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H_2/HD Molecular Clouds in the Early Universe. An Independent Means of Estimating the Baryon Density of the Universe

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Abstract—A review of molecular hydrogen H_2 absorption systems identified in quasar spectra is presented. The analysis of such systems allows the determination of the chemical composition of the interstellar medium and the physical conditions existing in the early Universe, about 10–12 billioin years ago. To date, 27 molecular hydrogen systems have been found, nine of which show HD lines. An independent method for estimating the baryon density of the Universe is described, and is based on the analysis of the relative abundances of H_2 and HD molecules. Among known H_2/HD systems, only the two systems detected in Q1232+082 and Q0812+320 quasar spectra satisfy the condition of self-shielding of the absorbing cloud $\log N_{H_2,HD} \gtrsim 15$. Under these conditions the local molecular fraction can reach unity, making it possible to estimate the relative deuterium abundance D/H using the ratio of the HD and H_2 column densities $N(HD)/2N(H_2)$. The analysis of the column densities for these two systems yields $D/H = HD/2H_2 = (3.26 \pm 0.29) \times 10^{-5}$. Comparison of this result with the prediction of BBN theory for D/H enables the determination of the baryon density of the Universe: $\Omega_b h^2 = (0.0194 \pm 0.0011)$. This is somewhat lower than the values $\Omega_b h^2 = (0.0224 \pm 0.0012)$ and (0.0221 ± 0.0003) obtained using other independent methods: (i) analysis of the relative D and H abundances in Lyman Limit Systems at high redshifts, and (ii) analysis of the anisotropy of the cosmic microwave background. Nevertheless, all three values agree within their 2σ errors.

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1. INTRODUCTION

The H_2 and HD molecules play a unique role in both the astrophysics of the interstellar medium and cosmology. H_2 is the most widespread molecule in the Universe. Due to this and the characteristics of the energy levels of this molecule, H_2 plays a key role in the formation of gas condensations and the first stars, because it is the main cooling agent in the early Universe, whose matter composition is close to primordial. The energy of the first excited level of atomic hydrogen, $E \simeq 10.2$ eV, does not allow gas condensations consisting solely of atomic hydrogen to be efficiently cooled to temperatures $T \lesssim 10^4$ K, so that the thermodynamic gas pressure stops the gravitational contraction of the cloud. However, the energy-level structure of molecular hydrogen is much richer, due to the presence of vibrational and rotational degrees of freedom, and the corresponding excitation energies are fractions of an electron volt; this enables the gas to be cooled to temperatures of the order of 200 K (see, e.g., [1]).

It would seem that the influence of HD molecules on the cooling of the interstellar medium should be negligible due to the considerably lower abundance of HD compared to H_2 ($N(HD)/N(H_2) < 10^{-4}$). However, by virtue of the symmetry of the H_2 molecule, dipole transitions in the ground electronic state are forbidden in H_2, and the lifetime of the levels reaches a thousand years. In contrast, since this symmetry is not present in the HD molecule, dipole transitions are permitted, and the lifetime of the levels decreases to a few days. This results in an increase in the photon-emission rate and makes HD a significant cooling agent compared to H_2 (see, e.g., [2]).

An observational manifestation of the properties of the energy structure of H_2 is that H_2 absorption spectra contain lines coming from excited rotational levels ($J \geq 1$), whereas HD molecules and

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other atoms and ions are mainly in the ground state under the conditions of the interstellar medium. This is due to the long lifetime of the excited H_2 levels and the properties of their population. The dissociation continuum of molecular hydrogen is higher than the ionization potential of atomic hydrogen. Therefore, photodissociation of H_2 in the interstellar medium does not occur directly, since atomic hydrogen depletes the radiation spectrum above 13.6 eV. Dissociation occurs by means of a mechanism that was first described in [3, 4]. After photoexcitation to upper energy levels in lines of the Lyman and Werner bands (∼912–1100 Å), about 87% of the molecules return to the ground electron state in upper vibrational–rotational levelsin in a time $\tau \sim 10^{-6}$ s, while 13% of the molecules make a transition to the continuum, i.e., they are dissociated [5]. The surviving molecules fall to the ground vibrational state via cascade transitions and occupy long-lived rotational levels [6]. This mechanism is called radiative pumping.

In addition to the fact that H_2 and HD are key components of the interstellar medium, they play an important role in studies of the physical conditions and chemical composition during the cosmological evolution of the Universe. Analyses of spectra of quasars containing H_2/HD absorption systems can be used to address such cosmological problems as: (a) estimating the primordial deuterium abundance, and thereby a key cosmological parameter—the baryon density in the Universe (see, e.g., [7, 8]); (b) obtaining constraints on the possible cosmological variations of fundamental physical constants; (c) measuring the temperature of the cosmic microwave background (CMB) radiation at cosmological epochs 10–12 billion years ago by means of analyses of the populations of the energy levels of atomic carbon CI and/or CO (see, e.g., [9]). Thus, molecular clouds at high redshifts represent unique cosmological laboratories.

2. OBSERVATIONS OF MOLECULAR CLOUDS

2.1. H_2 and HD in the Interstellar Medium of our Galaxy

H_2 is the most widespread molecule in the Universe (its abundance exceeds those of other molecules by at least a factor of 10^4), however, some difficulties are encountered with its observation. H_2 has no resonance lines suitable for observations in either the visible or the radio. This hindered the detection of molecular hydrogen for a long time. Only with extra-atmospheric space observations with the Copernicus Orbiting Astronomical Observatory (NASA, 1972) did detailed studies of absorption lines of interstellar molecular hydrogen in the UV spectra of hot stars become possible, in the Lyman ($X^1\Sigma_g^+ \rightarrow B^1\Sigma_u^+$) and Werner ($X^1\Sigma_g^+ \rightarrow C^1\Pi_u^\pm$) series with wavelengths $\lambda \sim 912$–1100 Å [10]. Together with the H_2 lines, UV absorption lines of HD were also visible in these spectra. Modern observations of H_2 and HD lines in our Galaxy were carried out using the Far Ultraviolet Spectroscopic Explorer (FUSE, NASA, 1999). One of the primary goals of this mission was studies of the deuterium abundance and its Galactic evolution with the aim of estimating the mean baryon density in the Universe, Ω_b. Observations of both H and D atomic lines and H_2 and HD molecular lines were observed for this purpose. These observations demonstrated that (a) the D/H abundance within 1 kpc of the Sun does not exceed 2.3×10^{-5} [11]; (b) the relative abundance $N(\mathrm{HD})/2N(\mathrm{H_2})$ along 41 lines of sight in our Galaxy varies from 6.6×10^{-7} to 7.4×10^{-6} [12, 13]. It is clear that the complexity of determining the primordial deuterium abundance from observations in our Galaxy is due to uncertainties in the Galactic evolution of chemical elements and molecules.

2.2. H_2 at High Redshift

The discovery of quasars [14] offered the opportunity to study clouds of molecular hydrogen located beyond our Galaxy (at cosmological distances), because at high redshifts[1] $z \gtrsim 2$, the H_2 lines fall in the blue ($\lambda \gtrsim 3000$ Å), and can be identified in the spectra obtained on ground-based telescopes. In addition, cosmological redshifts correspond to much earlier epochs, when the relative abundances of elements in the interstellar medium were closer to their primordial values than to their modern values.

One of the problems that has been solved by analyzing quasar spectra is determining the physical conditions in clouds of the interstellar and intergalactic media at large cosmological distances corresponding to high redshifts z. Since the populations of different vibrational–rotational levels of molecules are extremely sensitive to physical conditions, H_2 and HD are extremely important indicators of the physical state of the interstellar medium.

For a long time (from 1985 to 1997) only one absorption system of molecular hydrogen was known in the spectrum of the quasar Q 0528–250. A spectrum

[1] The physical meaning of cosmological redshift z is determined by the ratio of the current scale factor of the Universe a_0 to the scale factor for an earlier epoch in the evolution of the Universe: $a_0/a(t) = 1 + z$. In practice, the observational manifestation of the cosmological redshift is a change in the wavelength of radiation emitted by a distant source λ_{em} compared to the wavelength observed by a telescope λ_{obs}. These are related by the relationship $\lambda_{\mathrm{obs}} = \lambda_{\mathrm{em}}(1 + z)$.

