

## ENHANCED DEUTERIUM FRACTIONATION IN DENSE INTERSTELLAR CORES RESULTING FROM MULTIPLY DEUTERATED $\text{H}_3^+$

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### ABSTRACT

In this Letter, we present the first results from updated models of interstellar deuterium chemistry that now include all possible deuterated isotopomers of  $\text{H}_3^+$ . We find that in regions of high density and heavy depletion, such as prestellar cores, the inclusion of  $\text{HD}_2^+$  and  $\text{D}_3^+$  enhances the fractionation of ionic and neutral species significantly. Our models are the first to predict the very high *atomic* D/H ratios ( $\geq 0.3$ ) necessary for grain-surface chemistry models to reproduce the high formaldehyde and methanol fractionation seen in star-forming regions.

*Subject headings:* ISM: clouds — ISM: individual (L1544) — ISM: molecules — molecular processes

### 1. INTRODUCTION

Models of deuterium chemistry are widely used in interpreting observational results in order to trace the chemical and physical processes occurring in interstellar clouds (as reviewed by Roberts, Herbst, & Millar 2002 and Ceccarelli 2002). Recently, though, it has seemed that the more observers look for deuterium, the more they find. In particular, dramatic enhancements in the fractionation of multiply deuterated species are creating problems for the chemical models.

Although the underlying abundance of deuterium is  $\sim 10^{-5}$  with respect to hydrogen,  $\text{NHD}_2/\text{NH}_3$  is 0.005 in the cold cloud L134N and 0.03 in the low-mass protostar 16293 E (Roueff et al. 2000; Loinard et al. 2001),  $\text{ND}_3/\text{NH}_3$  is  $\sim 10^{-3}$  in the Class 0 protostar NGC 1333 IRAS4A and the cold dense Barnard 1 cloud (Lis et al. 2002; van der Tak et al. 2002), while  $\text{D}_2\text{CO}/\text{H}_2\text{CO}$  is between 0.01 and 0.4 in a range of low-mass protostars and prestellar cores (Loinard et al. 2002; Bacmann et al. 2003). One of these protostars, IRAS 16293–2422, also has a total abundance of deuterated methanol that actually exceeds that of the main isotopomer (Parise et al. 2002).

Deuterium-bearing molecules can become highly fractionated in the gas phase at low temperatures, an effect thought to be due primarily to  $\text{H}_2\text{D}^+$ , which forms efficiently from the reaction between  $\text{H}_3^+$  and HD, then transfers its deuteron to neutral species such as CO, O, and  $\text{N}_2$ . If these species are depleted from the gas, the  $\text{H}_2\text{D}^+/\text{H}_3^+$  ratio, and thus deuterium fractionation throughout the cloud, becomes very large (Brown & Millar 1989a; Roueff et al. 2000; Roberts & Millar 2000b, hereafter RM00b; Rodgers & Charnley 2001). Recent observational studies strongly support this link among high densities, depletion of CO, and enhanced deuterium fractionation. The prestellar cores observed by Bacmann et al. (2002, 2003) indicate that  $\text{D}_2\text{CO}$  fractionation increases with CO depletion. Hatchell (2003) has observed enhanced  $\text{NH}_2\text{D}/\text{NH}_3$  ratios close to the dust peaks of protostellar sources, while Caselli et al. (2003) have actually detected a high  $\text{H}_2\text{D}^+$  abundance in the dense, heavily depleted central region of L1544.

There is a limit, though, to the deuterium enrichment that can be produced in the gas phase. The accretion model of RM00b predicted maximum fractionation for singly and doubly

deuterated species of 0.25–0.4 and 0.04–0.08, respectively, but this is only for short time periods, at extreme depletions that are not always supported by observations. In any case, for  $\text{D}_2\text{CO}/\text{H}_2\text{CO}$  the predicted ratios were still significantly lower than many of the observations.

Another way of enhancing D/H ratios is via an active surface chemistry (Brown & Millar 1989b; Charnley, Tielens, & Rodgers 1997). In this view, the deuteration is caused by a chemistry based on H and D atoms adsorbing from the gas phase. To produce the relative abundances of deuterated methanol and formaldehyde seen in IRAS 16293, however, an initial D/H ratio of 0.2–0.3 is required (Caselli et al. 2002a; Parise et al. 2002). This is a serious problem, since previous accretion models produce a *maximum* atomic D/H ratio  $\leq 0.1$  (Roberts et al. 2002) and this for only a short time. In addition, surface chemistry cannot explain high deuterium fractionation in the prestellar cores, where low temperatures make it unlikely that significant amounts of material have desorbed from grains.

