# Radiative Association of $CH_3^+$ and $H_2$ at 13 K

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This paper reports the first observation and measurement of two-body ion-neutral association at low temperatures and densities. The rate at 13 K for $CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$ has been measured to be $(1.8 \pm 0.3) \times 10^{-13}$ cm$^3$/s for a normal (3 to 1) mix of ortho and para hydrogen. The reaction conditions were such that the process could only have proceeded by radiative stabilization of the collision complex.

The importance of gas-phase ion-molecule reactions in the chemical evolution of the interstellar medium (ISM) has been recognized for some time, and Refs. 1–5 are representative of the many papers on this subject. The ability to model observed abundances of some interstellar molecules from laboratory data is impressive, and substantial progress has been made in measuring or deducing the needed data. Until recently, however, no rates have been measured below 80 K, and most have not been measured below room temperature. Much of the ISM is characterized by $T \sim 10$–50 K. Workers have had to rely on extrapolation of rate coefficients from higher-temperature data. Some processes have not yielded to measurement at any temperature, and these must be estimated theoretically.

The radiative association process is an important case in point. Its role was discussed in the earliest[1] ISM models. By 1977 Black and Dalgarno[3] included $C^+ + H_2 \rightarrow CH_2^+ + h\nu$ as one of the fundamental starting reactions for molecule formation, despite the fact there had been no laboratory observation of this type of process. This remains an anchor in most present models[5] as well—still with no measurements. Other radiative associations have been incorporated into subsequent models.[4,5] Recognition of the importance of the mechanism led to experimental efforts to observe and measure the process, and success was achieved for ion–polar-molecule systems near room temperature. Woodin and Beauchamp[6] reported rates for $Li^+$ colliding with several moderate size molecules (small aldehydes and ketones). MeEwan *et al.*[7] reported a rate for $CH_3^+ + HCN \rightarrow CH_3 \cdot HCN^+$.

The radiative association process can be represented as

$$A^+ + B \underset{\tau_d}{\overset{k_1}{\rightleftarrows}} (AB^+)^* \overset{A_r}{\rightarrow} AB^+ + h\nu. \tag{1}$$

$$\underset{k_r}{\longrightarrow}$$
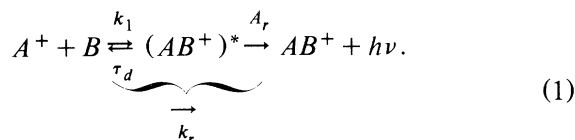
The lifetime $\tau_d$ of the complex $(AB^+)^*$ generally decreases with temperature[8] and for most such processes $k_r$ is too small at room temperature to be measured. Thus, until the present work, no observations or measurements of radiative association have been made involving small, nonpolar neutrals—particularly $H_2$, the most abundant molecule in the ISM. Further, no measurements have been made at the low temperatures (10–50 K) thought to be characteristic of the ISM.

In some important work[7,9-11] a third body $M$ has been introduced into the collision which stabilizes the complex $(AB^+)^*$. By observing the product $AB^+$ versus the concentration of $M$, workers were able to infer information on $\tau_d$, and by estimating $A_r$ and $k_1$, they could then estimate $k_r$.

In the absence of laboratory data for radiative association, much theoretical effort has gone into making estimates of rates for the process for species of astrophysical importance. The two most recent calculations by Bates[12] and by Herbst[13] predict the radiative association rate for $CH_3^+ + H_2$ to be $1 \times 10^{-14}$ and $3.3 \times 10^{-14}$ cm$^3$/s, respectively.

In this Letter we report a rate measurement at 13 K of the process $CH_3^+ + H_2 \rightarrow CH_5^+ + h\nu$ for a normal mix (3 to 1) of ortho and para hydrogen. The detailed rate value is important for determining $CH_4$ (methane)[5,10] and $H_2CO$ (formaldehyde)[14] concentrations in the ISM, but the rate and its measurement are equally important as prototypes for the process.

The measurement was made with a trapped-ion technique which has been described elsewhere.[15] The trap, shown schematically in Fig. 1, is cooled to 11 K and is centered in the 2.4-T field of a superconducting solenoid. The $CH_3^+$ ions were made *in situ* by a two-step process. First $He^+$ ions were created by electron bombardment. A small quantity of methane was then introduced through the 170-K gas pipe. A large fraction of the $He^+$ reacted with the methane to form $CH_3^+$. Ion clouds created in this way have densities of $10^5$–$10^6$/cm$^3$ and life-
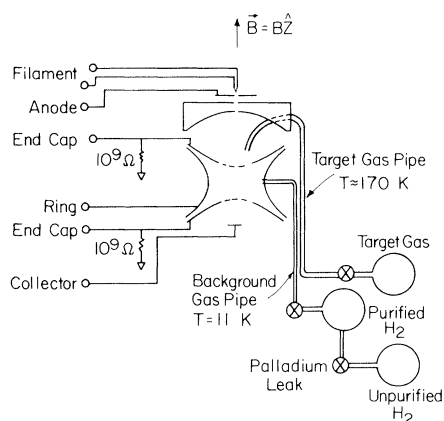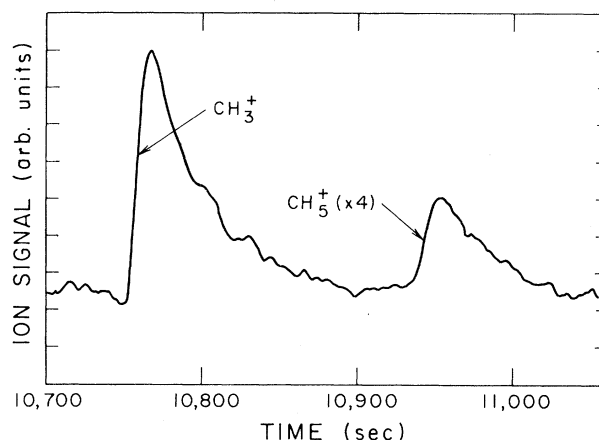
FIG. 1. Schematic of the ion trap.