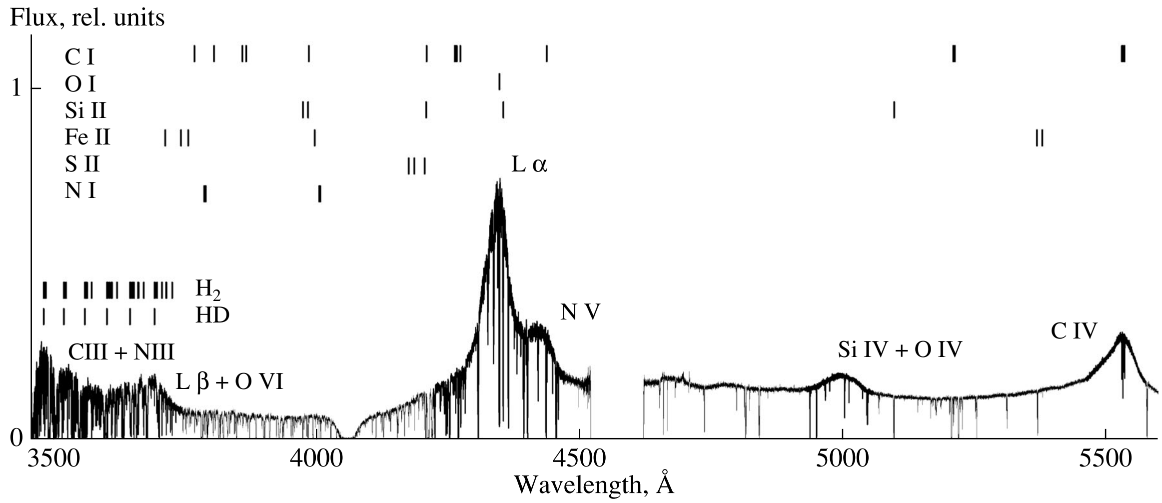

Fig. 1. Spectrum of the quasar Q 1232+082 obtained on the 8.2-m VLT telescope with the UVES high-resolution spectrograph. Broad emission lines formed in the vicinity of the central supermassive black hole and directly characterizing the redshift of the quasar $z_{\rm em} = 2.57$ are prominent in the spectrum. The positions of absorption lines of various atoms and ions, as well as the H_2 and HD molecules, belonging to the absorption system $z_{\rm abs} = 2.3377$ are shown by vertical dashes. The other absorption lines are mainly lines of the Lα forest and rarer lines of other heavy elements with other redshifts.

of this quasar was obtained in 1980 by Morton et al. [15]. However, the H_2 lines in this spectrum could not be identified before 1985, as these lines fell in the wavelength range with numerous Lα absorption lines (1215.67 Å) corresponding to clouds of the interstellar and intergalactic media shifted relative to each other due to their cosmological redshift (Fig. 1). These collected lines are called the Lα forest [16, 17]. In 1985, Levshakov and Varshalovich [18] found an H_2 absorption system with the redshift $z_{\rm abs} = 2.811$ in the spectrum of this quasar. It is interesting that the redshift of the quasar, $z_{\rm em} = 2.78$, is less than the redshift of the absorption system. This could mean that the system has a blueshift relative to the quasar; i.e., the molecular cloud is moving away from the observer toward the quasar at a velocity not less than 2500 km/s.

A second H_2 absorption system with redshift $z_{\rm abs} = 1.97$ was detected 12 years later, in 1997, in the spectrum of the quasar Q 0013−004 by Ge and Bechtold [19]. The small number of detected molecular-hydrogen absorption systems was due to the fact that most quasar spectra were taken with low resolution, whereas the identification of an H_2 system requires high-resolution spectra with high signal-to-noise ratio (SNR). It became possible to obtains such spectra with the commissioning of large optical telescopes such as the 10-m Keck Telescope and 8.2-m VLT, together with essential modifications of receiving instrumentation (the replacement of photographic plates with CCD matrices).

The first systematic search for molecular hydrogen was carried out on the 8.2-m telescope of the European Southern Observatory (VLT/ESO, Chile) [20]. The spectra of quasars containing Damped Lyman Alpha (DLA) systems were selected; these are absorption systems of neutral hydrogen with high column densities, $>2 \times 10^{20}$ cm^{-2}, that are associated with galaxies and protogalaxies at high redshifts [21]. Precisely in such systems is the amount of neutral hydrogen sufficient to block the UV background and thereby provide the conditions required for the formation of molecular clouds. However, the compactness of molecular clouds, i.e., their small sizes compared to clouds of atomic hydrogen, result in a fairly low probability for their detection. The statistics of studies of sucy systems demonstrates that only ∼10% of quasar spectra contain DLA systems, and in only ∼10% of these are molecular systems identified [22, 23].

More than 400 000 quasars have been detected (the VERONCAT catalog [24] includes 130 000 quasars, and the SDSS [25] contains 316 000 quasars), and in only 27 of them have systems of molecular-hydrogen lines been identified (Table 1).

Note that not all 400 000 quasars have been checked for the presence of H_2 systems. This is currently virtually impossible, since the vast majority of the quasars have been identified using low-resolution spectra or based on photometric data, whereas the detection of molecular systems requires high-quality, high-resolution spectra.

2.3. HD Molecules at High Redshifts

Lines of HD shifted to a high redshift ($z_{\rm abs} = 2.33771$) were first identified in the spectrum of

Table 1. Known molecular-hydrogen absorption systems observed in the spectra of high-redshift quasars. The column densities and mean degree of molecularization are listed. Nine absorption systems containing HD molecules are given in the upper part of the table

No.	Quasar	z_{abs}	z_{em}	$\log N$(HI)	$\log N(H_2)$	f_{H_2}	$\log N$(HD)	Reference
1	Q0120−284	0.19	0.43	20.50	20.00	0.39	14.82	[26]
2	Q0528−250	2.81	2.81	21.1	18.11	0.003	13.32	[27]
3	Q0812+320	2.63	2.70	21.4	19.9	0.06	15.70	[8, 28]
4	Q1232+082	2.34	2.57	20.9	19.7	0.11	15.53	[7]
5	Q1237+064	2.69	2.78	20.0	19.21	0.24	14.48	[29]
6	Q1331+170	1.78	2.08	21.2	19.71	0.06	15.03	[8, 30]
7	Q1439+113	2.42	2.58	20.1	19.68	0.29	14.87	[31]
8	Q2100−064	3.09	3.14	21.1	18.76	0.01	13.83	This study
9	Q2123−005	2.06	2.26	19.2	17.6	0.05	13.8	[32]
10	Q0013−004	1.97	2.09	20.8	18.9	0.02		[33]
11	Q0027−184	2.42	2.55	21.7	17.3	8.0×10^{-5}		[34]
12	Q0107−023	0.56	0.73	19.50	17.27	0.012		[35]
13	Q0203+113	3.39	3.61	21.3	14.8−16.6	10^{-7}–10^{-5}		[36]
14	Q0347−383	3.02	3.21	20.6	14.5	1.6×10^{-6}		[37, 38]
15	Q0405−443	2.59	3.00	20.9	18.2	0.004		[20]
16	Q0515−441	1.15	1.71	19.88	16.94	0.002		[39]
17	Q0551−366	1.96	2.32	20.5	17.4	0.002		[40]
18	Q0643−504	2.66	3.09	21.0	18.5	0.006		[22, 33]
19	Q0816+144	3.29	3.84	22.0	18.7	9.1×10^{-4}		[41]
20	Q0918+164	2.58	3.07	21.0	16.2−19.0	10^{-5}–10^{-2}		[42]
21	Q1337+315	3.17	3.17	21.4	14.1	1.0×10^{-7}		[43]
22	Q1443+272	4.22	4.42	21.0	18.3	0.004		[44]
23	Q1444+014	2.08	2.21	20.1	18.3	0.03		[20]
24	Q2318−111	1.99	2.56	20.7	15.5	1.3×10^{-5}		[45]
25	Q2340−00	2.05	2.09	20.35	18.20	0.014		[46]
26	Q2348−011	2.42	3.02	20.5	18.4	0.02		[45]
27	Q2343+125	2.43	2.52	20.4	13.7	4.0×10^{-7}		[47]

the quasar Q 1232+082 [48]. After additional spectral observations of this quasar on the 8.2-m telescope (VLT/ESO), we estimated the HD abundance. The HD/H_2 column-density ratio proved to be $(7.1^{+3.7}_{-2.2}) \times 10^{-5}$ [7]. This value considerably exceeds the corresponding values in our Galaxy, $(0.1-1.4) \times 10^{-5}$ [13].

HD lines have now already been detected in nine of the 27 known molecular-hydrogen absorption systems (Table 2).