In this Letter, we show that deuterium fractionation via gas-phase chemistry can be far more efficient than previously estimated if the role of multiply deuterated isotopomers of  $\text{H}_3^+$  is taken into account. This increased efficiency leads to a sufficiently high atomic D/H ratio such that the role of surface chemistry in deuterium fractionation is also enhanced.

### 2. THE MODELS

Our models of deuterium chemistry have been updated from those presented in Roberts & Millar (2000a, hereafter RM00a) and RM00b and now contain more multiply deuterated species, including all deuterated analogs of  $\text{H}_3^+$ ,  $\text{NH}_3$ , and  $\text{CH}_3\text{OH}$ . Full details of the updates will be presented in a future paper.

To include  $\text{HD}_2^+$  and  $\text{D}_3^+$ , we have added the fractionation reactions involving HD and  $\text{D}_2$  from Giles, Adams, & Smith (1992) to the list given in RM00a. The forward rate coefficients were measured at 80 K, while the rate coefficients of the reverse reactions are estimated from endothermicities. Entropy and nonthermal effects are likely to change the rates of the reverse reactions, though, and more studies are clearly needed for future work.

The fractionation of  $\text{H}_2\text{D}^+$  is most easily understood in terms

of its steady state value (Roberts et al. 2002), which is now given approximately by the equation

$$\frac{[\text{H}_2\text{D}^+]}{[\text{H}_3^+]} = \frac{k_{f(1)}[\text{HD} + \text{D}_2]}{k_{f(2)}[\text{HD} + \text{D}_2] + k_e[e^-] + k_{\text{CO}}[\text{CO}]} \quad (1)$$

The rate coefficient  $k_{f(1)}$  represents the formation of  $\text{H}_2\text{D}^+$  from either HD or  $\text{D}_2$  reacting with  $\text{H}_3^+$ , while  $k_{f(2)}$  stands for its destruction to form  $\text{HD}_2^+$  and  $\text{D}_3^+$  (assuming that the rate for destruction by  $\text{H}_2$  is negligible at 10 K, compared with  $k_{f(2)}$ ). Equivalent equations can be written for  $\text{HD}_2^+$  and  $\text{D}_3^+$  fractionation and would also serve to show that at low temperatures and extreme depletions, the deuterium fractionation will depend mainly on the forward rates of the fractionation reactions,  $k_f$ , on the ionization fraction,  $[e^-]$ , and on the rates for recombination of  $\text{H}_3^+$  and its analogs with electrons,  $k_e$ . For  $\text{H}_3^+$ ,  $k_e$  has been reduced by a factor of  $\sim 3$  from previous models because of recent measurements by McCall et al. (2003), and we assume that  $k_e$  for  $\text{HD}_2^+$  and  $\text{D}_3^+$  is the same as that measured for  $\text{H}_2\text{D}^+$  (Sundström et al. 1994).

In RM00b, we stated that  $\text{HD}_2^+$  was unlikely to contribute significantly to the overall deuterium fractionation, even in regions of the interstellar medium where accretion is active, since it will form from  $\text{H}_2\text{D}^+$ , lowering its abundance, while reacting in a similar way to  $\text{H}_2\text{D}^+$ , transferring only one deuteron per reaction. Table 1, which shows peak D/H ratios for selected species from a model without  $\text{HD}_2^+$  and  $\text{D}_3^+$  (model 1) and from our complete model (model 2), confirms this for accretion models with  $T_{\text{kin}} = 10$  K and  $n(\text{H}_2) = 10^4 \text{ cm}^{-3}$ .

It has long been known, however, that an increase in density increases deuterium fractionation (e.g., RM00a), since the ionization fraction will be lower and depletion will be enhanced. Tafalla et al. (2002) obtain a density of a few times  $10^6 \text{ cm}^{-3}$  for the core of L1544, and so D/H ratios for selected molecules from models 1 and 2, using  $n(\text{H}_2) = 1.5 \times 10^6 \text{ cm}^{-3}$ , are also listed in Table 1. The  $\text{H}_2\text{D}^+$  fractionation does, indeed, become very large,  $\sim 30$ , in model 1 at higher densities, but this fractionation has not translated to the other species. The peak  $\text{DCO}^+$  and  $\text{N}_2\text{D}^+$  fractionation ratios, for example, which we expect to be closely related to  $\text{H}_2\text{D}^+$ , are only approximately twice as high as in the lower density model.

