HD/H$_2$ Molecular Clouds in the Early Universe: The Problem of Primordial Deuterium

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Received 15 April, 2010

Abstract

We have detected new HD absorption systems at high redshifts, $z_{\text{abs}} = 2.626$ and $z_{\text{abs}} = 1.777$, identified in the spectra of the quasars J0812+3208 and Q1331+170, respectively. Each of these systems consists of two subsystems. The HD column densities have been determined: $\log N_{\text{HD}}^1 = 15.70 \pm 0.07$ for $z_{\text{abs}} = 2.626443(2)$ and $\log N_{\text{HD}}^2 = 12.98 \pm 0.22$ for $z_{\text{abs}} = 2.626276(2)$ in the spectrum of J0812+3208 and $\log N_{\text{HD}}^3 = 14.83 \pm 0.15$ for $z_{\text{abs}} = 1.77637(2)$ and $\log N_{\text{HD}}^4 = 14.61 \pm 0.20$ for $z_{\text{abs}} = 1.77670(3)$ in the spectrum of Q1331+170. The measured HD/H$_2$ ratio for three of these subsystems has been found to be considerably higher than its values typical of clouds in our Galaxy. We discuss the problem of determining the primordial deuterium abundance, which is most sensitive to the baryon density of the Universe $\Omega_b$. Using a well-known model for the chemistry of a molecular cloud, we have estimated the isotopic ratio D/H=HD/H$_2$=(2.97±0.55)×10^{-5}$ and the corresponding baryon density $\Omega_b h^2 = 0.0205^{+0.0025}_{-0.0020}$. This value is in good agreement with $\Omega_b h^2 = 0.0226^{+0.0006}_{-0.0006}$ obtained by analyzing the cosmic microwave background radiation anisotropy. However, in high-redshift clouds, under conditions of low metallicity and low dust content, hydrogen may be incompletely molecularized even in the case of self-shielding. In this situation, the HD/H$_2$ ratio may not correspond to the actual D/H isotopic ratio. We have estimated the cloud molecularization dynamics and the influence of cosmological evolutionary effects on it.

Key words. cosmology, primordial composition of matter, molecular clouds in early Universe, qso: J0812+3208, Q1331+170.

1. Introduction

Being the main coolant of the primordial gas, molecular hydrogen (both H$_2$ and HD) plays a central role in the creation of gas condensations and the formation of the first stars in the post-recombination Universe (see, e.g., Puy et al. 1993; Palla and Galli 1995; Lepp et al. 2002; McGreer and Bryan 2008; Bromm et al. 2009). Observations of these molecules in high-redshift absorption clouds allow the physical conditions existed in the early Universe to be determined.

The fact that measuring the HD column density makes it possible to independently determine the primordial D/H isotopic ratio is important too (Noterdaeme et al. 2008a; Ivanchik et al. 2010). Among the light nuclides produced by primordial nucleosynthesis $^2$D, $^3$T, $^3$He, $^4$He, $^6$Li, $^7$Li, and $^7$Be, the primordial deuterium abundance is the most sensitive indicator of one of the key cosmological parameters – the baryon-to-photon ratio, $\eta \equiv n_b/n_{\gamma}$, or the corresponding baryon density of the Universe $\Omega_b$ (see, e.g., Sarkar 1996; Olive et al. 2000; Coc et al. 2005; Fields and Olive 2006).

Until recently, the D/H ratio has been determined mainly only from H$^1$ and D$^1$ atomic lines in the absorption spectra of quasars. However, such measurements run into a number of difficulties. The optical D$^1$ and H$^1$ spectra are almost identical; only the wavelengths of their lines are shifted by 0.027%. At the same time, the number densities of these atoms differ by four or five orders of magnitude. Therefore, if the H$^1$ column density is low, then the D$^1$ lines are not seen at all. If, alternatively, the hydrogen column density is too high, then the H$^1$ lines are saturated, broadened, and overlap the D$^1$ lines (blend them). Moreover, the lines identified as D$^1$ ones can in principle be produced by a small H$^1$ cloud that moves relative to the cloud being studied with a velocity of $\sim 80$ km/s, especially since there are actually many such clouds moving with different velocities (the so-called Lyman-α forest) on the line of sight. These factors may also be responsible for the significant spread in the D/H values obtained by this method.

