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THE EFFECT OF AN INCREASED ELEMENTAL D/H RATIO ON DEUTERIUM FRACTIONATION IN THE COLD INTERSTELLAR MEDIUM

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ABSTRACT

Measurements using the *Far Ultraviolet Spectroscopic Explorer* (*FUSE*) show that the gas-phase D/H ratio in the solar neighborhood is highly variable and suggest that the elemental abundance of deuterium in the Galactic disk may be higher than previously thought. We investigate in this Letter the possible consequences of such an enhanced D/H ratio on the deuterium fractionation in singly and multiply deuterated molecules in cold, dense gas. We show that a modest increase in the elemental abundance of deuterium can lead to significant enhancements in abundances of multiply deuterated species.

Subject headings: Galaxy: abundances — ISM: abundances — ISM: molecules

1. INTRODUCTION

Chemical models of deuterium fractionation in the cold, dense interstellar medium (ISM) assume an elemental D/H ratio of $\sim 1.5 \times 10^{-5}$, as suggested by absorption spectroscopy measurements toward stars in the vicinity of the Sun. However, Linsky et al. (2006) argue that these "Local Bubble" measurements may not be representative of the correct deuterium abundance in the local disk. In a plot of the D/H ratio as a function of the H I column density, they introduce three distinct regions. The Local Bubble, $\log N(\mathrm{H\,I}) < 19.2\ \mathrm{cm}^{-2}$, is characterized by a relatively low D/H ratio of $(1.56 \pm 0.04) \times 10^{-5}$, with little scatter. The "intermediate regime," $\log N(\mathrm{H\,I}) = 19.2$–$20.7\ \mathrm{cm}^{-2}$, shows significant scatter in the measured D/H ratios, by a factor of 4–5, with several lines of sight having values as high as $\sim 2.2 \times 10^{-5}$. The "distant regime," $\log N(\mathrm{H\,I}) > 20.7\ \mathrm{cm}^{-2}$, is again characterized by a low D/H ratio, nearly a factor of 2 below the Local Bubble. Linsky et al. attribute the large scatter in the D/H measurements beyond the Local Bubble to spatial variations in the depletion of deuterium onto dust grains.

In the Linsky et al. model, deuterium is depleted from the gas phase onto dust grains over time (Jura 1982; Draine 2004, 2006) until the D-bearing grains are eroded or destroyed by sputtering or grain-grain collisions in strong shocks from supernova remnants, or by strong UV radiation from nearby hot stars. In this picture, the Local Bubble was last reheated or shocked 1–2 Myr ago; therefore, D-bearing grains are only partially evaporated. The intermediate regime exhibits a mixture of recently shocked and quiescent gas, which explains the large scatter in the observed D/H values. The distant regime consists mostly of cool H I gas, where deuterium is largely depleted onto dust grains. Linsky et al. argue that observed correlations of gas-phase D/H ratios with depletions of the refractory metals iron and silicon, and with the H_2 rotational temperature, are consistent with their model. One important implication is that the points with the highest D/H ratio give the more correct deuterium abundance in the local disk, $\mathrm{D/H} = (2.31 \pm 0.24) \times 10^{-5}$.

The recent measurement of a high D/H ratio toward HD 41161 with $\log N(\mathrm{H\,I}) > 21\ \mathrm{cm}^{-2}$ (Oliveira & Hébrard 2006) calls into question the existence of the "distant regime" as a distinct region. It appears instead that all lines of sight beyond the Local Bubble exhibit large variations in the measured D/H ratio. An alternative explanation for the large variations in the observed D/H ratios in the diffuse ISM, due to proximity to cold, dense regions exhibiting chemical fractionation, has also been proposed (Phillips & Vastel 2003). This also suggests that the upper bound of the existing D/H measurements represents a more correct deuterium abundance in the local disk. The corresponding elemental abundance of deuterium is a factor of 1.5 higher than the value commonly assumed in the chemical models of the cold ISM chemistry. Since interstellar chemical processes, including those involving deuteration, are highly nonlinear, it is reasonable to assume that a 50% increase in the elemental D abundance will have more pronounced effects on the abundances of multiply deuterated species. We thus consider the effects of such an enhancement in the present Letter. We describe our standard gas-phase model in § 2 and present model results for three different densities and metallicities. A simple estimate is presented in § 3 and used to explain the isotopic effect. Finally, our summary is contained in § 4.