3. PROPERTIES OF INDIVIDUAL ABSORPTION SYSTEMS

3.1. Absorption System in the Spectrum of Q 2100−064

The DLA system in the spectrum of the quasar Q 2100−064 was first identified in [50]. Later, lines

Table 2. H_2/HD absorption systems in quasar spectra: the primordial deuterium abundance estimated from two systems that satisfy the self-shielding criterion

Quasar	z_{abs}	$\log N(H_2)$	$\log N(HD)$	$N(HD)/2N(H_2)$	Reference
Q1232+082	2.33771	19.68 ± 0.09	$\mathbf{15.53^{+0.17}_{-0.11}}$	$\mathbf{(3.55^{+1.85}_{-1.10}) \times 10^{-5}}$	[7]
Q0812+320	2.62644	19.93 ± 0.04	$\mathbf{15.70^{+0.04}_{-0.04}}$	$\mathbf{(2.97^{+0.55}_{-0.55}) \times 10^{-5}}$	[8]
	2.62638	18.82 ± 0.37	12.98 ± 0.22	7.23×10^{-7}	
Q0120−284	0.18562	20.00 ± 0.10	14.82 ± 0.15	3.30×10^{-6}	[26]
Q0528−250	2.81112	*16.56 ± 0.02*	*13.27 ± 0.07*	*2.56×10^{-4}*	[49]
		17.85 ± 0.02	13.32 ± 0.02	1.47×10^{-5}	[27]
J1237+064	2.68956	19.21 ± 0.13	14.48 ± 0.05	1.86×10^{-5}	[29]
Q1331+170	1.77637	19.43 ± 0.10	14.83 ± 0.15	2.51×10^{-5}	[8]
	1.77670	19.39 ± 0.11	14.61 ± 0.20	1.66×10^{-5}	
Q1439+113	2.41837	19.68 ± 0.10	14.87 ± 0.03	1.55×10^{-5}	[31]
J2100−064	3.09145	18.76 ± 0.04	13.83 ± 0.06	5.87×10^{-6}	This study
J2123−005	*2.05933*	*15.76 ± 0.10*	*12.95 ± 0.03*	*7.67×10^{-4}*	[32]
		17.55 ± 0.05	*13.69 ± 0.05*	*0.69×10^{-4}*	
		17.64 ± 0.15	*13.84 ± 0.20*	*0.79×10^{-4}*	[28]
$D/H = HD/2H_2 = (3.26 \pm 0.29) \times 10^{-5}$					

Figures in italics are very uncertain.

of neutral carbon CI (three components) associated with this system were also identified [46]. CI (ionization potential 11.3 eV) is usually located in the cool phase of interstellar matter, and is therefore spatially related to molecular hydrogen. Using this fact, we carried out a search in order to identify H_2 lines associated with one of the CI components, with redshift $z_{abs} = 3.09145$ [51]. The molecular-hydrogen column density is $\log N_{H_2} = 18.76 \pm 0.04$. Spectra of Q 2100−064 were recorded on the Keck telescope with the HIRES spectrograph in 2005, 2006, and 2007 as part of the programs U17H (principal investigator J.X. Prochaska), G400H (principal investigator S.L. Ellison), and U149Hr (principal investigator A.M. Wolfe), respectively. We retrieved the freely accessible exposures from the Keck telescope archive. We used the MAKEE software[2] to process and add the exposures; this software was especially developed to process spectra obtained on the Keck HIRES spectrograph. We identified HD lines in the molecular-hydrogen absorption system in the spectrum of Q 2100−064, shown in Fig. 2. We used the L4-0R(0), L7-0R(0), L8-0R(0), W1-0R(0), and L16-0R(0) HD absorption lines in our analysis. The HD column density was found to be $\log N_{HD} = 13.83 \pm 0.06$.

[2] http://www.astro.caltech.edu/~tb/makee

3.2. Absorption System in the Spectrum of Q 0812+320

A DLA system ($z_{abs} = 2.626$) was detected in the spectrum of the quasar Q 0812+320 ($z_{em} = 2.701$) in 2000 [52]. Lines of molecular hydrogen were subsequently detected in this system. This, together with the analysis of lines of neutral carbon CI, suggested the absorption was associated with a cold interstellar cloud with $T < 78$ K [53].

We carried out an independent analysis of this absorption system [8]. The molecular-hydrogen lines in this system demonstrate the presence of two subsystems with redshifts $z_A = 2.626443(2)$ and $z_B = 2.626276(2)$, corresponding to a relative shift of $\sim$14 km/s. This two-component structure is most prominent in H_2 lines associated with excited rotational levels $J = 2, 3, 4$ of the ground state. In total, we used about 50 lines belonging to the Lyman (from L0-0 to L17-0) and Werner (from W0−0 to W4−0) bands in this analysis. The Doppler parameter b was assumed to be identical for all levels; note that this is not always the case (see, e.g., [54], for

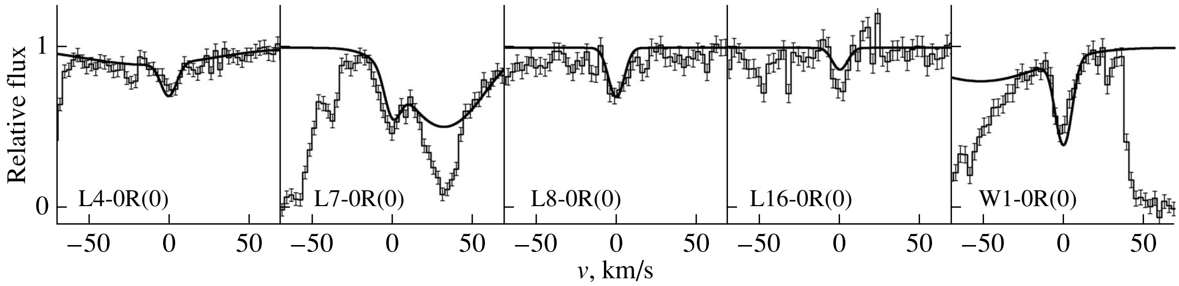

Fig. 2. Synthetic spectrum of HD in the absorption system with $z_{\rm abs} = 3.09145$ fitted to the normalized spectrum of the quasar Q 2100–064.

the effect of broadening). However, the main goal of our analysis of this molecular-hydrogen system was to determine the H_2 column density, which is not sensitive to the parameter b in strongly saturated (damped, with Lorentz wings) systems. An example of a synthetic molecular-hydrogen spectrum and the observed spectrum of the quasar are shown in Fig. 3.

We also identified lines of HD in this system (Fig. 4). In contrast to [28], where only six HD lines corresponding to the transitions from the ground state ($J = 0$) are identified, we managed to find nine HD lines ($J = 0$). This enabled us to determine the HD column density more accurately: the value obtained in [28] is $\log N_{\rm HD} = 15.38 \pm 0.25$, while the value obtained in our paper [8] is $\log N_{\rm HD} = 15.71 \pm 0.07$. This considerable improvement in the accuracy of the column density is due to the fact that, in the case when different HD lines have different oscillator strengths, the addition of even one line to the analysis can result in a considerably narrower probable interval for the column densities (in our case, there were three additional HD lines).

Moreover, we managed to identify lines belonging to the first excited rotational level $J = 1$ of the HD molecule for the first time for an extragalactic object. This enabled us to independently estimate the volume density in the interstellar cloud [8].

3.3. Absorption System in the Spectrum of Q 1331+170

The DLA system in the spectrum of the quasar Q 1331+170 ($\log N_{\rm HI} = 21.18$) was identified in 1975 [55]. This was one of the first DLA systems found at high redshift ($z_{\rm abs} = 1.777$). The redshift of this system is such that the molecular-hydrogen lines fall in the UV ($\lambda < 3000$ Å), which is actively absorbed by the Earth's atmosphere and is inaccessible to observations with ground-based telescopes. Only in the Hubble Space Observatory Telescope (HST) spectrum did it become possible to identify a line of molecular hydrogen in this system [30]. Bearing in mind the high column density of molecular hydrogen ($N_{\rm H_2} \approx 4 \times 10^{19}$ cm^{-2}), we carried out an independent analysis of this system with the aim of searching for HD lines, which yielded detections of a several HD lines in this system. These are present up to the Lyman L18–0 and Werner W4–0 bands. However, due to the low SNR in this spectrum ($S/N \lesssim 7$), we could use only four HD lines to determine the physical parameters: L3–0R(0), L4–0R(0), L7–0R(0), and L8–0R(0). Two subsystems are present in these lines, whose redshifts coincide within the errors with the redshifts found from the H_2 lines. The HD column densities are $\log N^{\rm A}_{\rm HD} = 14.83 \pm 0.15$ and $\log N^{\rm B}_{\rm HD} = 14.61 \pm 0.20$.

3.4. Absorption System in the Spectrum of Q 0528–250

The quasar Q 0528–250 was the first in which a molecular-hydrogen system was detected [18]. Since its discovery, this quasar has been observed by various groups on various telescopes, and the results obtained varied widely. For example, depending on the spectrum quality and the model used for the absorption system, the molecular-hydrogen column densities varied over two orders of magnitude (3×10^{16}–3×10^{18} cm^{-2}). Our independent analysis yielded the H_2 column density $\log N_{\rm H_2} = 18.28 \pm 0.02$. The H_2 system consists of two saturated components separated in velocity by $\Delta v \sim 9$ km/s. HD lines were identified in only one component, with $z_{\rm abs} = 2.811124$; the column density found from these lines is $\log N_{\rm HD} = 13.32 \pm 0.02$. This enabled us to estimate the HD abundance, $N({\rm HD})/2N({\rm H_2}) = (1.47 \pm 0.13) \times 10^{-5}$. This quantity is an order of magnitude lower than the value $(2.7 \pm 0.6) \times 10^{-4}$ obtained earlier for this system in [49], which exceeds the estimates primordial deuterium abundance by almost an order of magnitude. A detailed analysis of the spectrum of this quasar is presented in [27].