FIG. 2. Demonstration of ion signature/signal vs time. The observed signal, the noise power in image currents at $\nu_z$, is proportional to product of ion number and temperature. The signal increases sharply (arrows) when cyclotron resonant power is applied thus increasing the temperature. Ions then cool by collisions with cold $H_2$, and the signal decreases. The power input [(rf amplitude)$^2 \times$ time] for heating $CH_5^+$ was 4 times greater than for $CH_3^+$.

times of $\sim 10^7$ s. (Residual neutral densities were $\lesssim 10^4/cm^3$.) Hydrogen was then introduced through the background gas pipe (Fig. 1) to bring the neutral density to $\sim 10^7/cm^3$; the ion-cloud lifetime fell to $\sim 10^4$ s. In the trap ions move with simple harmonic motion along the $z$ axis at frequency $\nu_z$, the ion cloud rotates uniformly about the $z$ axis with the magnetron frequency $\nu_-$, and the ions execute cyclotron motion in the $B$ field with the offset cyclotron frequency $\nu_+ = \nu_c - \nu_-$, where $\nu_c = qB/2\pi m$.

The ions are nondestructively detected by observing the noise power in the image currents induced in the trap end caps at $\nu_z$. This signal is proportional to the product of ion number and temperature. The relative number of ions of a particular $q/m$ can be measured by applying a small amount of rf power at $\nu_+$; ion-ion collisions rapidly bring the ion cloud into thermal equilibrium, and one observes an increase in signal which is proportional to the number of resonant absorbers times the applied power.

Sequential heating of each species in a period short compared to the reaction time is used to establish the relative amount of each ion present at the measurement time. Figure 2 shows a typical measurement cycle. The cooling rate after each heating is also determined to give a measurement of the neutral density. A typical data run consists of five to nine heating and cooling measurements spaced at approximately 30-min intervals for each sample.

Typically, ions were "created" long enough (3000–5000 s) before measurements began so that internal modes could thermalize both by collision and by radiation. Before measurements began, unwanted ions—e.g., $CH_4^+$ (which can form $CH_5^+$) and $CH_5^+$ (the product ion)—were ejected from the

trap by cataclysmic cyclotron heating in a time so short that nonresonant ions could not be heated. Since it was necessary to establish whether ions could act as a third body in stabilizing the collision complex, $CH_3^+ \cdot H_2$, the ion density in the trap was varied by ejecting or leaving various "benign" ions, $C_2H_4^+$, etc., in the sample.

After monitoring the parent and daughter ions at selected times over about $10^4$ s, the total ion signal $N_T(t) = \sum_{i=1}^{l} N_i(t)$ was least-squares fitted by an exponential of the form $N_T(t) = N_0 \exp(-t/\tau_a)$, where $N_0$ is the initial value at some arbitrary zero of time and $\tau_a$ is the time constant for diffusion or other loss from the trap. This exponential fit for a typical data run is shown in Fig. 3(a). Now the number of product ions is