A long-standing assumption in modeling deuterium chemistry is that the  $[\text{DCO}^+]/[\text{HCO}^+]$  and  $[\text{N}_2\text{D}^+]/[\text{N}_2\text{H}^+]$  ratios will be approximately one-third of the  $[\text{H}_2\text{D}^+]/[\text{H}_3^+]$  ratio, since they form via reactions from  $\text{H}_2\text{D}^+$  and  $\text{H}_3^+$  with the assumption of statistical distribution of products. This approximation is correct, however, only when  $[\text{H}_2\text{D}^+] \ll [\text{H}_3^+]$ , so that most of the normal isotopomers come from  $\text{H}_3^+$ ; it begins to break down when  $[\text{H}_2\text{D}^+]/[\text{H}_3^+]$  is about 0.5. In the limit that  $[\text{H}_2\text{D}^+]$  becomes much larger than  $[\text{H}_3^+]$ , as is the case at high densities and extreme depletions, the reactions of  $\text{H}_2\text{D}^+$  with CO, for example, produce twice as much  $\text{HCO}^+$  as  $\text{DCO}^+$ . For this reason, the highest  $\text{DCO}^+$  (and  $\text{N}_2\text{D}^+$ ) fractionation that can possibly result from reaction with  $\text{H}_2\text{D}^+$  is 0.5, as seen in Table 1 for model 1.

The inclusion of  $\text{HD}_2^+$  and  $\text{D}_3^+$  in the chemical models changes this analysis, allowing more deuterium to transfer to other species. The efficient fractionation at 10 K causes  $\text{D}_3^+$  to become the most abundant form of deuterated  $\text{H}_3^+$  at higher density, with  $[\text{D}_3^+]/[\text{H}_3^+]$  peaking at  $\sim 20$ . The other molecules also become highly fractionated, as Table 1 shows. The peak atomic  $[\text{D}]/[\text{H}]$  ratio is greater than 1, while  $[\text{ND}_3]$  rises to almost equal  $[\text{NH}_3]$ , at which time they still have an appreciable

TABLE 1  
PEAK MOLECULAR D/H RATIOS FOR SELECTED SPECIES FROM ACCRETION  
MODELS AT 10 K

| SPECIES                      | $n(\text{H}_2) = 10^4 \text{ cm}^{-3}$ ,<br>$t = 10^6 \text{ yr}$ |         | $n(\text{H}_2) = 1.5 \times 10^6 \text{ cm}^{-3}$ ,<br>$t = 2 \times 10^4 \text{ yr}$ |         |
|------------------------------|-------------------------------------------------------------------|---------|---------------------------------------------------------------------------------------|---------|
|                              | Model 1                                                           | Model 2 | Model 1                                                                               | Model 2 |
| $\text{H}_2\text{D}^+$ ..... | 0.938                                                             | 0.580   | 27.37                                                                                 | 1.787   |
| $\text{HD}_2^+$ .....        | ...                                                               | 0.154   | ...                                                                                   | 2.077   |
| $\text{D}_3^+$ .....         | ...                                                               | 0.046   | ...                                                                                   | 20.79   |
| $\text{N}_2\text{D}^+$ ..... | 0.215                                                             | 0.264   | 0.484                                                                                 | 7.813   |
| $\text{DCO}^+$ .....         | 0.217                                                             | 0.265   | 0.492                                                                                 | 8.122   |
| D .....                      | 0.075                                                             | 0.087   | 0.355                                                                                 | 1.830   |
| $\text{NH}_2\text{D}$ .....  | 0.313                                                             | 0.315   | 1.208                                                                                 | 2.580   |
| $\text{NHD}_2$ .....         | 0.021                                                             | 0.026   | 0.258                                                                                 | 2.672   |
| $\text{ND}_3$ .....          | 0.001                                                             | 0.001   | 0.017                                                                                 | 0.959   |
| $\text{HDCO}$ .....          | 0.133                                                             | 0.133   | 0.381                                                                                 | 0.722   |
| $\text{D}_2\text{CO}$ .....  | 0.003                                                             | 0.003   | 0.021                                                                                 | 0.144   |

gas-phase abundance of  $\sim 10^{-12}$  with respect to  $\text{H}_2$ . The  $\text{D}_2\text{CO}/\text{H}_2\text{CO}$  ratio exceeds 0.1 for the time period  $(2-4) \times 10^4 \text{ yr}$ .

