Pressure Broadening of Gas Phase Molecular Ions at Very Low Temperature

J. C. Pearson,* L. C. Oesterling, Eric Herbst,† and F. C. De Lucia
Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio 43210-1106
(Received 5 July 1995)

A novel apparatus has been developed to produce large quantities of thermal molecular ions at temperatures well below the freezing points of their precursor neutrals. This apparatus has been used to study the pressure broadening of the $J = 3$-2 rotational transition of HCO^+ in H_2 gas at temperatures in the range 11–30 K.

PACS numbers: 34.20.Gj

A knowledge of rotationally inelastic scattering cross sections for collisions between ions and neutral species at temperatures under 50 K is crucial for a proper interpretation of radio astronomical spectral lines from dense interstellar clouds [1–3]. In these sources, the dominant gas phase constituent is H_2 while the most abundant molecular ion is HCO^+, making collisions between the two species important [4].

One method of investigating these low temperature inelastic collisions, using techniques pioneered in this laboratory for neutral species, is to study the pressure broadening of rotational spectral lines and to analyze the data to constrain the intermolecular potential [5]. However, the pressure broadening of molecular ions, even at higher temperature, has been little studied because of the experimental difficulties associated with producing large quantities of molecular ions and determining their temperature in the electrical discharge environment where they are typically produced. To the best of our knowledge, only two previous microwave studies have been reported. The first reported a pressure broadening coefficient γ of 29.6 ± 3 MHz/Torr for the $J = 1$-0 rotational transition of HCO^+ in H_2 gas at 100 K [6]. This coefficient is about 3 times larger than what would be expected from a neutral species with a large dipole moment colliding with H_2. The second study reported the J-dependent broadening of HCO^+ in Ar at liquid nitrogen temperature and determined broadening coefficients of 21.49, 17.51, and 14.56 MHz/Torr for the $J = 1$-0, 2-1, and 4-3 transitions, respectively [7].

In this work, we report a detailed experimental study of the pressure broadening of the $J = 3$-2 transition of HCO^+ by H_2 from 11.2 to 30 K. The challenge for the studies described in this paper was the development of a system which produces an adequate number density of molecular ions at temperatures far below the freezing point of their neutral precursors while simultaneously allowing the pressure and temperature of the collisional environment to be controlled and characterized. This was achieved by the development of a novel cell which is based on the magnetic enhancement of ion production in an abnormal glow discharge [8] and on collisional cooling [9]. The collisional cooling technique was originally developed to facilitate studies of the quantum nature of gas phase molecular collisions at temperatures of few kelvin [9,10]. More recently this method has been adopted by a number of workers for a variety of studies ranging from the observation of a gas dynamic NH_3 maser at very low temperature [11] to the simplification of infrared spectra [12]. The ion production technique uses a magnetic field parallel to an abnormal glow discharge to increase the average ion density by 2 orders of magnitude. The magnetic field dramatically lengthens the ion-rich negative glow region by preventing the ionizing electrons from colliding with the cell walls. This method has been widely used to facilitate the study of molecular ions [13,14].

In our earlier work on ion production [8], we pointed out that the cathode region in a magnetically enhanced abnormal glow discharge is functionally equivalent to an electron gun injecting keV electrons into an electric-field-free negative glow region [15–17]. However, the requirements to sustain the magnetically enhanced abnormal glow discharge significantly limit the combinations of pressure, voltage, gas mixture, and cell geometry that can be used. The allowed parameter space is further narrowed if the constraints imposed by collisional cooling are considered. We have therefore designed an apparatus in which the energetic electrons are produced by a simple electron gun, which decouples the electron energy and densities from the gas mixture and pressure while leaving the chemistry in the ion production region unaffected. We have tested and demonstrated the equivalence of the two approaches.