2. MODEL CALCULATIONS

Thirty interstellar and circumstellar molecules containing deuterium have been detected to date, with several doubly and triply deuterated isotopologues. The fractionation ratio, defined as the ratio of the column density of a deuterated molecule to its hydrogen counterpart, is often found to be orders of magnitude higher than the elemental abundance ratio, which is typically from 1.5×10^{-5} to 2.3×10^{-5}, as discussed above. This deuterium enhancement results from chemical processes, which can involve both gas-phase (Roberts et al. 2003, 2004; Roueff et al. 2005) and surface reactions (Lipshtat et al. 2004). The key gas-phase process involves the reaction

$$H_3^+ + HD \rightleftharpoons H_2D^+ + H_2, \qquad (1)$$

which proceeds preferentially to the right (Gerlich et al. 2002), owing to differences in zero-point vibrational energies, as well as the nonexistence of the ground rotational state of H_3^+ due to the Pauli exclusion principle. The resulting exoergicity is 232 K. The deuteration proceeds further via formation of D_2H^+ and D_3^+ in reactions with HD and D_2 (Gerlich & Schlem-

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mer 2002). The transfer of deuterons then occurs efficiently, producing the observed deuterated molecules. The contribution of solid-phase processes is less quantitative. However, Lipshtat et al. (2004) discuss the enhancement of HD and D_2 production on grain surfaces, caused by the stronger sticking of D atoms and differences in surface reaction rates under conditions of low flux. In other models, large abundances of atomic deuterium, produced in the gas phase, are transferred to grain surfaces and lead to high abundances of deuterated isotopologues (Charnley et al. 1997; Stantcheva & Herbst 2003). The respective importance of gas-phase versus solid-phase processes in the formation of interstellar deuterated molecules is still a subject of debate.

We consider here a comprehensive steady state gas-phase chemical model, which includes all deuterium substitutes of H, H_2, H_n^+, CH_n^+, H_nO, H_nCO, H_nCO^+, NH_n, NH_n^+, HCN, HNC, H_nCS, and H_nS, leading to saturated, stable molecules such as ammonia, formaldehyde, water, etc., and their ions. We do not consider gas-phase mechanisms involving methanol, because they cannot explain the observed abundance of this molecule. The chemical network includes 216 species and 3291 gas-phase chemical reactions. We also introduce the formation of H_2, HD, and D_2 on surfaces by using the formalism described in Le Bourlot et al. (1995) where the formation rate is expressed by the geometric cross section of the grains. Relevant quantities are the dust-to-gas mass ratio (1%) and the grain volume density (3 g cm^{-3}); we consider spherical grains of 0.1 μm radius. We introduce here a range of gas densities and depletions, pertaining to different dark cloud conditions as in Roueff et al. (2005). We consider three different molecular hydrogen densities (10^4, 10^5, and 10^6 cm^{-3}) and a kinetic temperature of 10 K. Different elemental abundances have been chosen for these three models, supposed to be representative, respectively, of TMC-1, Barnard 1, and a highly depleted core, such as LDN 1544 (models A, B, and C, respectively). The abundance of elemental nitrogen is kept fixed to the "standard" dark cloud value (2×10^{-5}), whereas those of carbon and oxygen decrease with increasing density. In this manner, we can account approximately for the observed increase of depletion of carbon and oxygen with increasing density, which appears not to occur for nitrogen (Bacmann et al. 2003; Roueff et al. 2005; Lis et al. 2006). The possibility that deuterium is trapped significantly in ices is not included in this simple model, because the deuterium content in ices has been found to be less than 1% (Dartois et al. 2003; Parise et al. 2003). The cosmic ionization rate is 2×10^{-17} s^{-1}. We also introduce separately the effect of the neutralization of ions on grain surfaces (Le Bourlot et al. 1995). We consider the role of the enhancement of the deuterium elemental abundance from 1.5×10^{-5} to 2.3×10^{-5}, and we display some corresponding model results in Table 1. These results show that the enhancement of the deuterium elemental abundance affects the abundances of deuterated isotopologues according to the number of deuterium atoms in the molecule, with the effect increasing with increasing number. This effect can be explained in a semi-quantitative manner, as discussed below.