$$N_p(t) = N_0 \exp(-t/\tau_a)[1 - \exp(-t/\tau_r)],$$

so that a plot of

$$X_p(t) = \ln\{1 - [N_p(t)/N_0]\exp(t/\tau_a)\}$$

versus time yields a line of slope $1/\tau_r$, where $\tau_r$ is the reaction time constant. Figure 3(b) shows a fit to the product data $N_p$ for the same data run as in Fig. 3(a). The probability per ion-neutral collision of a reaction occurring is simply the ratio of the ion-neutral collision time to the reaction time, $\tau_r$. The ion-neutral collision time $\tau_c$ is related to the observed equilibration or cooling time, $\tau_e$, by
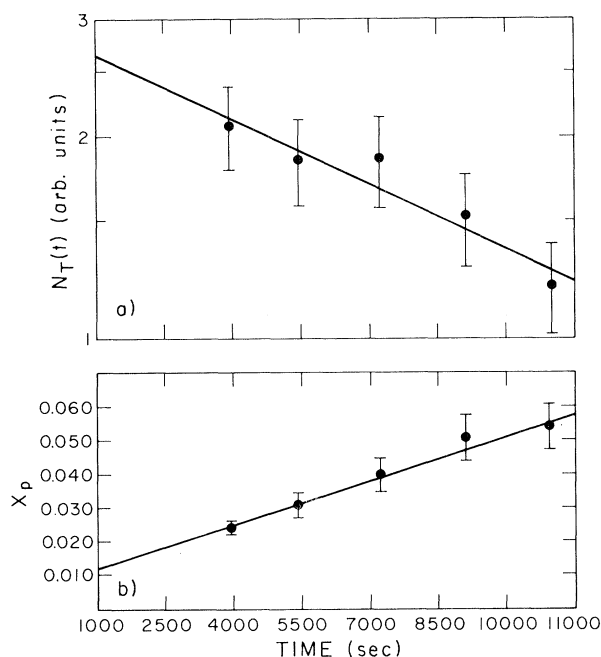
FIG. 3. (a) Total ion number vs time; line is least-squares fit. (b) $X_p(t) = -\ln[1 - N_p(t)/N_t(t)]$ vs time, with least-squares fitted line of slope $1/\tau_r$.

$\tau_c = \frac{8}{3}[m_i m_n/(m_i + m_n)^2]\tau_e$, where $m_i$ is the ion mass and $m_n$ is the neutral mass.[16] The reaction probability is then $P_r = \tau_c/\tau_r$. One then proceeds to the reaction rate coefficient from $k_r(T) = k_c(T)P_r(T)$, where $k_c(T)$ is the collision rate coefficient and is taken from the quantum calculation of Arthurs and Dalgarno.[17] This leads finally to

$$k_r(T) = 4.45 \times 10^{-9}\mu^{-1/2}(T^{-1/6} + 0.117)P_r(T),$$

where $\mu$ is in atomic mass units.

Three measurements were made with total ion densities varying over a factor of 2.5 and neutral densities varying over a factor of 1.6. The largest deviation between any two measurements was only 12%. Thus, the role of ions as a third-body stabilizer is precluded. The neutral density of $\sim 10^7$ is far below the $10^{11}$ or $10^{12}$ needed for complex-neutral collisions to be important, as is borne out by the observations.

The results of the measurements give

$$P_r(13\text{ K}) = (7.0 \pm 1.0) \times 10^{-5},$$

and

$$k_r(13\text{ K}) = (1.8 \pm 0.3) \times 10^{-13}\text{ cm}^3\text{ s}^{-1},$$

where the uncertainties are the quadrature sums of the deviaton of the mean of three measurements

and estimated systematic uncertainties.

Smith and Adams[9-11] extensively studied collisions of $CH_3^+$ with $H_2$, using a third-body (e.g., He) $M$ to stabilize the complex $(AB^+)^*$. With the assumption that a fraction, $f$, of collisions of $M$ with $(AB^+)^*$ leads to stabilization, the dependence of the three-body rate on $M$ concentration will yield $\tau_d$, the lifetime of the complex. Referring to Eq. (1) we see that $k_r = k_1[\tau_d/(\tau_d + A_r^{-1})]$, and from this and the $k_r$ measured here, the value of $A_r$ can be determined. Assuming the collision rate as given by the Arthurs and Dalgarno theory mentioned earlier, and extrapolating the most recent data of Smith and Adams[11] for the three-body rate coefficient by assuming the commonly used[8,10,11] simple $1/T^n$ dependence, we obtain $\tau_d = 1.3 \times 10^{-7}$ s and $A_r = 560$ s$^{-1}$ for $f = 0.5$. Experimentally determined[9] $f$'s fall in the range 0.1 to 0.5 and deduced values of $A_r$ are effectively proportional to $f$. The radiative rates are in qualitative agreement with estimates in the literature.[12,18] On the other hand, Bates[19] has said that assuming a $1/T^n$ dependence is not correct. If one uses the temperature dependence of $k_r$ calculated by Bates[12] as the basis for extrapolating the three-body rates of Smith and Adams,[11] there results $\tau_d \approx 9.8 \times 10^{-9}$ s and $A_r \approx 7 \times 10^3$ s$^{-1}$ for $f = 0.5$. Such a large value of $A_r$ is more characteristic of electronic transitions than the vibrational ones normally assumed to be involved in radiative association. McEwan et al.[7] also found a surprisingly large $A_r$ for $CH_3^+ + HCN$.

The value of $k_r$ found here is about an order of magnitude larger than the most recent theoretical values.[12,13] Values of $k_r$ for this process used for modeling the ISM range from[20] $1 \times 10^{-16}$ to[13] $7 \times 10^{-11}$ cm$^3$ s$^{-1}$. The specific effects of this measured value on modeling the ISM await evaluation. Some care should be exercised when these data are applied to the ISM, as the effect of the ortho-para hydrogen ratio on radiative association has not been determined.

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