The experimental apparatus used in this experiment is shown in Fig. 1. The central region, in which the observations are made, is a collisional cooling cell with open ends to accommodate the electron beam. In this region, H_2 is maintained between 4 and 30 K by contact with the liquid or vapor cooled copper walls regulated by a feedback loop. In the middle of the central region, trace amounts of CO are continuously injected at ~200 K into the cold H_2 buffer gas, and cooled within 10–100 collisions to the measured cell wall temperature. The CO is effectively cryopumped by the helium temperature walls and, as was confirmed experimentally, has significant concentration only in the middle of the central region, as does the CO reaction product HCO^+. The central helium

 0031-9007/95/75(16)/2940(4)$06.00

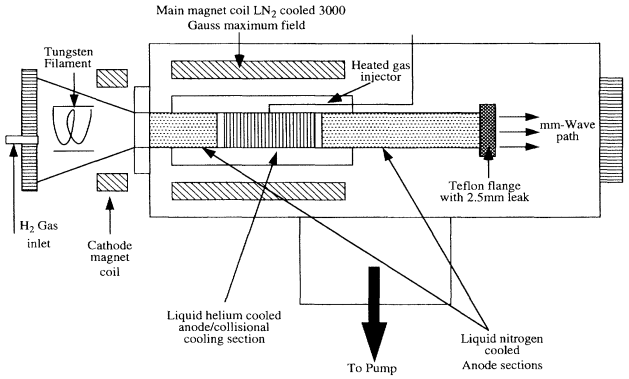

FIG. 1. The experimental apparatus, combining magnetic enhancement of ion concentrations, collisional cooling, and an electron gun ionization source.

cooled region is surrounded by a 77 K heat shield and thermally isolated at both ends from the 77 K cylindrical sections by Mylar cylinders sealed with indium. The H_2 buffer gas inlet is at one end and a cap with a 1 mm diameter hole is used at the other to maintain a pressure differential between the experimental region and the guard vacuum region.

The electron gun consists of a ac-heated tungsten filament located in a glass appendage to the main vacuum chamber for thermal and electrical isolation. A potential of $\sim$1 keV is maintained between the filament and the entrance to the 77 K cylinder. In addition to the axial magnetic field provided by the main solenoid, a separately adjustable magnetic field in the region of the cathode was used to optimize the trajectories of the electrons through the experimental region.

In operation, electrons are produced by the heated filament, accelerated by the electric field to $\sim$1 keV, guided to and through the collisional cooling region by the axial magnetic field, and collected in the 77 K exit region with most of their energy intact. In the collisional cooling region, HCO^+ is formed by several different ion-molecule reactions [18], such as $H_3^+ + CO$.

There are several important differences between this experiment and a standard collisional cooling experiment, chiefly the open cell ends and the electron beam. Consequently, special care is required to characterize the pressure and temperature of the collision partners. In order to understand the temperature in the cold region, we developed a quantitative model of heat flow [19]. This model shows that the H_2 thermal conduction between the two regions raises the temperature along the central axis a maximum of 0.5 K in the region populated by HCO^+. The electron beam deposits energy throughout the volume in proportion to current and gas density; nevertheless, it is possible to identify large regions of pressure, temperature, and current space where the electron beam has a negligible effect on the measured parameters. Additionally, it was possible to subject the model to independent experimental tests, including comparison with earlier studies of CO pressure broadening and comparison of observed HCO^+ linewidths as a function of electron beam current. The independence of linewidth on current demonstrates that the HCO^+ broadening is not increased noticeably by collisions with electrons.

The klystron-based millimeter or submillimeter wave spectrometer used here has been described in detail elsewhere [20,21]. All data were recorded in a fast sweep (20 ms) mode with sufficient postdetection bandwidth to preserve the true line shape. Pressure was measured by an MKS-690 baratron calibrated with an ion gauge as a zero reference; a geometry dependent transpiration correction was automatically applied. The temperature was measured by a calibrated Lake Shore Cryogenics 4-lead germanium thermometer.

Data sets at 11.2–30 K were taken at 1° intervals below 20 K, with no 17 K point, and 2° intervals above 20 K. The temperature of the gas is assumed to be the wall temperature and, for the data included in the fit, the absolute temperature accuracy is estimated to be 0.5 K. Any systematic error would result in a higher temperature than reported based on the heat sources discussed above. For the data included in the fit, a 0.5 K temperature error represents only a 5% relative error at the lowest temperatures. The uncertainty in the pressure broadening parameters from all sources in the overall measurements is estimated at 10%, with the largest contribution being the temperature uncertainty.