No difficulty with the identification of lines arises if the relative abundance of not the D$^1$ and H$^1$ atoms but the HD and H$_2$ molecules is measured, because their spectra differ significantly and most narrow absorption lines do not overlap. However, the detection of molecules at high redshifts is a fairly rare event. For example, H$_2$ molecules are observed only in $\sim 10\%$ of the DLA systems (Noterdaeme et al. 2008b) (damped Lyman-α systems – those with a high atomic hydrogen column density, $N_{\text{HI}} \gtrsim 10^{20}$cm$^{-2}$, Wolfe et al. 2005) and only 19 high-redshift H$_2$ systems have been detected to date. Only in three of them have HD lines been detected as well (the first system is Q1232+0815 (Varshalovich et al. 2001; Ivanchik et al. 2010); the second system is
of the quasar J 0812+3208 (log \( N_{\text{H}} \)) considered as a search criterion for HD systems. Therefore, the absorption systems at \( z = 1.777 \) were analyzed by Prochaska et al. (2003). Analysis of the molecular hydrogen lines in the spectrum of the quasar J 0812+3208 (\( \log N_{\text{H}} = 19.88 \), Jorgenson et al. 2009) and \( z_{\text{abs}} = 1.777 \) in the spectrum of the quasar Q 1331+170 (\( \log N_{\text{H}} = 19.65 \), Cui et al. 2005). Having analyzed these systems, we detected two new HD systems (each of them consists of two subsystems).

2. Observational Data

J 0812+3208. A spectrum of J 0812+3208 was taken with the HIRES echelle spectrograph at the Keck I telescope. This quasar was observed in the wavelength range 3300–6200 Å in 2005 under Ellison’s and Wolfe’s programs (four 1-h and two 1.5-h exposures) and in 2007 and 2008 under Prochaska’s program (four 1-h and four 40-min exposures). The data are in free access from the Keck/HIRES archive[1]. We reduced and added these exposures using the MAKEE software package[2] specially developed by Barlow for Keck/HIRES. The total exposure time was 13.7 h, which allowed a signal-to-noise ratio of \( \sim 45 \) to be achieved at a resolution of \( \sim 46,000 \) for the part of the spectrum containing H2 and HD absorption lines.

Q 1331+170. A high-resolution spectrum of Q 1331+170 in the wavelength range 2280–3370 Å, within which the molecular hydrogen lines at \( z = 1.777 \) fall, was taken with the STIS spectrograph on the Hubble Space Telescope (HST) (program 7271 in 1999 and program 9172 in 2002–2003, the principal investigator is Bechtold). The data are in free access from the HST archive[3]. The exposures were reduced and added using the CALSTIS procedures of the IRAF software package. The total exposure time was 14.5 h at a resolution of \( \sim 25,000 \) and the best signal-to-noise ratio of \( \sim 7 \).

3. Data Analysis

J 0812+3208. A DLA system was identified in the spectrum of J 0812+3208 (\( \text{zem} = 2.701 \)) in 2000 (White et al. 2000). The heavy-element abundance in this system was analyzed by Prochaska et al. (2003). Analysis of the C I absorption lines in this system (Jorgenson et al. 2009) revealed a cold cloud at redshift \( z_{\text{abs}} = 2.626 \). The upper limit on the cloud temperature \( T < 78 \text{ K} \) was estimated from the Doppler parameter of neutral carbon lines. Molecular hydrogen lines associated with the absorption system were also detected in the spectrum of this quasar.

Q 1331+170. A DLA system with \( \log N_{\text{H}} = 21.18 \) was identified in the spectrum of Q 1331+170 (Carswell et al. 1975). The redshift of this system, \( z = 1.777 \), does not allow the part of the quasar spectrum with molecular hydrogen lines to be obtained by ground based telescopes. Only HST observations allowed molecular hydrogen lines to be identified in this system (Cui et al. 2005).