3. SIMPLE ESTIMATE

We assume, as a first approximation, that deuteration of species is caused primarily by reactions involving H_2D^+, the most abundant deuterating ion, followed for neutral species by dissociative recombination with electrons. The estimated steady state abundance of H_2D^+ to that of H_3^+ is given by the equation (Roberts et al. 2002, 2003)

$$\frac{[H_2D^+]}{[H_3^+]} = S(H_2D^+)\frac{[HD]}{[H_2]}, \tag{2}$$

where the "enhancement factor" S is

$$S(H_2D^+) = \frac{k_1}{k_2[HD] + k_{dr}[e^-] + \sum k_i[M_i]}. \tag{3}$$

Here k_1 is the rate coefficient for the reaction between H_3^+ and HD, which leads to H_2D^+ and H_2, k_2 is the rate coefficient for the destruction of H_2D^+ via reaction with HD to form $HD_2^+ + H_2$, k_{dr} is the dissociative recombination rate coefficient for H_2D^+, and the $k_i[M_i]$ are the rates of depletion of H_2D^+ by reactions with heavy species (e.g., CO, O). If the rate of destruction of the H_2D^+ ion by reactions with HD is significantly smaller than the sum of the rates of the other depletion mechanisms, then the ratio of the abundance of H_2D^+ to that of H_3^+ is proportional to the fractional abundance of HD, as long as small changes in HD do not affect the other abundances.

One can similarly derive the abundance ratio of the doubly deuterated isotopologue, D_2H^+, to that of H_2D^+, as it is mainly formed through the reaction

$$H_2D^+ + HD \rightleftharpoons D_2H^+ + H_2, \tag{4}$$

which proceeds preferentially to the right because the exoergicity of the reaction is 187 K. The D_2H^+ ion is then destroyed in the same manner as H_2D^+. The corresponding reaction rate coefficient k_2 is slightly smaller than k_1 (Gerlich et al. 2002). Then the steady state fractionation ratio can be written as

$$\frac{[D_2H^+]}{[H_2D^+]} = S(D_2H^+)\frac{[HD]}{[H_2]}, \tag{5}$$

where $S(D_2H^+)$ is expressed as

$$S(D_2H^+) = \frac{k_2}{k_3[HD] + k_{dr}[e^-] + \sum k_i[M_i]}. \tag{6}$$

Here k_3 is the rate coefficient for the destruction of D_2H^+ via reaction with HD to form $D_3^+ + H_2$.

Finally, one can derive a similar expression for the steady state abundance ratio of D_3^+ to D_2H^+, where the term in the denominator involving a reaction with HD is no longer present.

The ratio is then given by

$$\frac{[D_3^+]}{[D_2H^+]} = S(D_3^+)\frac{[HD]}{[H_2]}, \tag{7}$$

with

$$S(D_3^+) = \frac{k_3}{k_{dr}[e^-] + \sum k_i[M_i]}. \tag{8}$$

Then, as long as the destruction of H_2D^+ and D_2H^+ by HD is negligible in comparison to the recombination and reactions of these ions with the other abundant neutrals, we find that the fractionation ratio of the various deuterated isotopologues, $H_{3-n}D_n^+/H_3^+$, scales as $(HD/H_2)^n$, close to $(2D/H)^n$. Moreover, if