The data at each temperature were fit by a Voigt or Lorentizian line shape, with the latter being used when the linewidth was more than eight Doppler widths. At each temperature, 200 to 300 line shapes were recorded at pressures ranging from 0.5 to 20 mTorr. For each, the baseline standing wave pattern was suppressed by recording $\sim$100 scans with the electron excitation on, followed by another 100 scans with the excitation off. These data files were filtered for excessive residual baseline and temperature or pressure drifts. The half-widths measured from acceptable files at each temperature were plotted versus pressure and fit to two straight lines with slope γ (MHz/Torr), one with the zero-pressure intercept fixed to zero and one with the intercept a free parameter.

Two of the half-width versus pressure plots are shown in Figs. 2 (11.2 K) and 3 (28 K) along with the linear fits and predictions based on our heating model. The range of pressures included in the linear fits was chosen to avoid the loss of collisional cooling efficiency at low pressure and electron beam heating at high pressure. The varied zero-pressure intercepts are small and consistent with statistical fluctuations in data sets and small drifts in the 0.2 mTorr absolute uncertainty in the pressure measurements. The high pressure points in all data sets

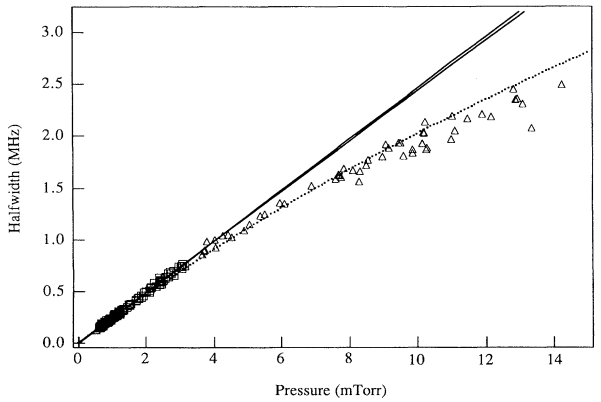

FIG. 2. Observed half-width for HCO^+ (J = 3-2) in collision with H_2 as a function of pressure at 11.2 K and 8 mA electron beam current. The two solid lines represent fits to the linear portion of the data and the dotted line the prediction of the electron beam heating model. The high pressure data clearly show the effects of electron beam heating.

suffer from the effects of very broad lines, which results in more scatter. The results with the zero-pressure intercept fixed at zero are believed to be slightly more accurate since they are less sensitive to scatter and possible loss of cooling at low pressure.

Figures 2 and 3 illustrate the different thermal effects nicely. Since γ varies roughly inversely as temperature in the 11–30 K region (see below), heating caused by the electron beam will decrease the value of γ. Figure 2 clearly shows this reduction due to beam heating at high pressures at 11.2 K. The lower density and higher conductivity combined with the less severe dependence of γ on temperature at 28 K result in the lack of observed high pressure features in Fig. 3. The low pressure "hook" apparent in Fig. 3 derives from loss of collisional cooling efficiency, a common low density effect in collisional cooling spectra [10], which is the result of the partially cooled Doppler widths being attributed to pressure broadening.

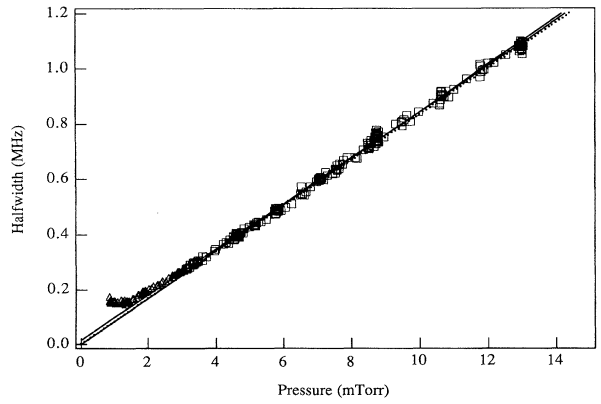

FIG. 3. Observed half-width for HCO^+ (J = 3-2) in collision with H_2 as a function of pressure at 28 K and 10 mA electron beam current. The two solid lines represent fits to the linear portion of the data and the dotted line the prediction of the electron beam heating model. The low pressure show the "hook" from the loss of cooling while the high pressure data show little effect from electron beam heating.