3.1. \( \text{H}_2 \) Column Densities

J 0812+3208. We performed an independent analysis of the molecular hydrogen absorption system in the spectrum of J 0812+3208. A synthetic spectrum was constructed to determine the \( \text{H}_2 \) column density. The molecular hydrogen lines show the presence of two subsystems in the spectrum, \( z_A = 2.626443(2) \) (subsystem A) and \( z_B = 2.626276(2) \) (subsystem B), with a relative shift of \( \sim 14 \text{ km/s} \). This structure is most pronounced in the \( \text{H}_2 \) lines associated with the excited \( J = 2, 3, 4 \) rotational levels of the \( X^1\Sigma^+ \), \( v = 0 \) ground state. The lines associated with the ground states of para- and orthohydrogen (\( J = 0 \) and 1) are strongly saturated; it is hard to resolve the two subsystems in them and to determine the Doppler parameter \( b \). Therefore, when determining the \( \text{H}_2 \) column density, we proceed as follows. First, we analyzed the \( J = 2, 3, 4 \) levels. A local continuum was constructed for each of the selected lines (a total of \( \sim 50 \) lines belonging to the Lyman (from L0-0 to L17-0) and Werner (from W0-0 to W4-0) bands were used). The Doppler parameter was assumed to be the same for all levels. It should be noted that the parameter \( b \) may grow with increasing rotational level number (see, e.g., Balashev et al. (2009) and references therein). Here, we disregarded this possibility, because our main objective was to determine the total hydrogen column density, which for this system is determined mainly by the ground rotational levels whose lines are strongly saturated and, as a result, are insensitive to the parameter \( b \). Once the values of the redshifts and Doppler parameters for the two subsystems had been obtained, we fixed these values and constructed a synthetic spectrum for the ground \( \text{H}_2 \) levels. The synthetic \( \text{H}_2 \) spectrum is shown in Fig. 4, and the parameters obtained from our analysis are presented in Table 4. For subsystem A, our \( \text{H}_2 \) results are in good agreement with those of Jorgenson et al. (2009). However, the latter authors determined the Doppler parameter \( b_{\text{H}_2} \) from the Doppler parameter of neutral carbon \( b_{\text{C I}} \), while we used it as an independent parameter being fitted.

For subsystem B, the derived column densities of \( \text{H}_2 \) molecules in the \( J = 0 \) and 1 ground states have large errors, because the column density in subsystem B is an order of magnitude lower than that in subsystem A. Therefore, the saturated lines are centered near \( z_A \) due to the small relative shift between subsystems A and B.
while subsystem B makes only a slight contribution to the asymmetry of the Lorentz wings.

Fig. 2 shows the relative populations of H$_2$ rotational states in the two subsystems. Using the ratio of the ortho-H$_2$ and para-H$_2$ (J = 0 and 1) column densities, we estimated the gas temperature in both subsystems: $T_A^{01} = 48 \pm 2$ K and $T_B^{01} = 50^{+38}_{-15}$ K.

Q 1331+170. In contrast to the analysis of the H$_2$ absorption system in Cui et al. (2005), where the authors fitted only one component ($z = 1.776553(3)$) into the spectrum, we constructed a synthetic spectrum by assuming the absorption system to consist of two components ($z_C = 1.77637(2)$ and $z_D = 1.77670(3)$). Two components with a relative shift of $\sim 35$ km/s are clearly seen in the H$_2$ lines originating from the J = 4 rotational level (Fig. 3) and in the HD lines we identified (see Fig. 6 below). The redshifts of both subsystems were determined by analyzing the H$_2$ (J = 4) lines. Since the lines associated with the J = 0 and 1 levels are strongly saturated for both subsystems, the column density of molecules at these levels can be obtained with a good accuracy. This cannot be said for the lines associated with the J = 2 and 3 levels, which fall into the logarithmic part of the curve of growth. As a result, the total molecular hydrogen column density for the two subsystems is $\log N_C^{\text{H}_2} = 19.43 \pm 0.10$ and $\log N_D^{\text{H}_2} = 19.39 \pm 0.11$.

3.2. HD Column Densities

J 0812+3208. To determine the HD column density, the Doppler parameter, and the redshift, we constructed a synthetic spectrum for each of the two subsystems (A and B). The parts of the quasar spectrum normalized to their statistical weights $g_J$ versus level energy $E_J$. The red and blue circles correspond to subsystems A and B in the spectrum of J 0812+3208. The straight lines correspond to $T_{01}$, the excitation temperatures of the J = 0 and J = 1 levels.
Table 1. Results of our analysis of the absorption system at \( z = 2.626 \) in the spectrum of J0812 + 3208

| Subsystem A | Subsystem B |
|-------------|-------------|
| \( z_A = 2.626443(2) \) | \( z_B = 2.626276(2) \) |
| \( \log(N) \) | \( \log(N) \) | \( b, \text{ km/s} \) | \( b, \text{ km/s} \) |
| \( \text{H}_2 \) | \( \text{H}_2 \) | \( J=0 \) | \( J=0 \) |
| \( J=0 \) | \( 19.83 \pm 0.05 \) | \( 0.81 \pm 0.10 \) | \( 18.71 \pm 0.45 \) |
| \( J=1 \) | \( 19.25 \pm 0.02 \) | \( 0.81 \pm 0.10 \) | \( 18.19 \pm 0.19 \) |
| \( J=2 \) | \( 16.47 \pm 0.10 \) | \( 0.81 \pm 0.10 \) | \( 16.79 \pm 0.10 \) |
| \( J=3 \) | \( 15.15 \pm 0.25 \) | \( 0.81 \pm 0.10 \) | \( 14.62 \pm 0.09 \) |
| \( J=4 \) | \( 13.95 \pm 0.12 \) | \( 0.81 \pm 0.10 \) | \( 13.39 \pm 0.14 \) |
| \( \sum J \) | \( 19.93 \pm 0.04 \) | \( \sum J \) | \( 18.82 \pm 0.37 \) |
| \( \text{HD} \) | \( \text{HD} \) | \( J=0 \) | \( J=0 \) |
| \( J=0 \) | \( 15.70 \pm 0.07 \) | \( 0.7 \pm 0.04 \) | \( 12.98 \pm 0.22 \) |
| \( J=1 \) | \( 13.77 \pm 0.15 \) | \( 0.7 \pm 0.04 \) | \( < 3.6^{1} \) |
| \( \sum J \) | \( 15.71 \pm 0.07 \) | \( \sum J \) | \( \sum J \) |