TABLE 1

Fractional Abundances relative to H_2 and Enhancement Factors

Species	Model A $n(H_2) = 10^4$ cm^{-3}		EF	Model B $n(H_2) = 10^5$ cm^{-3}		EF	Model C $n(H_2) = 10^6$ cm^{-3}		EF
C/H	3.5(−5)			7.0(−6)			7.0(−7)		
N/H	2.0(−5)			2.0(−5)			2.0(−5)		
O/H	1.0(−4)			2.0(−5)			2.0(−6)		
S/H	1.8(−7)			1.8(−7)			1.8(−8)		
Fe/H	1.5(−8)			1.5(−8)			1.5(−8)		
D/H	1.5(−5)	2.3(−5)		1.5(−5)	2.3(−5)		1.5(−5)	2.3(−5)	
H	2.24(−04)	2.24(−04)		2.23(−05)	2.22(−05)		2.19(−06)	2.16(−06)	
CO	6.70(−05)	6.70(−05)		1.32(−05)	1.32(−05)		1.21(−06)	1.21(−06)	
H_2O	7.99(−07)	7.95(−07)		1.92(−07)	1.87(−07)		2.39(−08)	2.30(−08)	
H_2CO	6.63(−08)	6.56(−08)		1.93(−08)	1.89(−08)		1.84(−09)	1.83(−09)	
NH_3	8.89(−08)	9.00(−08)		1.09(−07)	1.13(−07)		1.60(−07)	1.78(−07)	
HCN	1.07(−07)	1.07(−07)		3.43(−08)	3.47(−08)		1.36(−08)	1.41(−08)	
HNC	4.43(−08)	4.43(−08)		1.57(−08)	1.61(−08)		7.38(−09)	7.80(−09)	
H_3^+	1.03(−08)	9.98(−09)		2.96(−09)	2.74(−09)		5.47(−10)	4.76(−10)	
HCO^+	1.02(−08)	1.00(−08)		1.27(−09)	1.22(−09)		5.28(−11)	5.09(−11)	
N_2H^+	5.14(−10)	5.08(−10)		9.21(−10)	8.83(−10)		6.13(−10)	5.82(−10)	
Simple analytic formula			1.52			1.52			1.52
D	9.95(−07)	1.51(−06)	1.52	3.90(−07)	5.72(−07)	1.47	8.56(−08)	1.19(−07)	1.41
HD	2.79(−05)	4.20(−05)	1.51	2.69(−05)	3.97(−05)	1.47	2.53(−05)	3.68(−05)	1.45
HDO	6.42(−09)	9.68(−09)	1.51	4.77(−09)	6.99(−09)	1.50	1.24(−09)	1.81(−09)	1.52
HDCO	1.53(−09)	2.38(−09)	1.57	7.43(−10)	1.13(−09)	1.55	1.10(−10)	1.70(−10)	1.55
NH_2D	4.32(−09)	6.58(−09)	1.50	1.19(−08)	1.84(−08)	1.49	2.50(−08)	4.17(−08)	1.50
DCN	1.70(−09)	2.70(−09)	1.59	1.81(−09)	2.95(−09)	1.61	1.87(−09)	3.22(−09)	1.66
DNC	2.78(−09)	4.31(−09)	1.55	2.59(−09)	4.10(−09)	1.54	2.05(−09)	3.37(−09)	1.55
H_2D^+	5.76(−10)	8.27(−10)	1.48	4.37(−10)	5.68(−10)	1.40	1.42(−10)	1.64(−10)	1.33
DCO^+	2.82(−10)	4.26(−10)	1.54	8.28(−11)	1.23(−10)	1.55	6.63(−12)	9.90(−12)	1.55
N_2D^+	1.48(−11)	2.25(−11)	1.54	6.49(−11)	9.61(−11)	1.54	8.08(−11)	1.19(−10)	1.55
Simple analytic formula			2.35			2.35			2.35
D_2	5.27(−07)	1.19(−06)	2.26	1.33(−06)	2.83(−06)	2.13	2.25(−06)	4.49(−06)	2.00
D_2O	1.64(−11)	3.73(−11)	2.29	2.48(−11)	5.45(−11)	2.26	6.52(−12)	1.48(−11)	2.36
D_2CO	8.86(−11)	2.06(−10)	2.35	4.52(−11)	1.00(−10)	2.26	7.93(−12)	1.76(−11)	2.23
ND_2H	1.40(−10)	3.25(−10)	2.29	9.46(−10)	2.20(−09)	2.24	2.83(−09)	7.33(−09)	2.33
D_2H^+	3.02(−11)	6.48(−11)	2.21	6.20(−11)	1.16(−10)	2.02	3.70(−11)	5.86(−11)	1.82
Simple analytic formula			3.58			3.58			3.58
ND_3	5.37(−12)	1.85(−11)	3.40	8.32(−11)	2.72(−10)	3.15	3.14(−10)	1.16(−09)	3.32
D_3^+	1.21(−12)	3.98(−12)	3.39	7.65(−12)	2.18(−11)	3.08	9.54(−12)	2.26(−11)	2.72

Note.—The first six rows list the input elemental abundances with respect to H. EF are the enhancement factors of the abundance ratios of the deuterated species to their normal counterparts, for D/H increasing from 1.5×10^{-5} to 2.3×10^{-5}.