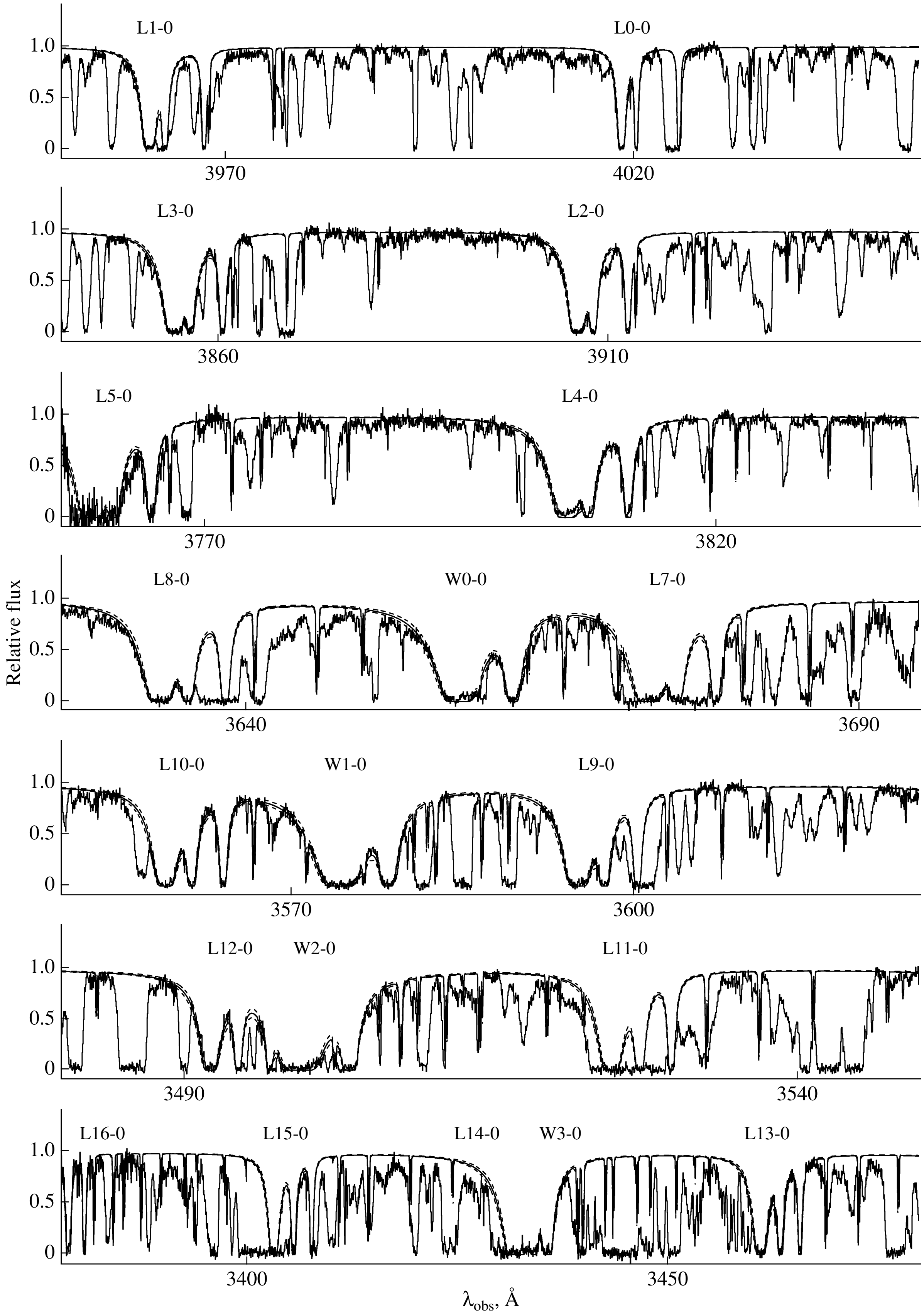

Fig. 3. Normalized spectrum of the quasar Q 0812+320 and the fitted synthetic spectrum of H_2 with redshift $z_{abs} = 2.626$. The spectrum was taken on the 10-m Keck I telescope with the HIRES spectrograph.

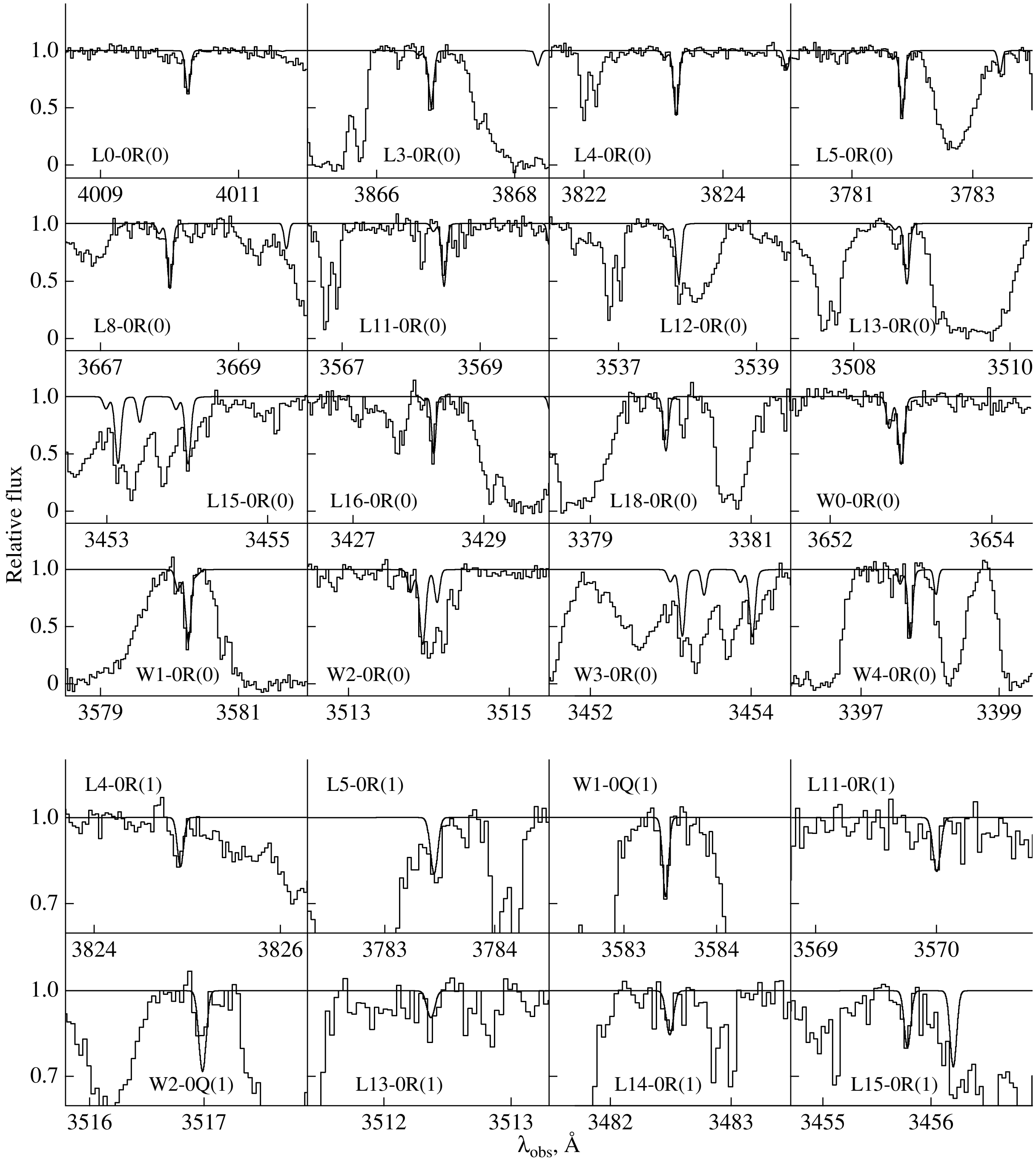

Fig. 4. Synthetic spectrum of HD in the absorption system with $z_{\rm abs} = 2.626$, fitted to the normalized spectrum of the quasar Q 0812+320. Top: lines of transitions from the ground state $J = 0$. Bottom: the R(1), P(1), and Q(1) lines for transitions from the excited rotational level $J = 1$.