\[ \text{HD}/2\text{H}_2 = 2.97^{+0.52}_{-0.50} \times 10^{-5} \]

\[ \text{HD}/2\text{H}_2 = 7.08^{+10.05}_{-4.26} \times 10^{-7} \]

\[ ^{1} - \text{The observed lines are insensitive to the parameter } b, \text{ because they are located at the linear part of the curve of growth.} \]

Figure 3. Synthetic H\(_2\) spectrum of the absorption system at \( z = 1.777 \) fitted into the observed spectrum of Q\( 1331+170 \) (STIS/HST). The two components of the synthetic spectrum are indicated by the dotted and dashed lines. These components are well resolvable for the lines originating from the \( J = 4 \) rotational level (bottom).

density in the cloud, \( n = 54^{+36}_{-22} \text{ cm}^{-3} \) (for more detail, see below). As far as we know, this is the first reliable detection of HD lines associated with the \( J = 1 \) level. This proved to be possible due to the high HD column density and good spectrum quality.

The HD molecular lines of the Lyman and Werner series are present in the spectrum up to \( L18-0 \) and \( W4-0 \) inclusively. In general, the HD wavelengths and oscillator strengths for \( \nu'' = 0 \) and \( W \nu'' = 0 \) lines with large \( \nu'' \) are not known well enough. The laboratory wavelengths were measured with a high accuracy, \( \delta \lambda/\lambda \sim 5 \times 10^{-8} \), only for the bands up to \( L9-0 \) and \( W0-0 \) (Ivanov et al. 2008). For shorter wavelength transitions, we used the laboratory data (Ivanov et al. 2010) kindly provided to us by Prof. W. Ubachs. The oscillator strengths were taken from the calculations by Abgrall and Roueff (2006); the wavelengths are also given there. However, comparison of the theoretical (Abgrall and Roueff 2006) and laboratory (Ivanov et al. 2008) values showed that the calculated wavelengths for some lines differ significantly from the laboratory ones. For example, the calculated wavelength of the \( L11-0\text{R}(0) \) line differs from the laboratory value by \( \sim 8 \text{ km/s} \) and does not fit into the general analysis. Using the data from Ivanov et al. (2010), we were able to determine the HD column density with a good accuracy.

The results of our determination of the parameters for the identified HD molecular lines in the spectrum of J0812+3208 are presented in Table 1. The redshifts of the HD lines in subsystems A and B coincide, within the error limits, with those determined by analyzing H\(_2\) lines. To determine the HD (\( J = 0 \)) column density in subsystem A, we chose the R(0) lines of the following bands: \( L6-0, L3-0, L4-0, L5-0, L8-0, L11-0, L18-0, W0-0, W4-0 \). The 1, 2, and 3\( \sigma \) confidence regions for \( N_{\text{HD}} \) and \( b_{\text{HD}} \) are shown in Fig. 5.
Figure 4. Synthetic HD molecular spectrum of the absorption system at $z = 2.626$ in the observed spectrum of J0812+3208. Two components are seen for the transitions from the $J = 0$ ground state. The $R(1), P(1),$ and $Q(1)$ lines of the transitions from the excited $J = 1$ rotational level are also shown.

We determined the HD column density in subsystem A, $\log N_{\text{HD}} = 15.71 \pm 0.07$. This is the highest value of $N_{\text{HD}}$ measured in the quasar spectra. The derived Doppler parameter $b_{\text{HD}} = 0.70 \pm 0.04 \, \text{km/s}$ agrees (within the error limits) with $b_{\text{C} I} = 0.33 \pm 0.05 \, \text{km/s}$ and $b_{\text{H}_2} = 0.81 \pm 0.10 \, \text{km/s}$ (if the thermal broadening is dominant, then the Doppler parameters are related as the square root of the ratio of the element masses).

