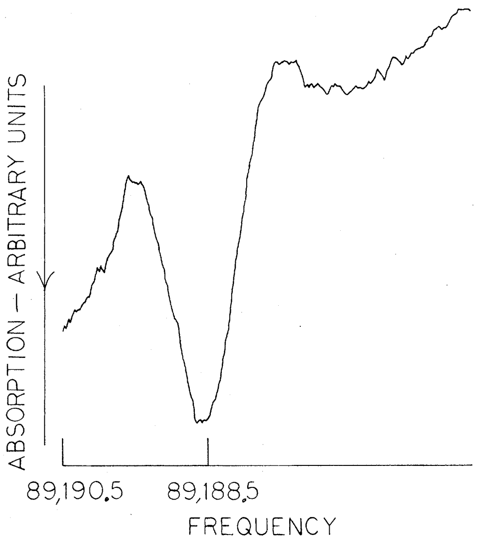

FIG. 1. The HCO^+ transition in a liquid-nitrogen cooled, 10-mTorr, 350-mA discharge in a CO-H_2 mixture with CO in excess. This is an average of 562 scans, each of 1000 points, taken at 1.5-msec intervals, with a 10-msec time constant. The 1,-2,1 intensity ratio is characteristic of the double-square-wave source-modulation method. The sloping baseline is the result of the inevitable detection, by any frequency-modulation method, of the variation of microwave power transmitted through the cell with frequency. This particular modulation method responds mainly to the second derivative, d^2P/df^2.

The precise frequency measurement was obtained from twelve separate averages of 100 scans each (with 3-msec time constant), six of them sweeping from low to high frequency, and six from high to low. On each the apparent frequency was determined from the relationship of the average marker position to the apparent line center assuming an i.f. of 57.1 MHz. The subsequent averaging of the high-to-low and low-to-high sweeps should then compensate for several obvious systematic errors such as uncertainty in the discriminator crossover frequency, time-constant distortion of the signal, finite time for the computer to sense the marker, etc. The frequency obtained in this way is 89188.545 ± 0.020 MHz, where the error is estimated from the scatter in the twelve separate determinations. There is, however, one systematic error, not taken into account in this procedure, which is specific to an ion. This is a Doppler shift due to the ion drift velocity in the dc discharge. The positive ions in this apparatus are drifting along the direction of the microwave propagation (towards the detector) with a drift velocity that is not known exactly. The magnitude to be expected for our pressure, temperature, etc., is several hundred meters per second[7] (300 m/sec corresponds to a Doppler shift of 90 kHz). Thus the true rest frequency is $\nu_r = 89188.545(1 - |v_d|/c)$ GHz. In future experiments we hope to reverse the polarity of the discharge and average to remove this ambiguity. For reasonable values of the drift velocity our measured frequency compares very well with Buhl and Snyder's original quoted value[1] of 89190 ± 2 MHz and their later refined value of 89189 ± 2 MHz,[8] and especially with three more recent astrophysical determinations: 89188.51 ± 0.15 MHz by Morris *et al.*,[9] 89188.65 ± 0.35 MHz by Hollis *et al.*,[10] and 89188.55 ± 0.10

MHz by Snyder and Hollis.[11] When our laboratory frequency is corrected for the drift velocity to obtain a true rest frequency, the astronomical data can be used to determine the velocity distribution of HCO^+ in various sources from the Doppler profile. The HCO^+ velocities can then be compared to those of the neutral species to see if there are any discrepancies, but the latter will obviously be rather small in general since the laboratory rest frequency is in such good agreement with the astronomical value derived from the assumption of equal ion and neutral velocities.

The line shape illustrated in Fig. 1 is sufficiently better than the best that was ever obtained in the CO^+ case that the linewidth may be estimated with somewhat greater confidence. From the data of Fig. 1 we obtain a half-width of 340 ± 25 KHz. In the HCO^+ case (as opposed to the CO^+ case) Zeeman broadening is not a factor, and we further expect wall broadening, modulation broadening, saturation broadening, and Stark broadening to be small relative to the observed width. In addition to pressure broadening, however, there is a fairly important contribution from the frequency instability, both long term and short term, of the unstabilized klystron. Furthermore if the ion kinetic temperature is not in thermal equilibrium with that of the background neutrals the Doppler broadening may be unusually large. The other major (but not insurmountable) problems in determining the pressure-broadening linewidth parameter (of HCO^+ broadened by H_2) are the measurement of the gas pressure within the discharge, the uncertainty of the true gas temperature, and the lack of knowledge of the actual gas composition, which may be different in different parts of the cell. Thus, for example, a small fraction of formaldehyde, which is a logical reaction product, would be expected to contribute considerable broadening because of the strong dipole-dipole interaction between the two strongly polar molecules, HCO^+ and H_2CO. In the future, however, we hope to define the conditions well enough to obtain at least an approximate value of the linewidth parameter of HCO^+ broadened by H_2 from this apparatus.