3.5. Absorption System in the Spectrum of Q 2123–005

The H_2/HD absorption system with $z_{\rm abs} = 2.058$ in the spectrum of the quasar Q 2123–005 was studied in [28, 32]. Unfortunately, the SNR in the spectrum was $\lesssim$20, and the absorption system has a complex, multi-component structure. Therefore, Tumlinson et al. [28] and Malec et al. [32] note major difficulties in determining the H_2 column densities. For example, according to [32], using a four-component model results in the unphysical (difficult to explain) temperature $T_{01} = -96$ K, based on the relative level populations of molecular para- ($J = 0$) and ortho- ($J = 1$) hydrogen.

In this relation, formal estimates of $HD/2H_2$ having the order of magnitude 10^{-4} (Table 2) are not physically reasonable, and are therefore not shown in Fig. 7.

4. THE PROBLEM OF PRIMORDIAL DEUTERIUM

4.1. Densities of Baryons and Photons in the Universe

One of the key parameters of modern cosmology is the mean baryon density in the Universe, characterized by the quantity $\Omega_b = \rho_b/\rho_{cr}$, i.e., the ratio of the baryon density to the critical density $\rho_{cr} = 3H_0^2/8\pi G$. Another cosmological parameter, the baryon–photon ratio $\eta \equiv n_b/n_\gamma$, is related to Ω_b; in the standard cosmological model, this ratio has not changed from the termination of primordial nucleosynthesis to the present time. The relationship between these two parameters is $\eta = 2.74 \times 10^{-8}\Omega_b h^2$, where $h \equiv \frac{H_0}{100\ \mathrm{km\,s^{-1}\,Mpc^{-1}}}$ is the dimensionless Hubble constant (which we have taken to be $h = 0.7$).

According to our current understanding, the baryon density, which constitutes the density of ordinary matter—atoms, molecules, planets, stars, and interstellar and intergalactic gas, does not exceed 5% of all matter in the Universe, whereas 95% of the density of the Universe consists of unknown forms of matter whose presence is manifest gravitationally.

The importance of determining Ω_b has grown considerably in the current epoch of "precision" cosmology. The detailed theory of primordial nucleosynthesis with the observed abundances of light elements (D, He, Li) leads to the estimate $\Omega_b = 4.35 \pm 0.20\%$ [56]. Independent estimation of Ω_b based on an analysis of the anisotropy of the CMB yields $4.51 \pm 0.06\%$ [57]. These estimates agree well with the errors, though they refer to different cosmological epochs.

4.2. Primordial Nucleosynthesis. Chemical and Isotopic Composition in the Early Universe

During the few minutes after the Big Bang, the Universe was a cosmic thermonuclear reactor that operated in the "opposite" sense: fusion reactions took place not when the material contracted and heated, but when it expanded and cooled. During the primordial nucleosynthesis, protons and neutrons, which constituted nearly all baryonic matter at that time, together with the remaining hydrogen (H $\sim$ 75%), formed primordial ^{4}He ($\sim 23\%$) and a small amount of deuterium D (^{2}H), ^{3}He, ^{7}Li, and ^{7}Be; this last substance was completely converted to ^{7}Li via electron capture much later. The process of primordial nucleosynthesis was so brief (due to the rapid expansion and cooling of the Universe) that only the above nuclei could be formed in significant amounts. Heavier nuclei were formed only later, in the course of stellar evolution.

The epoch of primordial nucleosynthesis is currenty the earliest stage in the evolution of the Universe for which a comparison of theoretical predictions with observations is possible.[3] The abundance of the relict nuclei formed during primordial nucleosynthesis can be calculated, since the rates of all relevant reactions are well known. The only free parameter in this calculation is the relative baryon density $\eta = n_b/n_\gamma$ (or Ω_b). This parameter can be determined by comparing the calculation results with astronomical data on the abundances of the relict nuclei.

The left-hand panel of Fig. 5 shows how the abundances of various nuclides change with the temperature T and time t, which were related at that epoch as $t = AT^{-2}$, where A was determined by the effective number of degrees of freedom of the relativistic particles (photons, electrons, all kinds of neutrinos and antineutrinos). The right-hand panel presents the results of calculating the final abundances of the relict nuclei as a function of the ratio of the baryon and photon densities $\eta(\Omega_b)$. The vertical band shows the estimate of $\eta(\Omega_b)$ obtained from the anisotropy of the CMB. One success of primordial nucleosynthesis theory is that, in the presence of a scatter of the predicted nuclide densities of several orders of magnitude, the observational results have the right orders of magnitude, and are currently consistent with the theory within the errors. However, with the increasing accuracy of the measurements obtained, some discrepancies between the observations and the values predicted by primordial nucleosynthesis theory have become apparent.

4.2.1. Primordial ^{4}He. Among light elements, primordial ^{4}He can be determined most accurately based on the available observations, to a relative accuracy of $\sim$2% [59], whereas the uncertainties in the relative abundances of deuterium and lithium are $\sim$10% and $\gtrsim 50\%$, respectively [60]. Owing to the weak logarithmic sensitivity of ^{4}He to Ω_b, helium is not considered a good "baryometer"; instead, deuterium is chosen for this purpose. However, ^{4}He is more sensitive to the expansion rate of the Universe than the other nuclides, which is mainly determined

[3] Measurements of the spectrum of relict neutrinos or the detection of primordial gravitational waves would make it possible to approach closer in time to the beginning of the Big Bang.

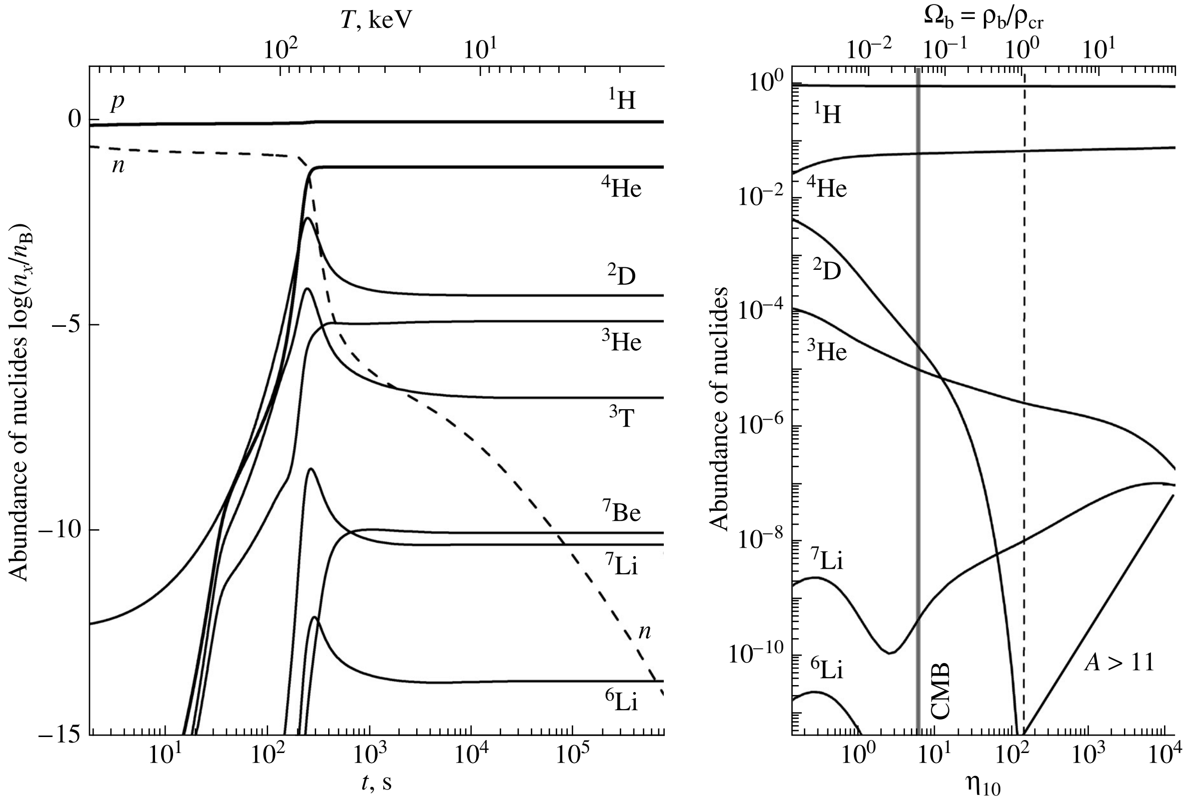

Fig. 5. Results of calculating the model for the primordial nucleosynthesis. Left: abundances of light elements as functions of the cosmological time t. Right: abundances of light elements after the termination of primordial nucleosynthesis processes as a function of the baryon/photon density ratio n_b/n_γ (or the baryon density of the Universe Ω_b, top scale). The vertical band shows the estimate of Ω_b obtained from the anisotropy of the CMB. The calculations of the primordial nucleosynthesis model were obtained using an original software package, and were taken from [58].

at the moment of primordial nucleosynthesis by the relativistic degrees of freedom. Recent observational results for the primordial helium abundance yield the mass fraction $Y_p = 0.2565 \pm 0.006$ [59], which exceeds the value $Y_p^{\rm CMB} = 0.2477 \pm 0.0001$ [57] obtained from the CMB anisotropy at the 1.5σ level. This can be interpreted as the presence of additional relativistic degrees of freedom (usually expressed in terms of the effective neutrino degrees of freedom $N_{\rm eff} = 3.6$–3.8) [59]. Moreover, analysis of the nine-year WMAP data on the CMB anisotropy together with the latest data on baryon acoustic oscillations and independent measurements of the Hubble parameter H_0 have resulted in an estimate of the effective neutrino degrees of freedom $N_{\rm eff} = 3.84 \pm 0.40$ [61]. Thus, the "helium problem" emerges; its resolution requires observations with improved accuracy related to both primordial nucleosynthesis and the CMB.