the major deuteration mechanism of ions, such as HCO^+, and neutral species, such as ammonia, is a reaction with H_2D^+:

$$NH_3 + H_2D^+ \rightarrow NH_3D^+ + H_2, \quad (9)$$

$$CO + H_2D^+ \rightarrow DCO^+ + H_2, \quad (10)$$

$$NH_3D^+ + e^- \rightarrow NH_2D + H, \quad (11)$$

then a similar albeit more complex analysis holds approximately for the abundance ratios of their deuterated isotopologues. Since the abundance of HD varies almost linearly with the elemental D/H abundance ratio, the abundance ratios of deuterated ions and neutrals to their normal counterparts are also proportional to the elemental deuterium abundance to the same power. Thus, when the elemental D/H ratio increases from 1.5×10^{-5} to 2.3×10^{-5}, a factor of 1.53, abundance ratios between singly deuterated isotopologues and the normal species rise by this factor, ratios involving doubly deuterated isotopologues rise by $1.53^2 = 2.35$, and ratios involving triply deuterated isotopologues rise by $1.53^3 = 3.58$.

Table 1 lists the simple estimate for enhancement of the fractionation ratio along with our detailed calculations for models A, B, and C as the deuterium elemental abundance is raised from 1.5×10^{-5} to 2.3×10^{-5}. If we look at the isotopologues H_2D^+, D_2H^+, and D_3^+, we see that the simple results do best for model A, because the destruction of the H_2D^+ and HD_2^+ ions by HD is least important. For most other species listed in Table 1, the simple estimate tracks the dependence of the fractionation ratio on the deuterium elemental abundance much better, because other factors come into play such as deuteration by ions other than H_2D^+. Overall, our simple estimate for the magnitude of the effect is in reasonable agreement with our detailed model.

The elemental deuterium may in some regions be higher than 2.3×10^{-5}, so we also consider a third value, 3.5×10^{-5}, larger by another factor of 1.53. With the three different deuterium elemental abundances, we ran a series of models as functions of H_2 density from 10^4 to 10^6 cm^{-3}. The results for the deuterated isotopologues of ammonia are depicted in Figure 1. The top and bottom panels show fractional abundances and fractionation ratios plotted vs. H_2 density, respectively. The dependence on the elemental abundance of deuterium is illustrated via solid, dotted, and dashed lines, which represent the standard (1.5×10^{-5}) and

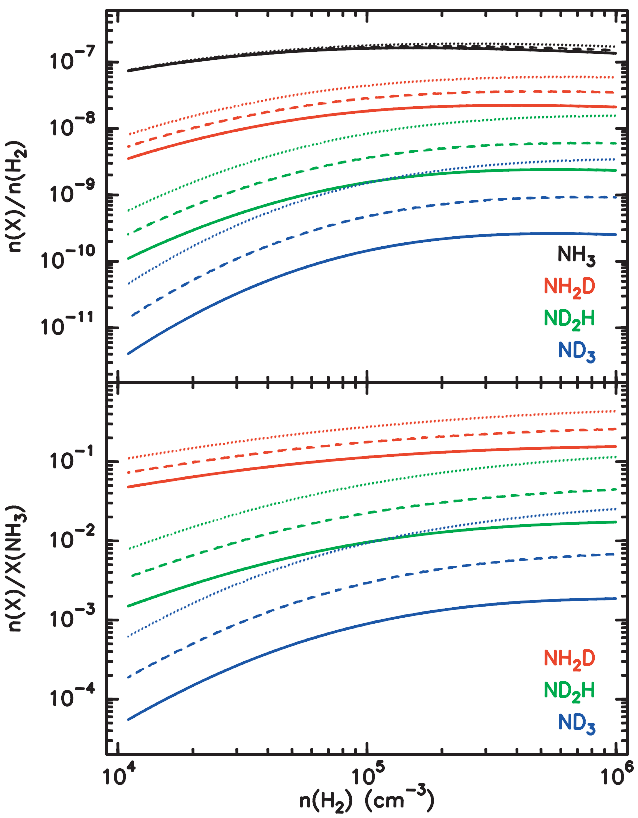

FIG. 1.—Fractional abundances of ammonia isotopologues (*top*) and fractionation ratios of deuterated ammonia isotopologues (*bottom*) vs. H_2 for models with varying density and C/O depletion, and a constant elemental abundance of N. The solid, dashed, and dotted lines in both panels correspond to an elemental D abundance of 1.5×10^{-5}, 2.3×10^{-5}, and 3.5×10^{-5}, respectively.

enhanced deuterium elemental abundances, respectively. The increase in fractionation as the number of deuterium atoms increases is easily seen in both panels, which are similar because the normal ammonia fractional abundance does not change appreciably with increasing density. The variation of the elemental deuterium abundance from the standard value to our highest value leads to an increase of the deuterium fractionation ratio by a factor of ≈10 for the triply deuterated species, close to the simple prediction of $(1.53 \times 1.53)^3 = 1.53^6 = 12.8$, and is not strongly density-dependent.