Given the increasing observational evidence that large amounts of deuterium are present in interstellar molecules and frozen onto grains, Phillips & Vastel (2003) suggested that the interstellar reservoir of deuterium, HD, could be depleted. As our models do not allow desorption from grain surfaces, the HD is, indeed, used up within a few times  $10^4 \text{ yr}$  in our high-density model, unless we make the assumption that a proportion of the atomic D that freezes out is returned to the gas as HD and  $\text{D}_2$ . In this Letter, we have made the (fairly arbitrary) assumption that 80% of the accreting D immediately forms HD and is evaporated. We note, however, that the peak D/H ratios (presented in Table 1) are not affected by this assumption. A coupled gas-grain chemical model is required in order to determine how much D forms HD and  $\text{D}_2$  and how much becomes incorporated into heavier species.

### 2.1. A Brief Comparison with L1544

Recent observations of prestellar cores indicate different spatial distributions for different molecules (e.g., Tafalla et al. 2002). For the well-studied source L1544, it seems that CO and CS freeze out at lower densities, while  $\text{N}_2$  stays in the gas longer, forming  $\text{N}_2\text{H}^+$  and  $\text{NH}_3$ , which trace the densest regions (Caselli et al. 2002b). Aikawa et al. (2001) and Aikawa, Ohashi, & Herbst (2003) have constructed a very detailed model of this source, which includes collapse, grain surface chemistry, and desorption but does not contain multiply deuterated species. Here we use our full high-density model to look at the effects on deuterium fractionation of keeping  $\text{N}_2$  in the gas while all other species heavier than  $\text{D}_3^+$  freeze out. The top panel of Figure 1 shows the evolution of selected fractional abundances, while the bottom panel shows the molecular D/H ratios.

With our assumption that 80% of the accreting D atoms are returned to the gas as HD, we obtain the result that most hydrogenic and nitrogenic species have fairly flat abundances from  $10^4$  to  $4 \times 10^5 \text{ yr}$ . Varying the 80% efficiency does not affect these abundances at times  $\leq 10^5 \text{ yr}$ . The calculated fractionation is large over the entire temporal range, although not as great as the peak values in Table 1. Eventually, the deuterated species are lost to the gas unless all accreting D atoms return to the gas in some form. Before the loss of fractionation,  $\text{N}_2\text{D}^+/\text{N}_2\text{H}^+$  is  $\sim 1$ , while  $\text{NH}_2\text{D}/\text{NH}_3$  rises from 0.3 to 0.8,  $\text{NHD}_2/\text{NH}_3$  from 0.07 to 0.25, and  $\text{ND}_3/\text{NH}_3$  to 0.03. The fractional electron abundance is  $\sim 2 \times 10^{-9}$ , and the most abundant ions