4.2.2. Primordial ^{7}Li. The relative abundance of ^{7}Li is estimated from observations of the atmospheres of low-mass stars, which are located mainly in the halo of our Galaxy. It is assumed that these stars have a thin convective zone, so that matter contained in their atmospheres has never passed through the central parts of the star, where lithium could be depleted. Observations of such stars indicate the presence of a Spite plateau: the lithium-to-hydrogen ratio Li/H does not depend on the variable iron-to-hydrogen ratio Fe/H. Elements such as iron are processed during the chemical evolution of the Galaxy as a result of nucleosynthesis in stars. Therefore, the lack of a correlation between Li/H and Fe/H means that the lithium density could be close to its primordial value. The most accurate estimate of the primordial ^{7}Li abundance is [62]:

$$\frac{^7\mathrm{Li}}{\mathrm{H}} = \left(1.23^{+0.68}_{-0.32}\right) \times 10^{-10}.$$

However, estimates of the baryon density obtained from the CMB anisotropy $\Omega_b^{\rm CMB}$ and the relative lithium abundance calculated using primordial nucleosynthesis theory with this value of $\Omega_b^{\rm CMB}$ yield a value that is a factor of 4.3 higher [63]:

$$\frac{^7\mathrm{Li}}{\mathrm{H}} = \left(5.24^{+0.71}_{-0.67}\right) \times 10^{-10}.$$

This is currently referred to as the "lithium problem," and no satisfactory solution has been found. Possible solutions of this problem are divided into three groups: (a) astrophysical solutions: revision of the estimates of the primordial lithium abundance in stars; (b) nuclear physics solutions: revision of the rates of reactions and of the primordial nucleosynthesis reactions affecting ^{7}Li production (consideration of new reactions); and (c) solutions beyond the framework of the standard model, which invoke new particle physics or nonstandard cosmological models.

4.2.3. Primordial D. Figure 5, which displays the production of light elements during primordial nucleosynthesis, shows that one of the most sensitive indicators of the relative baryon density $\eta(\Omega_b)$ is the primordial deuterium abundance $(D/H)_{Pr}$. For example, if the baryon density is equal to the critical density ($\rho_b = \rho_{cr}$), we would not see deuterium at all, since its abundance would be eight orders of magnitude lower than the existing value, which is inaccessible to observations with the sensitivity of modern instruments (telescopes, spectrographs, etc.).

During the subsequent evolution of the Universe, the isotope ratio $(D/H)_{Pr}$ formed at the end of primordial nucleosynthesis could only decrease: as interstellar matter gets incorporated into stellar interiors, deuterium is readily and rapidly depleted. Processes in which deuterium could form are not sufficiently intensive to appreciably change its abundance (see, however, [64]). In this sense, any estimate of D/H is a lower limit for the primordial value $(D/H)_{Pr}$. Therefore, finding $(D/H)_{Pr}$ requires measurements of the isotopic composition of interstellar matter that existed at the earliest epoch of cosmological evolution. The absorption spectra of quasars at high redshifts are used for this purpose. A typical spectrum of such a quasar is shown in Fig. 1. Absorption lines of the Lyα forest associated with the intergalactic medium are located to the left of the broad Lα hydrogen emission lines characterizing the redshift of the quasar. Among the Lα forest, systems with high HI column density ($\log N = 17-20$) are found, called Lyman Limit Systems (LLSs). LLSs are used to estimate the primordial deuterium abundance. The same spectral region includes lines of H_2 and HD. Their analysis represents an independent method for estimating the primordial deuterium abundance (labeled MC, "molecular clouds," in Table 3). Both these methods and their advantages and drawbacks are described in the following subsections.

4.3. Determining D/H from Lines of Atomic DI and HI

Until recently, the D/H abundance was determined from absorption lines of atomic hydrogen and deuterium observed in the spectra of quasars. However, such measurements encounter a number of difficulties. The DI and HI optical spectra are virtually identical: the wavelengths of their lines are shifted by only 0.027% (~80 km/s). At the same time, the column densities of these atoms differ by four to five orders of magnitude. Therefore, if the HI column density is small, the DI lines become completely invisible. This means that most lines of the Lα forest are not suitable for estimating the primordial deuterium abundance. If the hydrogen column density is too high, the HI lines are saturated, broadened, and overlap with the DI lines. In addition, lines identified as those of DI could be produced by a small HI cloud moving relative to the studied cloud at a velocity of ~80 km/s, since there could be numerous such clouds moving at various velocities in the line of sight. This could explain the considerable scatter of the D/H values obtained using this method. For example, some of the first D/H estimates yielded values an order of magnitude higher than modern estimates [65, 66]; this again demonstrates the complexities of this method.

At present, 14 LLSs with low heavy-element abundances have been detected and studied in the spectra of quasars. Lines of atomic deuterium DI have also been identified in these systems, enabling meaurement of the D/H ratio. The resulting ratios are consistent with the predictions of the standard cosmological model to order of magnitude; at the same time, obvious problems were also noted. Pettini et al. [56] used only seven of the 11 systems known at that time for their D/H estimate, in which they believed the relative deuterium abundances had been determined most reliably. The resulting value was $D/H = (2.82 \pm 0.20) \times 10^{-5}$. However, even for this sample, the scatter of the D/H values about their mean value considerably exceeded the errors of the individual measurements (Fig. 6). It is believed that the scatter in the deuterium abundances in such clouds can be explained both by star-forming processes and the deposition of deuterium onto dust granules [11]. In the above seven systems, interstellar gas that was little affected by chemical enrichment, as suggested by their low abundances of heavy elements, $[O/H] < 0.1$ (compared to the value for the Solar System), was studied. In the modern models for the chemical evolution of the Galaxy, the decrease in the D/H ratio should be negligible for such clouds. Therefore, the most probable explanation for the wide scatter in the observational data is underestimation of the statistical and/or systematic errors [56, 67] or actual physical processes that change the D/H ratio locally (in each particular cloud). However, the criteria for choosing the systems to be included were

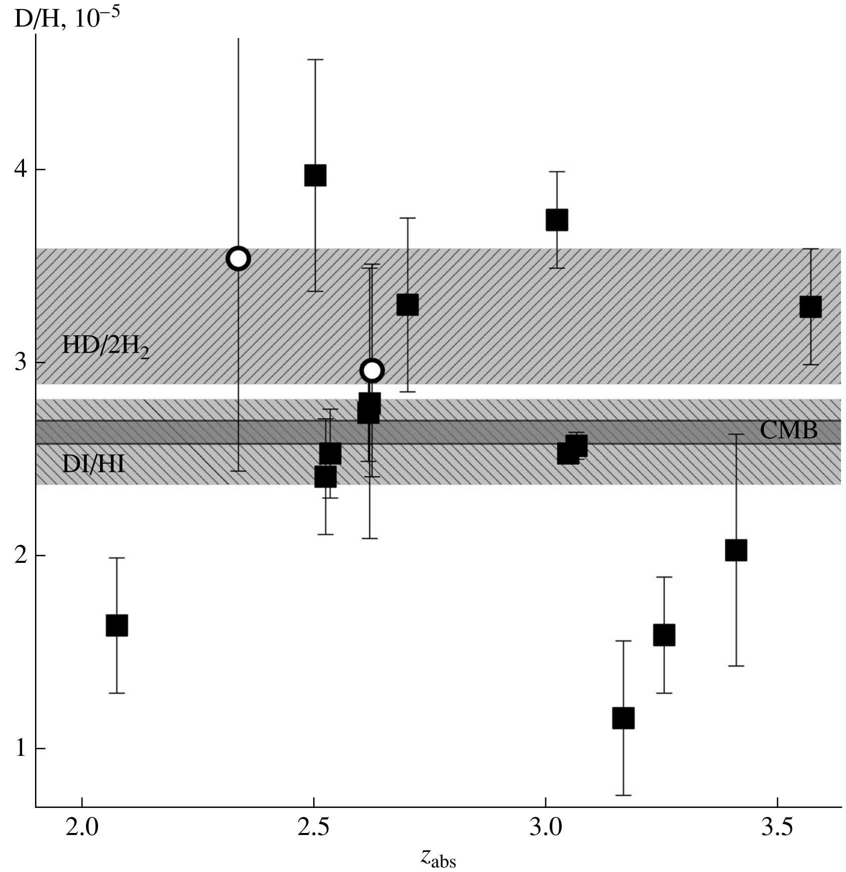

Fig. 6. Estimates of the relative deuterium abundance obtained for 14 LLS systems (squares) and two molecular systems (circles). The bands mark the corresponding mean values and their confidence intervals. The darkest band represents the estimate of D/H obtained from the CMB anisotropy.

revised in [68], and this yielded a different estimate, $D/H = (3.02 \pm 0.23) \times 10^{-5}$. Three new systems can now be added to the 11 previously known ones.