Number density in the subsystem J0812+3208A. The relative populations of the HD $J = 0$ and $J = 1$ rotational levels determined in the absorption subsystem J0812+3208A allow the number density of the molecular cloud to be estimated. This requires considering the level population balance equations. The $J = 1$ level can be populated by the direct radiative transition from the $J = 0$ level,
radiative pumping through excited electronic states, and collisions. Typically, the particle number density in a diffuse cloud is \( n \approx 10 - 500 \text{ cm}^{-3} \). At such number densities and the Galactic mean intensity of ultraviolet radiation, collisions will be the dominant \( J = 1 \) level population channel for the bulk of the cloud. Indeed, at such a high measured column density in the cloud, \( \log N_{\text{HD}} = 15.7 \), the rate of the \( 0\rightarrow1 \) population by radiative pumping inside the cloud falls by more than two orders of magnitude through selfshielding. The direct radiative \( 0\rightarrow1 \) population can also be neglected. The dominant channel of the \( 1\rightarrow0 \) transition is spontaneous relaxation characterized by the radiative transition probability \( A_{01} \). Thus, we can estimate the number density from the formula

\[
n = \frac{N_{J=1} A_{01}}{N_{J=0} C_{01}}
\]

The main collisional parter of HD for a molecular cloud will be \( \text{H}_2 \); the values of the collisional probability coefficient \( C_{01} \) were taken from Flower et al. (2000). Using a temperature estimate in the cloud of \( T_{01} = 48 \pm 2 \text{ K} \), we obtained the following estimate for the number density in the cloud: \( n = 54^{+36}_{-22} \text{ cm}^{-3} \) it agrees with typical values for diffuse clouds (Rachford et al. 2002). Note, however, that if the cloud is not molecularized, then the main collisional partner is atomic hydrogen and the number density estimate doubles.

**Q1331+170.** The HD molecular lines are present in the spectrum up to the L18-0 Lyman and W4-0 Werner bands, respectively (some of these lines are shown in Fig. 6). Because of the low signal-to-noise ratio, we were able to use only the L3-0R(0), L4-0R(0), L7-0R(0), and L8-0R(0) lines to determine the HD parameters. Two subsystems whose redshifts coincided, within the error limits, with those determined by analyzing \( \text{H}_2 \) are seen in the chosen lines. The HD column densities determined by synthetic spectrum construction were found to be \( \log N_{\text{NC}} = 14.83 \pm 0.15 \) and \( \log N_{\text{HD}} = 14.61 \pm 0.20 \).

### 3.3. HD/\( 2\text{H}_2 \) Ratio

Until now, HD lines (at high redshifts) have been identified only in three of the 19 \( \text{H}_2 \) absorption systems. Figure [7] shows the HD, \( \text{H}_2 \), and D, \( \text{H}_1 \) column densities measured in interstellar clouds of our Galaxy and absorption systems of quasars. Determining the column densities of HD and \( \text{H}_2 \) or \( \text{D} \) and \( \text{H}_1 \) at high redshifts allows the primordial D/H isotopic ratio and, hence, \( \Omega_2 \) to be estimated. The oblique straight lines in Fig. 6 indicate the column densities that correspond to the mean D/H and HD/\( 2\text{H}_2 \) ratios for the Galactic and extragalactic systems. In our Galaxy, the D/H ratio measured from the column densities of atomic D and H\(_1\) lines (Linsky et al. 2006) is systematically lower than its mean value obtained by analyzing the quasar spectra (Pettini et al. 2008). In principle, this can be explained by the astration of deuterium in stars. We also see that there is a significant difference between the values of D/H and HD/\( 2\text{H}_2 \) measured in our Galaxy. This may be because in contrast to \( \text{H}_2 \), the HD molecules are not always shielded from ultraviolet radiation and, hence, deuterium is molecularized to a lesser extent. Another explanation for the shortage of the HD molecular fraction can be complex chemistry of molecular clouds, where deuterium can effectively enter into other, more complex molecules, H\(_2\)O, NH\(_3\), HCN, polyaromatic hydrocarbons, etc. No significant difference is observed for the D/H ratios in the spectra of quasars measured from the molecular and atomic components (Fig. 7). However, the statistics for quasar spectra is much poorer than that for systems in our Galaxy.