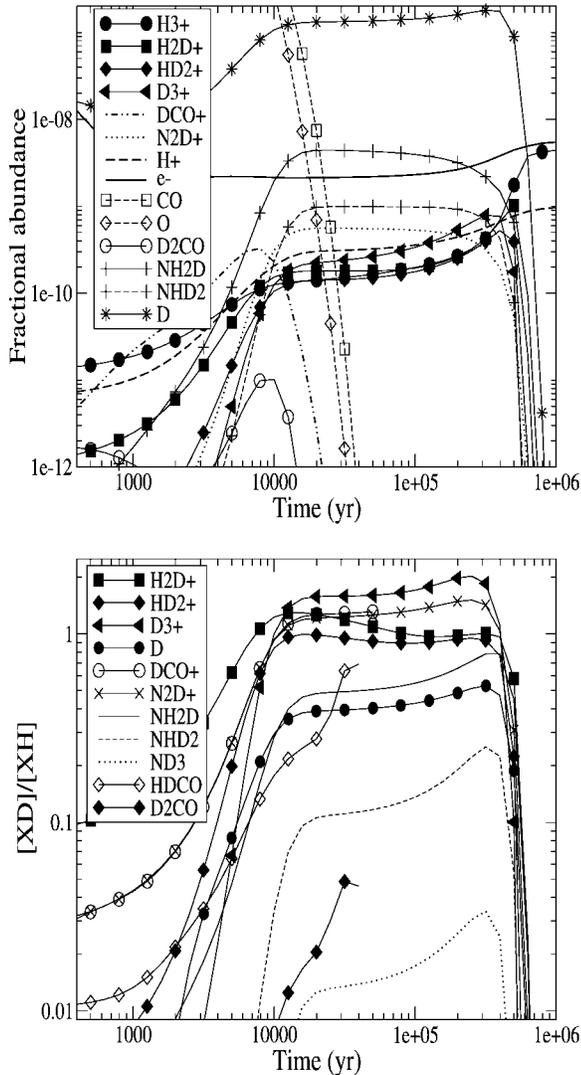


FIG. 1.—Results from the accretion model at 10 K,  $n(\text{H}_2) = 3 \times 10^6 \text{ cm}^{-3}$  when  $\text{N}_2$  does not freeze out. *Top*: Abundances relative to  $\text{H}_2$ ; *bottom*: molecular D/H ratios.

are  $\text{N}_2\text{D}^+$ ,  $\text{N}_2\text{H}^+$ ,  $\text{H}^+$ , and  $\text{D}_3^+$ . Specifically, we calculate that  $[\text{N}_2\text{H}^+] \sim [\text{N}_2\text{D}^+] \sim 5 \times 10^{-10}$  at  $10^5$  yr, while  $[\text{H}_2\text{D}^+]$  is  $2 \times 10^{-10}$ . These results are in only partial agreement with the observations of Caselli et al. (2003) for the center of L1544. They estimate  $[\text{H}_2\text{D}^+]$  to be  $(5-10) \times 10^{-10}$ , 2–5 times larger than our result, and  $[\text{N}_2\text{H}^+]$  to be approximately one-third  $[\text{H}_2\text{D}^+]$ , while our value is  $2.5 \times [\text{H}_2\text{D}^+]$ . Moreover, our value of 1 for  $\text{N}_2\text{D}^+/\text{N}_2\text{H}^+$  is  $\sim 5$  times higher than the observed value. Despite this excessive fractionation, our calculated  $\text{D}_2\text{CO}/\text{H}_2\text{CO}$  ratio reaches only the observed value of 0.04 (Bacmann et al. 2003) for a very short time when almost all the formaldehyde has frozen out. Another result that we do not reproduce is the difference between  $\text{DCO}^+$  and  $\text{N}_2\text{D}^+$  fractionation that Caselli et al. (2003) observed. In our models,  $\text{DCO}^+$  is highly fractionated, and the  $\text{N}_2\text{D}^+/\text{N}_2\text{H}^+$  and  $\text{DCO}^+/\text{HCO}^+$  ratios remain the same until  $\text{DCO}^+$  and  $\text{HCO}^+$  freeze out completely.

Although this model qualitatively supports the theory that  $\text{N}_2$  remains in the gas while CO depletes onto the dust grains, its major achievement is to show that the problem of producing high deuteration levels in quiescent and prestellar cores no longer exists. In fact, for the N-bearing species, the fraction-

ation now becomes *too* high. This discrepancy could be caused by our overestimating the rates for the forward fractionation reactions for a 10 K source (cf. Gerlich, Herbst, & Roueff 2002; Roberts et al. 2002) and/or by underestimating the rates of the backward reactions. However, a reduction in  $\text{H}_3^+$  fractionation would also lower the atomic D/H and  $\text{D}_2\text{CO}/\text{H}_2\text{CO}$  ratios. It is more likely that the assumption of constant physical conditions is unrealistic: the  $\text{DCO}^+$  emission from L1544, for example, may well be coming from a lower density region, so a much more complex model, such as that of Aikawa et al. (2001, 2003), is required.

## 2.2. The Atomic D/H Ratio

Given that our new models still reproduce neither the highest  $\text{D}_2\text{CO}/\text{H}_2\text{CO}$  ratios nor the abundances of methanol that have been observed in protostellar sources, it is almost certain that grain surface chemistry, followed by desorption, has affected the molecular composition. It is an important result, therefore, that our high-density accretion models, applicable to *prestellar* cores, predict  $[\text{D}]/[\text{H}] \geq 0.3$  for at least  $10^5$  yr. As the heavy species freeze onto the grains, D and H also stick, at least partially, causing surface hydrogenation and deuteration, until rising temperatures enable the high degree of fractionation in the ices to be transferred to the gas.