Figure 1 shows that for the standard dark cloud nitrogen abundance of 2×10^{-5}, steady state models with the standard elemental deuterium abundance of 1.5×10^{-5} underestimate the observed deuterium fractionation ratio of ND_3 (~1×10^{-3} in Barnard 1 and LDN 1689N and ~5×10^{-3} in the highly depleted core LDN 1544; Roueff et al. 2005). Increasing the elemental deuterium abundance is one way to improve the agreement between the observations and model predictions.

4. SUMMARY

Steady state gas-phase models show that a change in the deuterium elemental abundance from 1.5×10^{-5} to 2.3×10^{-5} leads to increases in the fractionation ratio of deuterated isotopologues to their normal counterparts. To a first approximation, the increase in fractionation ratio depends simply on the increase in the elemental deuterium abundance raised to a power that equals the number of deuterium atoms. As an example, the ND_3/NH_3 abundance ratio is estimated to increase by the factor $2.3/1.5 = 1.53$ raised to the power 3. Another increase in the deuterium abundance by a factor of 1.53 leads to a similar enhancement. Thus, multiply deuterated isotopologues are a particularly sensitive indicator of changes in the elemental deuterium abundance.

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REFERENCES

Bacmann, A., Lefloch, B., Ceccarelli, C., Steinakcer, J., Castets, A., & Loinard, L. 2003, ApJ, 585, L55
Charnley, S. B., Tielens, A. G. G. M., & Rodgers, S. D. 1997, ApJ, 482, L203
Dartois, E., Thi, W. F., Geballe, T. R., Deboffle, D., d'Hendecourt, L., & van Dishoeck, E. 2003, A&A, 399, 1009
Draine, B. T. 2004, in Carnegie Observatories Centennial Symp., Origin and Evolution of the Elements, ed. A. McWilliam & M. Rauch (Cambridge: Cambridge Univ. Press), 317
———. 2006, in ASP Conf. Ser. 348, Astrophysics in the Far Ultraviolet: Five Years of Discovery with *FUSE*, ed. G. Sonnebom, H. Moos, & B-G Andersson (San Francisco: ASP), 58
Gerlich, D., Herbst, E., & Roueff, E. 2002, Planet. Space Sci., 50, 1275
Gerlich, D., & Schlemmer, S. 2002, Planet. Space Sci., 50, 1287
Jura, M. 1982, in Advances in UV Astronomy: 4 Years of *IUE* Research, ed. Y. Kondo, J. M., Mead, & R. D. Chapman (NASA CP-2238; Greenbelt: NASA), 54
Le Bourlot, J., Pineau des Forêts, G., Roueff, E., & Flower, D. R. 1995, A&A, 302, 870
Linsky, J. L., et al. 2006, ApJ, 647, 1106
Lipshtat, A., Biham, O., & Herbst, E. 2004, MNRAS, 348, 1055
Lis, D. C., Gerin, M., Roueff, E., Vastel, C., & Phillips, T. G. 2006, ApJ, 636, 916
Oliveira, C. M., & Hébrard, G. 2006, ApJ, 653, 345
Parise, B., Simon, T., Caux, E., Dartois, E., Ceccarelli, C., Rayner, J., & Tielens, A. G. G. M. 2003, A&A, 410, 897
Phillips, T. G., & Vastel, C. 2003, in SFChem 2002: Chemistry as a Diagnostic of Star Formation, ed. C. L. Curry & M. Fich (Ottawa: NRC Research Press), 3
Roberts, H., Herbst, E., & Millar, T. J. 2002, MNRAS, 336, 283
———. 2003, ApJ, 591, L41
———. 2004, A&A, 424, 905
Roueff, E., Lis, D. C., van der Tak, F. F. S., Gerin, M., & Goldsmith, P. F. 2005, A&A, 438, 585
Stantcheva, T., & Herbst, E. 2003, MNRAS, 340, 983