By comparing the signal strength of the HCO^+ line to that of the nearby $^{18}OC^{34}S$ $J=7\rightarrow 8$ transition we obtain an estimate of $\gamma \simeq 1\times 10^{-6}$ cm^{-1} for the peak absorption coefficient of the HCO^+ transition. The theoretical estimate of this quantity comes from the standard formula[12]

$$\gamma_{\max} = 8\pi^2 N f |\mu_{ij}|^2 \nu_0^2 / 3ckT\,\Delta\nu.$$

We have made an *ab initio* self-consistent-field calculation of the dipole moment of HCO^+ using a double-zeta-plus-polarization basis with the program POLYATOM[13] and have obtained a dipole moment of 4.3 D and a total energy of -112.9844 hartrees. Experience with neutral molecules whose dipole moments are known experimentally indicates that this self-consistent-field calculation overestimates μ by about 1 D. If we substitute $\mu = 3.3$ D, $T = 100°$K, and $\Delta\nu = 500$ kHz into this formula and solve for N assuming $\gamma_{\max} = 1\times 10^{-6}$ cm^{-1}, we obtain $N = 3\times 10^9$ cm^{-3} for the density of HCO^+ ions. We have previously made interferometric measurements of the plasma density in this discharge tube (at similar pressure but at room temperature) using several gases including pure CO and pure H_2 and obtained values in the range $(2-8)\times 10^9$ cm^{-3}. Thus the above estimate of the HCO^+ density appears consistent with the assumption that HCO^+ is one of the most abundant ions in the discharge.

Although a failure of the klystron has prevented immediate continuation of observations on HCO^+, the strength of the signal suggests that when microwave power of the necessary frequency and isotopically enriched samples are available observation of the corresponding spectra for each of the singly substituted isotopic variants will be quite practical. This will then permit a very precise determination of the bond distances in the free HCO^+ molecular ion.

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Alignment and Orientation Effects in Beam-Foil Experiments*

Yehuda B. Band†
James Franck Institute, University of Chicago, Chicago, Illinois 60637

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I present a theory of the orientation and alignment of atoms observed upon emergence from tilted foils. The interaction with the foil surface is taken into account in the production process of particular states. Once they are produced, the evolution of these states, under the influence of the residual field near the surface, is calculated in the fashion introduced by Eck. The most general effect of this evolution is presented.

Light emitted from fast atoms emerging from foils tilted with respect to the beam axis has a nonvanishing component of circular polarization.[1, 2] This indicates a net angular momentum of the excited electronic state along the axis of the circular polarization. I present the theory predicting and describing the orientation and alignment of excited atoms or molecules that are produced in collisions with foil targets.

Let the normal to the plane of the foil ($\hat{u}$) make an angle α with the beam axis ($\hat{z}$), as in Fig. 1 of Ref. 1, and let the light be viewed along the $\hat{x}$ axis. The circular polarization is proportional to the atomic orientation parameter defined by[3,4]

$$O_0^{\mathrm{det}} = \langle (i' | J_x | i) \rangle / j_i(j_i+1)$$

where the states $|i\rangle$ refer to the excited states produced and j_i is the angular momentum quantum number of the states. If we quantize the angular momentum of the excited state about the viewing axis $\hat{x}$,

$$O_0^{\mathrm{det}} = \textstyle\sum_i m_i \sigma(m_i) / j_i(j_i+1) \sum_k \sigma(m_k) ,$$

where $\sigma(m_i)$ is the cross section for producing a state with azimuthal quantum number m_i. Unequal populations of states with quantum number m and $-m$, a requirement if O_0^{det} is to be nonvanishing, can arise only if an axial vector can be constructed in the direction of the $\hat{x}$ axis. Such a vector is given by $\vec{k} \times \hat{u}$ where $\vec{k}$ is the momentum of the fast particle. The circular polarization dependence and thus the atomic orientation effects must therefore originate with the interaction of the incident particles with the surface as a whole. This is true of the alignment parameter A_{1+}[4]. This interaction must be included in the description of the *production* process of the excited states. The energy associated with the interaction of the beam with the foil surface is quite large and thus its inclusion in the production process is imperative. The effect of the foil-surface interaction upon departing atoms in their final excited states, if the interaction is divorced from the *creation* process,[5] is not sufficient to explain the observed phenomena.[6] That is, the precession of the multipole moments of excited states due to this interaction potential does not describe the observations.

Consider the excitation of the atoms or molecules in the beam from some initial electronic state $|\beta\rangle$ to a particular state of the manifold $|i\rangle$ of interest.[7] Assume the excited states of interest can be characterized as excitations of only one electron. The "active" electron of state $|\beta\rangle$ may interact with electrons in the foil to cause excitation. However, there are interactions with the surface as a whole, as well as the interactions within the interior of the foil between electrons bound in the projectile and foil electrons. Inside the solid electrons experience an average potential determined by the work function φ plus the Fermi energy ϵ_F. Positively charged particles encounter the negative of this potential. These potentials which abruptly end at the vicinity of the surface are also capable of producing excitation of $|\beta\rangle$. The essential difference between the atom-surface interaction and the interactions between atom and bulk electrons must be stressed.

The cumulative foil-surface interaction with the atomic core plus active electron must be described by a separate term in the transition ma-