**J 0812+3208.** The ratios of the HD and \( \text{H}_2 \) column densities in the spectrum of J 0812+3208 were found to be HD/\( 2\text{H}_2 = 2.97^{+0.52}_{-0.50} \times 10^{-5} \) and HD/\( 2\text{H}_2 = 7.08^{+1.05}_{-4.26} \times 10^{-7} \) for the absorption systems A and B, respectively. The HD/\( 2\text{H}_2 \) ratio in subsystem B is definitely unsuitable for the D/H estimate, because the HD column density in this subsystem (\( \log N_{\text{HD}} = 12.98 \)) is two orders of magnitude lower than the value necessary for the self-shielding of molecules and, as a result, deuterium may be incompletely molecularized. According to the calculations by Le Petit et al. (2002), if HD and \( \text{H}_2 \) are self-shielded from ultraviolet radiation, then both components are completely molecularized and the universal ratio D/H = HD/\( 2\text{H}_2 \) is established in the cloud. In our case, only subsystem A can be completely shielded in HD, because it has a relatively high HD column density: \( \log N_{\text{HD}} = 15.7 \). Besides, this subsystem has a low metallicity (relative to the solar one), \( \lesssim -1.0 \) (Prochaska et al. 2003). This means a low level of deuterium astration in stars and makes it possible to estimate the primordial D/H ratio. On the other hand, a low metallicity also means a low dust content; since molecular hydrogen is formed mainly on dust, this leads to a lower formation rate of \( \text{H}_2 \) and HD and, in contrast to the calculations by Le Petit et al. (2002), the cloud molecularization may be incomplete. Since there is an additional, fairly efficient formation channel for HD, HD + D\(_+\rightarrow HD + H^+\) at a low \( \text{H}_2 \) formation rate on dust this can lead to a significant increase in the HD/\( 2\text{H}_2 \) ratio and it will not correspond to the true D/H isotopic ratio (see, e.g., Ferlet et al. 2000). Besides, at a low dust content, the process of gas molecularization in...
the cloud slows down. Therefore, the matter in the observed clouds may not have time to reach a steady state in chemical equilibrium and the HD/2H$_2$ ratio can then be different for clouds of different ages (see the Section 4 and Fig. S).

Q 1331+170. The ratios of the HD and H$_2$ column densities in the spectrum of Q 1331+170 were found to be HD/2H$_2$ = $1.24^{+0.60}_{-0.40} \times 10^{-5}$ and HD/2H$_2$ = $0.83^{+0.54}_{-0.33} \times 10^{-5}$ for the absorption systems C and D, respectively. Note that the large errors in the parameters compared to the previous system are attributable to a poorer spectrum quality.

3.4. Peculiarities of the HD/H$_2$ Absorption Systems

**J 2123-0050.** According to Malec et al. (2010), the absorption system in the spectrum of J2123-0050 has the highest HD/2H$_2$ ratio, $\sim 7 \times 10^{-5}$. However, in our opinion, this system requires an additional study of the column densities and its physical parameters, because the ortho-to-parahydrogen ratio obtained by these authors, $\sim 16:1$, exceeds considerably the ratio 3:1, appears very strange, and has never been observed before.

**J 1439+1117.** The metallicity of this system is nearly solar and HD/2H$_2$ = $1.5 \times 10^{-5}$ is close to the D/H ratio measured in our Galaxy (Noterdaeme et al. 2008a).

**Q 1232+0815, J 0812+3208.** This system has a low metallicity, $\sim -1.5$ (Balashev et al. 2010; Prochaska et al. 2003), and high HD column densities. This makes the derived values for these HD/2H$_2$ systems a good estimate of the primordial D/H ratio.

**Q1331+170.** The metallicity of this system is also low, $\sim -1.5$ (Prochaska and Wolfe 1999). However, incomplete shielding in HD is quite possible for the two derived HD/H$_2$ systems, because the HD column density is low. Besides, the spectrum has a low signal-to-noise ratio and, hence, the estimate of the primordial D/H ratio based on these systems is ambiguous.

The results for all the systems are summarized in Table S.