Figure 6 presents estimates of D/H obtained for all 14 LLS systems (data for nine systems were taken from [56, 68]; more recent data for five systems were taken from [43, 69–72]). If the scatter of the points is due to actual system-to-system variations in the deuterium abundance, we should take the highest value for the estimate of the primordial D/H ratio, since (see the previous subsection) deuterium is only destroyed during the subsequent evolution of the Universe after the primordial nucleosynthesis, so that any measurements are only lower limits. If the fact that the scatter of the points exceeds the individual measurement errors is due to underestimation of the statistical and/or systematic errors, the most adequate estimate of the mean D/H value is the unweighted average: $D/H = (2.60 \pm 0.22) \times 10^{-5}$. All the above issues contribute to the deuterium problem.

4.4. Estimation of D/H from the HD/2H_2 Ratio

The difficulties with line identification do not arise if D/H is estimated using the relative abundances of HD and H_2, since the spectra of these molecules differ substantially and most narrow absorption lines do not overlap. This method was not used until recently, because HD molecules could not be detected in high-redshift systems. Observations of absorption systems containing HD lines represent a more difficult problem than the observation of H_2 absorption systems, since the HD density is several orders of magnitude lower than the H_2 density. In order for HD lines to be visible in the spectrum of a quasar, the H_2 column density must be sufficiently high: $\log N(H_2) \gtrsim 18$. This inequality can be considered a search criterion for the detection of HD molecules in such systems.

In general, determining the D/H isotope ratio based on the estimated HD/2H_2 ratio requires taking into account all channels for the formation and loss of these molecules. The dominant destruction channel for H_2 and HD is dissociation by UV radiation in resonance lines. Under the action of UV radiation,

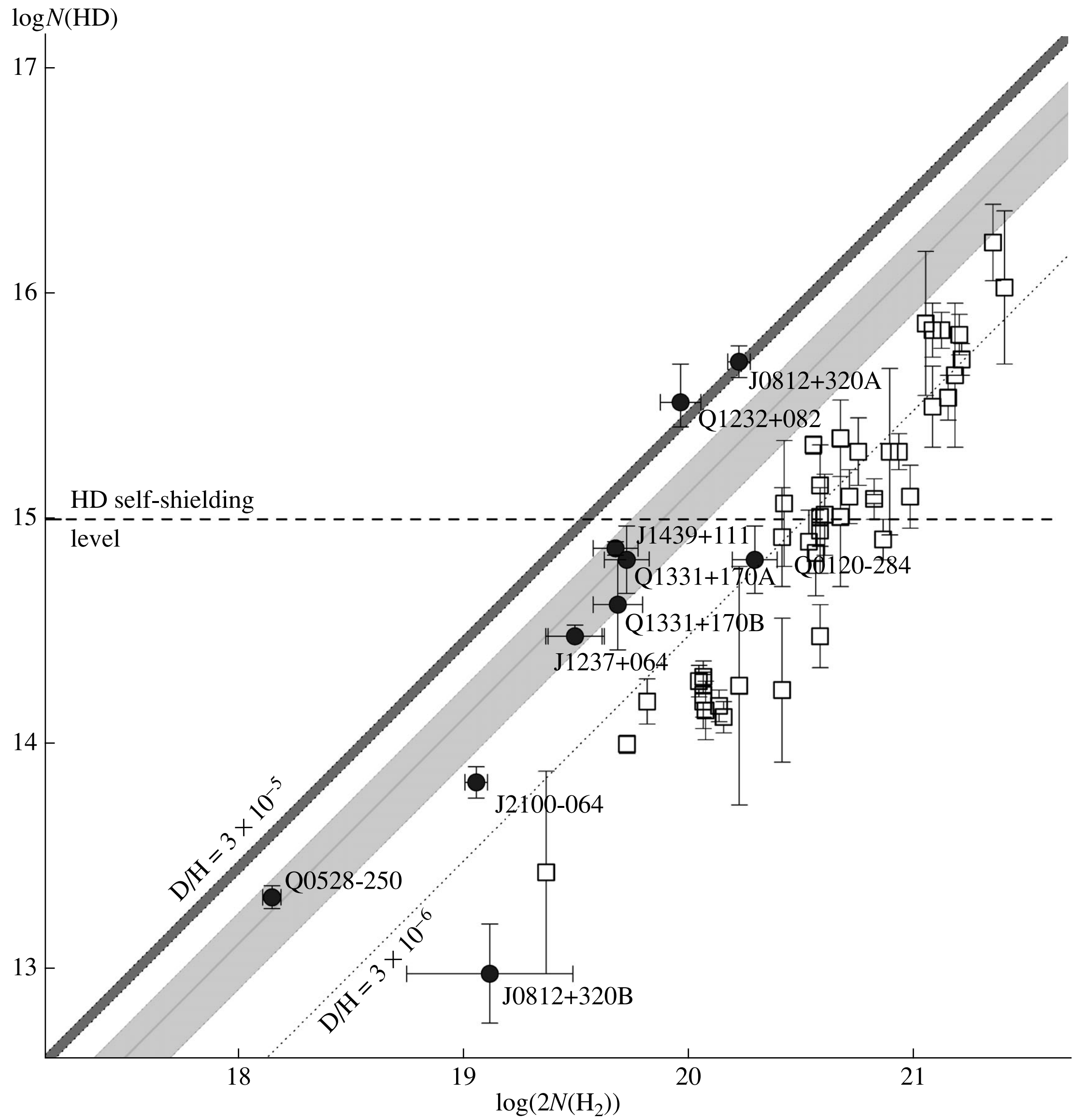

Fig. 7. Joint measurements of the column densities of HD and H_2 molecules in our Galaxy and in quasar spectra. The circles denote measurements in quasar spectra, and the squares observations of HD and H_2 in our Galaxy [12, 13]. The gray band corresponds to the D/H value obtained from atomic data (DI and HI) in our Galaxy, together with its uncertainty [11]. The dark band represents the D/H value obtained from the atomic data (DI and HI) in quasar spectra and adopted as an estimate of the primordial ratio $(D/H)_P$, together with its uncertainty [56]. The two molecular systems that satisfy the self-shielding criterion agree well with the band corresponding to the estimate of the primordial ratio $(D/H)_{Pr}$.

the molecules are excited from their ground state to upper electronic states; i.e., the excitation takes place in the lines of the Lyman and Werner bands in the range 912–1120 Å (precisely these lines, shifted into the optical, are observed in the spectra of quasars). About 87% of molecules excited by UV radiation return to the ground electronic state in various vibration–rotation levels, while about 13% of the molecules are dissociated. However, as it penetrates into the cloud, the radiation in the Lyman and Werner bands is absorbed, and the lines become saturated, so that H_2 and HD molecules inside the cloud are shielded from the destructive UV radiation.