## 3. CONCLUSIONS

We have shown that an extraordinarily high degree of deuterium fractionation can occur via gas-phase chemistry in dense objects with a significant depletion of heavy species. The key basis for this result is the inclusion of the ions  $\text{HD}_2^+$  and  $\text{D}_3^+$  in our chemical network. This result suggests future theoretical, experimental, and observational research to test our assumptions and conclusions. It is now very important, for example, to measure and/or calculate the low temperature rates of all reactions involved in the conversion of  $\text{H}_3^+$  to partially and totally deuterated forms and the dissociative recombination rates of the two new “primary” ions. A coupled gas-grain chemistry, which includes desorption from the grain surfaces, also seems necessary in order to make the model physical at late times. The models predict that in dense depleted regions, the abundance of  $\text{HD}_2^+$  will be similar to that of  $\text{H}_2\text{D}^+$ , so, observationally, it is critical to attempt to find the  $1_{1,0}-1_{0,1}$  line of  $\text{HD}_2^+$ , for which accurate predictions are available (Polyansky & McKellar 1990; J. Tennyson 2003, private communication). It would also be useful to observe all deuterated analogs of other molecules in each source.

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## REFERENCES

- Aikawa, Y., Ohashi, N., & Herbst, E. 2003, *ApJ*, in press
- Aikawa, Y., Ohashi, N., Inutsuka, S., Herbst, E., & Takakuwa, S. 2001, *ApJ*, 552, 639
- Bacmann, A., Lefloch, B., Ceccarelli, C., Castets, A., Steinacker, J., & Loinard, L. 2002, *A&A*, 389, L6
- Bacmann, A., Lefloch, B., Ceccarelli, C., Steinacker, J., Castets, A., & Loinard, L. 2003, *ApJ*, 585, L55
- Brown, P. D., & Millar, T. J. 1989a, *MNRAS*, 237, 661
- . 1989b, *MNRAS*, 240, 25
- Caselli, P., Stantcheva, T., Shematovich, V., Shalabiea, O., & Herbst, E. 2002a, *Planet. Space Sci.*, 50, 1257
- Caselli, P., van der Tak, F. F. S., Ceccarelli, C., & Bacmann, A. 2003, *A&A*, 403, L37
- Caselli, P., Walmsley, C. M., Zucconi, A., Tafalla, M., Dore, L., & Myers, P. C. 2002b, *ApJ*, 565, 344
- Ceccarelli, C. 2002, *Planet. Space Sci.*, 50, 1267
- Charnley, S. B., Tielens, A. G. G. M., & Rodgers, S. D. 1997, *ApJ*, 482, L203
- Gerlich, D., Herbst, E., & Roueff, E. 2002, *Planet. Space Sci.*, 50, 1275
- Giles, K., Adams, N. G., & Smith, D. 1992, *J. Phys. Chem.*, 96, 7645
- Hatchell, J. 2003, *A&A*, 403, L25
- Lis, D. C., Roueff, E., Gerin, M., Phillips, T. G., Coudert, L. H., van der Tak, F. F. S., & Schilke, P. 2002, *ApJ*, 571, L55
- Loinard, L., Castets, A., Ceccarelli, C., Caux, E., & Tielens, A. G. G. M. 2001, *ApJ*, 552, L163
- Loinard, L., et al. 2002, *Planet. Space Sci.*, 50, 1205
- McCall, B. J., et al. 2003, *Nature*, 422, 500
- Parise, B., et al. 2002, *A&A*, 393, L49
- Phillips, T. G., & Vastel, C. 2003, in *Chemistry as a Diagnostic of Star Formation*, ed. C. L. Curry & M. Fich, in press
- Polyansky, O. L., & McKellar, A. R. W. 1990, *J. Chem. Phys.*, 92, 4039
- Roberts, H., Herbst, E., & Millar, T. J. 2002, *MNRAS*, 336, 283
- Roberts, H., & Millar, T. J. 2000a, *A&A*, 361, 388 (RM00a)
- . 2000b, *A&A*, 364, 780 (RM00b)
- Rodgers, S. D., & Charnley, S. B. 2001, *ApJ*, 553, 613
- Roueff, E., Tiné, S., Coudert, L. H., Pineau des Forêts, G., Falgarone, E., & Gerin, M. 2000, *A&A*, 354, L63
- Sundström, G., et al. 1994, *Science*, 263, 785
- Tafalla, M., Myers, P. C., Caselli, P., Walmsley, C. M., & Comito, C. 2002, *ApJ*, 569, 815
- van der Tak, F. F. S., Schilke, P., Müller, H. S. P., Lis, D. C., Phillips, T. G., Gerin, M., & Roueff, E. 2002, *A&A*, 388, L53