### 4. Cloud Molecularization Model

To estimate the influence of incomplete molecularization on the HD/H$_2$ ratio, we calculated the chemical evolution of an HD/H$_2$ molecular cloud (this model will be presented in detail in Balashev et al. (2010)). Figure S presents the results of our calculations of the chemical evolution of a typical interstellar cloud with a temperature $T = 80$ K and a total hydrogen number density $n = 100$ cm$^{-3}$. We consider a cloud composed of H, He, D, their ions, electrons, H$_2$ and HD molecules, and some amount of dust on which these molecules are efficiently formed. The chemical reaction rates were taken from Stancil et al. (1998) and Glover and Jappsen (2007). We also took into account more complex molecules, H$^+3$, H$_2$D$^+$, HeH$^+$, HeD$^+$, etc., but their influence on the HD/H$_2$ evolution of interest to us proved to be insignificant in the case of a diffuse molecular cloud. The cloud was assumed to be in the field of external ultraviolet radiation, which leads to an efficient dissociation of molecules in the cloud surface layers. Its intensity was taken to be equal to the mean intensity of ultraviolet radiation in our Galaxy. The function of cloud self-shielding from ultraviolet radiation was taken from Draine and Bertoldi (1996). We also assumed that the cloud was irradiated by cosmic rays, which leads to gas ionization that provides ionmolecular reactions. The cosmic-ray ionization rate was taken to be equal to its Galactic mean value. The dust content was taken to be $1$ (Fig. 8, left) or $0.01$ (Fig. 8 right) of the mean dust content in our Galaxy. These values were chosen so as to qualitatively explain the difference between the observed clouds in our Galaxy and high-redshift DLA systems. The total hydrogen column density in the system $N_{\text{tot}} = N_{\text{HI}} + 2N_{\text{H}_2}$ was chosen from the condition $N_{\text{H}_2} \approx 10^{20}$cm$^{-2}$, which corresponds to the column density for the absorption subsystem A of the quasar J0812+3208.

We see that this model can explain the observational data, provided that the cloud age is greater than $10^7$ yr. At the Galactic dust content, the cloud reaches almost...
Figure 7. D1, H1 and HD, H2 column density measurements. The circles indicate the results of HD and H2 measurements in the quasar spectra (the red circles correspond to the data obtained in this paper); the squares represent the results of HD and H2 measurements in our Galaxy (Snow et al. 2008; Lacour et al. 2005); the blue and light blue squares indicate the points for which the HD column density is higher and lower than log N_{HD} = 15, respectively. The solid straight line indicates the mean HD/2H2 ratio determined from points with log N_{HD} > 15; the green stripe indicates the results of H1 and D1 measurements taken from Linsky et al. (2006) (the mean D/H ratio for these values is indicated by the dotted line). The D/H ratio in the quasar spectra measured from H1 and D1 lines (Pettini et al. 2008) is indicated by the yellow stripe.

Figure 8. Time variation of the HD/2H2 abundance ratio (top panels) and the molecular fraction (bottom panels) during the evolution of an interstellar cloud with a number density n = 1000 cm^{-3} and T = 80 K. The calculations are presented for the Galactic dust content (left panels) and 0.01 of the Galactic dust content (right panels). The vertical line marks the characteristic dynamical lifetime of clouds, \sim 3 \times 10^{7} yr.
complete molecularization in H$_2$, $f_{H_2} = \frac{2N_{H_2}}{N_{H_2} + N_{HD}} \approx 1$ (Figs. 8 bottom left); the HD molecular fraction ($f_{HD} = \frac{N_{HD}}{N_{H_2} + N_{HD}}$) is lower, because HD is shielded more weakly against ultraviolet radiation than H$_2$. The situation is different at a low dust content. The hydrogen molecular fraction is low ($f_{H_2} < 0.05$); the ion reaction of HD formation becomes more efficient than the formation of HD on dust and, as a result, the molecular fraction of HD can be higher than that of H$_2$ (Figs. 8 bottom right).

It is important to note that HD/H$_2$ depends significantly on the cloud age at a low dust content (Figs. 8 top panels). In addition, the HD/H$_2$ ratio also depends on other factors, namely, the ultraviolet radiation background, the cosmic-ray intensity, the gas number density, and the total column density. Therefore, the HD/H$_2$ ratio may not correspond to the actual D/H isotopic ratio and its estimation requires developing a model for the cloud molecularization dynamics (Balashev et al. 2010). Note that for the two most saturated (in HD) systems (J 0812+3208A and Q 1331+170, see Fig. 7), the HD/H$_2$ ratios turned out to be coincident (within the error limits) and close to the primordial D/H determined by analyzing the cosmic microwave background radiation anisotropy (Komatsu et al. 2010). It is hoped that increasing the statistics of high-redshift molecular clouds will clarify this situation.

In molecular cloud models, the D/HD transition is assumed to occur at larger penetration depths of the emission into the cloud than the H/HD transition (see, e.g., Le Petit et al. 2002). However, under conditions of low dust content, a situation where the D/HD transition in the cloud will begin more early than the H/HD transition is possible. This will occur via the ion reaction of HD formation under incomplete H$_2$ molecularization conditions.