This self-shielding of the cloud begins when the optical depth in the resonance lines reaches unity, which corresponds to column densities of $N_{H_2,HD} \gtrsim 4 \times 10^{14}$ cm^{-2}. For typical conditions in diffuse and semi-transparent molecular clouds, the self-shielding is complete, since the column densities are $N_{H_2,HD} \sim 10^{15}$ cm^{-2}. According to calculations of static models for interstellar molecular clouds [73], nearly all the gas inside the cloud should be

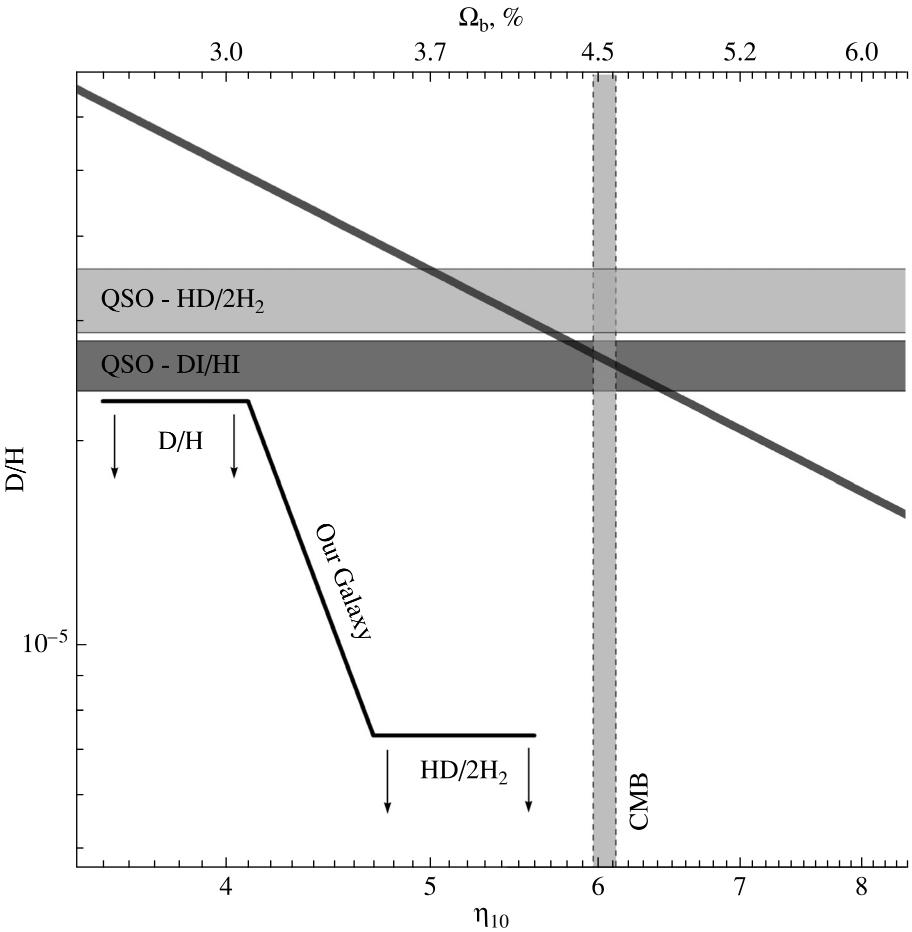

Fig. 8. Deuterium abundance as a function of the relative baryon density $\eta_{10} = 10^{10}(n_b/n_\gamma)$ (bottom scale) or Ω_b (top scale). The slanted band shows the results of primordial nucleosynthesis calculations. The upper horizontal band represents our estimate obtained from a joint analysis of molecular systems in two quasars, Q 1232+082 and Q 0812+320. The lower horizontal band corresponds to the atomic DI and HI data derived from quasar spectra. The vertical band corresponds to the data derived from the CMB anisotropy.

molecularized under these conditions; i.e., all the D should be in HD and all the H in H_2. In this case, the universal relationship, $D/H = HD/2H_2$ is established. Of the nine H_2 absorption systems detected up to now and containing HD,[4] only in two subsystems do the measured column densities of H_2 and HD substantially exceed the critical value required for self-shielding (Table 2). This enabled us to estimate the isotope ratio for these two systems: $D/H = (3.55^{+1.85}_{-1.10}) \times 10^{-5}$ for the absorption system in Q 1232+082 and $D/H = (2.97^{+0.55}_{-0.55}) \times 10^{-5}$ for the absorption system in Q 0812+320. These two estimates yield the joint estimate of the primordial deuterium abundance $D/H = (3.26 \pm 0.29) \times 10^{-5}$, which is slightly higher than but coincident within the errors with the values derived from the CMB anisotropy and DI and HI meaurements in quasar spectra (Table 3).

Figure 7 presents the HD and H_2 column densities for interstellar clouds of our Galaxy and at high redshift. Figure 7 shows that the D/H ratios measured from the column densities of DI and HI atomic lines in our Galaxy are systematically lower than the mean D/H value obtained from quasar spectra. The lower D abundance can be explained, e.g., by deuterium burning in stars. We can also see that the $HD/2H_2$ ratio in our Galaxy is much lower than the mean Galactic value of D/H. This difference could be due to several factors. In contrast to H_2, HD molecules could be insufficiently shielded from UV radiation, making D less molecularized. Another factor could be the complex chemistry of molecular clouds at the current epoch, where deuterium may be efficiently included into other, more complex molecules: $H_2O \rightarrow (HDO, D_2O)$, $NH_3 \rightarrow (NH_2D, NHD_2, ND_3)$, polyaromatic

[4] Two systems consist of two subsystems; thus, this yields 11 estimates of the relative HD/H_2 abundance.

Table 3. Estimates of the baryon density obtained using various methods

Method	D/H	$\Omega_b h^2$	Ω_b, %	Reference
CMB	$(2.65 \pm 0.06) \times 10^{-5}$	0.0221 ± 0.0003	4.51 ± 0.06	[57]
DI/HI (14-LLS)	$(2.60 \pm 0.22) \times 10^{-5}$	0.0224 ± 0.0012	4.57 ± 0.24	This work
$HD/2H_2$ (2-MC)	$(3.26 \pm 0.29) \times 10^{-5}$	0.0194 ± 0.0011	3.96 ± 0.22	This work

Here, we have adopted $h = 0.7$. The primordial D/H ratio predicted by primordial nucleosynthesis theory for the value of $\Omega_b h^2$ obtained from the CMB anisotropy is given in italics.

hydrocarbons, etc., reducing the abundance of HD molecules.

4.5. Estimate of the Mean Baryon Density in the Universe Ω_b

Assuming that our estimate of the deuterium abundance $D/H = (3.26 \pm 0.29) \times 10^{-5}$ reflects the primordial value, we can estimate the mean baryon density in the Universe by comparing the derived D/H value with the predictions of primordial nucleosynthesis theory. Figure 8 shows a comparison of our result and the results of other studies. The slanted line demonstrates the result of the values from the primordial nucleosynthesis calculations. The upper horizontal band represents our estimate of the primordial deuterium abundance obtained from a joint analysis of the molecular systems in the two quasars Q 1232+082 and Q 0812+320, $D/H = (3.26 \pm 0.29) \times 10^{-5}$. The intersection of this band with the slanted theoretical line yields the value $\Omega_b h^2 = 0.0194 \pm 0.0011$. The lower horizontal band corresponds to the data for DI and HI atomic lines in 14 LLS systems observed in the quasar spectra ($D/H = (2.60 \pm 0.22) \times 10^{-5}$); its intersection with the slanted line yields $\Omega_b h^2 = (0.0224 \pm 0.0012)$. The vertical band corresponds to the data derived from the CMB anisotropy: $\Omega_b h^2 = 0.0221 \pm 0.0003$ [57]. All three estimates obtained using independent methods coincide within 2σ.

5. CONCLUSION

We have presented a systematic review of absorption systems of molecular hydrogen H_2/HD observed in the spectra of quasars. Twenty-seven H_2 systems are currently known, in nine of which HD lines have been detected. We have included new original data obtained by reprocessing data for the absorption system in the spectrum of the quasar PKS 0528−250 and analyzing the new H_2/HD system in the spectrum of the quasar Q 2100−064. We have also estimated the primordial deuterium abundance from the data for 14 LLS systems containing DI and HI lines.

The analyses of the systematized data lead to the following main conclusions.

- The relative abundance of HD in interstellar clouds in the early Universe exceeds the values measured for our Galaxy corresponding to the current epoch by at least an order of magnitude.
- We have used an independent method to estimate the baryon density in the Universe, $\Omega_b h^2 = 0.0194 \pm 0.0011$. This is slightly lower than the values obtained from DI and HI atomic lines observed in quasar spectra ($\Omega_b h^2 = 0.0224 \pm 0.0012$) and from the CMB anisotropy ($\Omega_b h^2 = 0.0221 \pm 0.0003$) [57]. However, all three estimates obtained using independent methods coincide within 2σ.
- The independent method for estimating Ω_b we have proposed could be fairly promising, since the uncertainty in the Ω_b estimate obtained using only two absorption systems is comparable to the uncertainty of the method based on the analysis of atomic lines. At the same time, the method developed by us earlier to search for H_2 systems [23] provides hope that it will soon become possible detection new H_2/HD systems, thereby significantly decreasing the uncertainty in future estimates of Ω_b using this method.
- A comparison of two independent estimates of Ω_b corresponding to different cosmological epochs—the epoch of primordial nucleosynthesis and the epoch of primordial hydrogen–helium recombination—would make it possible to investigate fundamental physics, or obtain constraints on various theories lying beyond the framework of the standard cosmological model.

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