The results of the fixed zero-intercept fits to all the data sets are plotted in Fig. 4, including two 19 K points taken at 5 and 25 mA beam current, respectively. In this figure, we have plotted the rate coefficient k vs temperature rather than plotting the pressure broadening parameter γ. The parameters k and γ are related via the relations [22,23]

$$1/\Delta\tau = kn = 2\pi\gamma P, \tag{1}$$

where $\Delta\tau$ is the interval between strong collision, which randomize the rotational phase, n is the gas density, and P is the pressure, which is here given by the ideal gas law. In temperature-dependent studies, use of the rate coefficient, though rare, is desirable because its temperature dependence and size arise solely from the intermolecular potential. Over the temperature range studied here, a horizontal k vs T plot leads to a noticeably hyperbolic γ vs T plot.

Reactive collisions between ions and nonpolar neutrals normally follow the simple long-range Langevin capture theory, which leads to a temperature-independent rate coefficient k_L ($cm^3\,s^{-1}$) given by the relation

$$k_L = 2\pi q\sqrt{\alpha/\mu}, \tag{2}$$

where μ is the reduced mass in grams, α (cm^3) is the polarizability of the neutral, and q (esu) is the electronic charge [24–26]. If we assume that nonreactive collisions obeying the capture criterion randomize the rotational phase of HCO^+, the Langevin treatment yields simple expressions for the pressure broadening parameters. In particular, the Langevin rate coefficient is calculated to

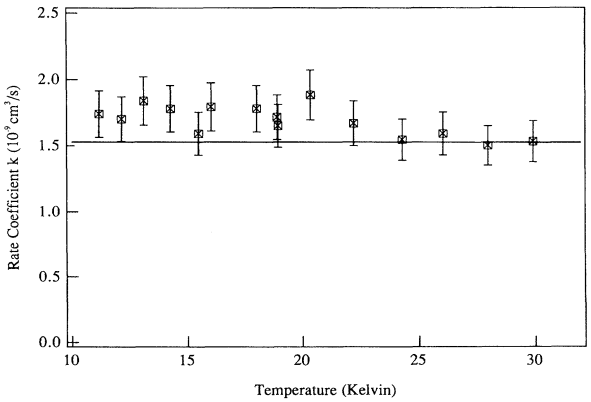

FIG. 4. The observed rate coefficient for HCO^+ (J = 3-2) collisions with H_2 over the range of temperatures from 11.2 to 30 K. The horizontal line is the Langevin rate coefficient.

be 1.53×10^{-9} cm^3 s^{-1} for HCO^+ colliding with H_2, independent of temperature.

The Langevin result is plotted as a horizontal line in Fig. 4. The experimental data points tend to lie above the Langevin line by as much as 20%, especially at temperatures below 24 K. In contrast, the Anderson theory result, which is approximately equal to the Langevin result at 77 K, is $\frac{1}{3}$ the size of the Langevin result at 11.2 K [27]. It is surprising that the lower temperature observed rate coefficients are slightly larger than a simple capture theory model predicts. This is opposite to neutrals where an analogous capture theory predicts larger pressure broadening parameters than observed.

There is clearly some structure to the data in Fig. 4. Whether or not this can be accounted for in a purely classical theory such as a higher order capture model, or whether these are quantum resonance effects, which are important in neutral pressure broadening at low temperature [28], remains to be seen. As a result, these data are very interesting and warrant further calculations [29], which might be based on a new potential for HCO^+ and H_2 [30].

This work has demonstrated a new technique for the observation of pressure broadening in molecular ions at low temperatures. The use of a metal collisional cooling cell coupled with a magnetically guided electron gun electron source has made characterization of low temperature and pressure possible and resulted in the direct measurement of pressure broadening parameters in a regime of fundamental interest for astrophysical molecular energy transfer calculations. It is our belief that this technique will find much broader application in studies of time resolved state-to-state collisions, time resolved studies of formation mechanisms, and the laboratory production of previously uncharacterized ionic species.