At a low dust content and high column densities, $N_{H_2} \gtrsim 10^{24}$ cm$^{-2}$, on long time scales ($\gtrsim 10^8$ yr), the cloud reaches complete molecularization in H$_2$ and HD and the HD/H$_2$ ratio will correspond to the D/H ratio. However, there will exist a long time interval ($\sim 10^7$ yr) in the cloud evolution in which the HD/H$_2$ ratio will exceed considerably the D/H ratio.

**5. Conclusions**

We identified HD molecular lines in the absorption systems at $z_{abs} = 2.626$ and $z_{abs} = 1.777$ in the spectra of the quasars J 0812+3208 and Q 1331+170, respectively. Each system consists of two clearly resolvable components. The HD and H$_2$ column densities were determined for all four subsystems (Table 2).

Since only one of the four identified subsystems, at $z = 2.626443(2)$, in the spectrum of J 0812+3208A has an HD column density exceeding its critical value for self-shielding, one would expect the HD/H$_2$ ratio in the steady-state model of a completely molecularized cloud to characterize the primordial D/H isotopic ratio. Under these conditions, D/H = ($2.97^{+0.52}_{-0.50}$) $\times 10^{-5}$, which corresponds to the baryonic matter density $\Omega_b h^2 = 0.0205^{+0.0025}_{-0.0020}$. This value is in good agreement with $\Omega_b h^2 = 0.0226^{+0.0006}_{-0.0006}$ obtained by analyzing the cosmic microwave background radiation anisotropy (Komatsuet al. 2010).

However, the cloud molecularization dynamics and the influence of cosmological evolutionary factors related to a change in dust content, ionizing radiation background, and cosmic-ray intensity on it can lead to a systematic shift in the estimate of the primordial D/H isotopic ratio.

We made preliminary estimates of the effects related to the cloud molecularization dynamics in the early

### Table 2. HD/H$_2$ absorption systems in the quasar spectra.

| QSO       | $z_{abs}$ | $N_{H_2}$, cm$^{-2}$ | $N_{ND}$, cm$^{-2}$ | Instrument | References$^*$ |
|-----------|-----------|----------------------|---------------------|------------|---------------|
| J 0812+3208 | 2.33714(3) | $4.78^{+0.96}_{-0.96} \times 10^{19}$ | $3.39^{+1.6}_{-0.8} \times 10^{15}$ | UVES       | 1, 2          |
| J 1439+1117$^2$ | 2.41837    | $2.40^{+0.49}_{-0.62} \times 10^{19}$ | $7.18^{+0.44}_{-0.44} \times 10^{14}$ | UVES       | 3             |
| J 2123+0050 | 2.0593276(5) | $3.68^{+0.33}_{-0.30} \times 10^{17}$ | $5.89^{+0.42}_{-0.33} \times 10^{13}$ | KECK     | 4             |
| Q 0812+3208 | 2.626443(2) | $8.54^{+0.83}_{-0.76} \times 10^{19}$ | $5.07^{+0.88}_{-0.75} \times 10^{15}$ | KECK     | 5             |
| Q 0812+3208 | 2.626376(2) | $6.74^{+0.36}_{-0.92} \times 10^{18}$ | $9.55^{+0.30}_{-1.80} \times 10^{12}$ | KECK     | 5             |
| Q 1331+170 | 1.77637(2) | $2.66^{+0.65}_{-0.53} \times 10^{19}$ | $6.61^{+2.73}_{-1.93} \times 10^{14}$ | HST      | 5             |
| Q 1331+170 | 1.77670(2) | $2.45^{+0.69}_{-0.54} \times 10^{19}$ | $4.07^{+1.38}_{-1.50} \times 10^{14}$ | HST      | 5             |

$^*$ Refs.: 1 Varshalovich et al. (2001), 2 Ivanchik et al. (2010), 3 Noterdaeme et al. (2008a), 4 Malec et al. (2010), 5 this paper.
Universe. Their allowance was shown to be necessary to properly determine the primordial D/H ratio.

Increasing the statistics of HD/H2 molecular systems will allow progress to be made both in understanding the chemical and isotopic evolution of molecular clouds as well as for determining the primordial D/H isotopic ratio. Significant progress in solving this problem may be expected when future extremely telescopes will be put into operation.

Acknowledgments

We thank Prof. W. Ubachs who kindly provided the HD wavelengths. This work was supported by the Russian Foundation for Basic Research (project no. 08-02-01246a) and the Program of the Russian President for Support of Leading Scientific Schools (NSh-3769.2010.2).

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Figure 9. Synthetic H$_2$ spectrum of the absorption system at $z = 1.777$ fitted into the observed spectrum of Q1331+170 (STIS/HST).