We would like to acknowledge NASA, the National Science Foundation, and the Army Research Office for their support of this research.

*Current address: Jet Propulsion Laboratory, Mail Stop 183-301, 4800 Oak Grove Drive, Pasadena, CA 91109-8099.

†Also at Department of Astronomy, The Ohio State University, 174 W. 18th Ave., Columbus, OH 43210-1106.

[1] E. Herbst and W. Klemperer, Astrophys. J. **188**, 255 (1974).

[2] B. E. Turner, Astrophys. J. **193**, L83 (1974).

[3] S. Green, Astrophys. J. **201**, 366 (1975).

[4] E. Herbst, Annu. Rev. Phys. Chem. **46**, 27 (1995).

[5] S. Green and P. Thaddeus, Astrophys. J. **205**, 766 (1976).

[6] T. G. Anderson, C. S. Gudeman, T. A. Dixon, and R. C. Woods, J. Chem. Phys. **72**, 1332 (1980).

[7] G. Buffa, O. Tarrini, G. Cazzoli, and L. Dore, Phys. Rev. A **49**, 3557 (1994).

[8] F. C. De Lucia, E. Herbst, G. M. Plummer, and G. A. Blake, J. Chem. Phys. **78**, 2312 (1983).

[9] J. K. Messer and F. C. De Lucia, Phys. Rev. Lett. **53**, 2555 (1984).

[10] D. R. Willey, R. L. Crownover, D. N. Bittner, and F. C. De Lucia, J. Chem. Phys. **89**, 1923 (1988).

[11] D. R. Willey, R. J. Southwick, B. K. Rapela, and W. A. Neff, Phys. Rev. Lett. **74**, 5216 (1995).

[12] P. Jin, G. E. Hall, and T. J. Sears, Int. Symp. Mol. Spectrosc. **50**, 282 (1995).

[13] H. E. Warner, W. T. Conner, R. H. Petrmichl, and R. C. Woods, J. Chem. Phys. **81**, 2514 (1984).

[14] G. A. Blake, , K. B. Laughlin, R. C. Cohen, K. L. Busarow, and R. J. Saykally, Astrophys. J. **316**, L45 (1987).

[15] J. J. Thompson and G. P. Thompson, *Conductivity of Electricity Through Gasses* (Cambridge University Press, London, 1928).

[16] A. Von Engel, *Ionized Gases* (Oxford University Press, Glasgow, 1965).

[17] A. K. Brewer and J. Westhaver, J. Appl. Phys. **8**, 779 (1937).

[18] V. G. Anicich and W. T. Huntress, Jr., Astrophys. J. Suppl. Ser. **62**, 553 (1986).

[19] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids* (Oxford University Press, London, 1959).

[20] W. C. King and W. Gordy, Phys. Rev. **90**, 319 (1953).

[21] P. Helminger, J. K. Messer, and F. C. De Lucia, Appl. Phys. Lett. **42**, 309 (1983).

[22] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (Dover, New York, 1975).

[23] J. I. Steinfeld, *An Introduction to Modern Molecular Spectroscopy* (MIT Press, Cambridge, MA, 1989).

[24] P. Langevin, Ann. Chim. Phys. **5**, 245 (1905).

[25] G. Gioumousis and D. P. Stevenson, J. Chem. Phys. **29**, 294 (1958).

[26] *Interaction Between Ions and Molecules,* edited by P. Ausloos (Plenum Press, New York, 1975).

[27] Q. Liao and E. Herbst (to be published).

[28] M. M. Beaky, T. M. Goyette, and F. C. De Lucia, Int. Symp. Mol. Spectrosc. **50**, 141 (1995).

[29] S. Green, *MOLSCAT Routine, National Resource for Computation in Chemistry Software Catalogue* (Lawrence Berkeley Laboratory, Berkeley, CA, 1980).

[30] E. J. Bieske, S. A. Nizkorodov, F. R. Bennett, and J. P. Maier, J. Chem. Phys. **102**, 5152 (1995).