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OXYGEN PUMPING: PROBING INTERGALACTIC METALS AT THE EPOCH OF REIONIZATION

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ABSTRACT

We consider the pumping of the 63.2 μm fine-structure line of neutral O I in the high-redshift intergalactic medium (IGM), in analogy with the Wouthuysen-Field effect for the 21 cm line of cosmic H I. We show that the soft UV background at ~1300 Å can affect the population levels, and if a significant fraction of the IGM volume is filled with "fossil H II regions" containing neutral O I, then this can produce a nonnegligible spectral distortion in the cosmic microwave background (CMB). O I from redshift z is seen in emission at $(1 + z)63.2$ μm, and in the range $7 < z < 10$ produces a mean spectral distortion of the CMB with $y = (10^{-9}$ to $3 \times 10^{-8})(Z/10^{-3}\ Z_\odot)(I_{\rm UV})$, where Z is the mean metallicity of the IGM and $I_{\rm UV}$ is the UV background at 1300 Å in units of 10^{-20} ergs s^{-1} Hz^{-1} cm^{-2} sr^{-1}. A measurement of this signature can trace the metallicity at the end of the dark ages, prior to the completion of cosmic reionization, and is complementary to cosmological 21 cm studies. While future CMB experiments such as *Planck* could constrain the metallicity to the $10^{-2}\ Z_\odot$ level, specifically designed experiments could potentially achieve a detection.

Subject headings: cosmic microwave background — cosmology: theory — intergalactic medium — ISM: abundances

The first sources of light that ended the cosmic dark ages are expected to have reionized the intergalactic medium (IGM) and polluted it with metals (e.g., Loeb & Barkana 2001). To use the metal enrichment as a potential probe of the reionization epoch, recent studies have concentrated on the neutral oxygen (O I) produced by the first massive stars (Oh 2002; Basu et al. 2004).

The ionization potential of O I is only 0.2 eV higher than that of hydrogen (H I), and the two species are in charge exchange equilibrium. Therefore, oxygen is likely to be highly ionized in regions of the IGM where hydrogen is ionized. However, the recombination time for oxygen (as for hydrogen) is shorter than the Hubble time at $z \gtrsim 6$, indicating that oxygen can be neutral even in regions where H has been ionized but where short-lived ionizing sources have turned off, allowing the region to recombine (Oh 2002). Numerical simulations that do not resolve the first generation of "minihalos" find a small volume filling factor of such "fossil" H II regions (Iliev et al. 2007; McQuinn et al. 2006; Ricotti et al. 2002). However, Oh & Haiman (2003) argued, in a semianalytical model, that minihalos are more susceptible to negative feedback and that they can produce fossil H II regions that occupy >50% of the volume of the IGM prior to reionization. More generally, the distribution of metals around early galaxies is poorly understood, but they may preferentially occupy denser regions around galaxies, where recombination time is short (Theuns et al. 2002; Miralda-Escudé et al. 2000; Cen & Ostriker 1999). Moderate wind velocities (10–100 km s^{-1}) suffice to pollute a significant fraction of the IGM volume, in principle (Haiman 2003), although the metal escape can be hindered by large-scale structures around the small galaxies. In fact, Becker et al. (2006) claim to have found evidence for significant O I absorption in quasar spectra corresponding to highly ionized patches of the IGM at $z > 6$. If correctly interpreted, then the trend in their data suggests that O I abundance may even increase at earlier stages of reionization.

Previous work has proposed exploiting the scattering of UV photons by O I, and the corresponding absorption features in the spectra of quasars: the O I forest (Oh 2002), analogous to the lower redshift H I Lyα forest (e.g., Becker et al. 2006). In the case of H I, another interesting signature from the high-redshift IGM is the 21 cm hyperfine-structure line, which is made detectable by UV pumping by the Lyα background (the so-called Wouthuysen-Field effect; see Field 1958 or Furlanetto et al. 2006 for a recent review). Here we examine whether a similar effect occurs for O I, and demonstrate that there exist O I lines with the required features: the fine-structure lines of the electronic ground state, 44.1, 63.2, and 145.5 μm, can be pumped by 1300 Å photons produced by the first stars or black holes, via the Baα line of O I. We compute the spectral distortion in the CMB created by this effect, and find that it can be as high as $y \sim 10^{-7}$ if $Z_{\rm O\,I}$ at $z \sim 7$, just prior to reionization, is $\sim 10^{-2.5}\ Z_\odot$. Values for the metal abundance of the order of $10^{-3}\ Z_\odot$ in $z \in [1, 4]$ (slightly increasing with redshift) have been observed (Schaye et al. 2003), and since there is less than 1 Gyr between $z = 4$ and 7, from now on we take $Z_{\rm O\,I} = 10^{-3}\ Z_\odot$ as our fiducial value.

This distortion could be detectable with future CMB experiments and opens the possibility of performing tomography of the reionization epoch using this effect. In combination with 21 cm studies, it could yield direct measurements of the abundance and spatial distribution of metals in the high-redshift IGM.[4]

The basic criteria for a line $0 \leftrightarrow 1$ of a metal species or their ions to produce an effect analogous to the Wouthuysen-Field pumping of the H I 21 cm line are as follows: (1) abundant metals in the IGM in the required ionization state; (2) the $0 \leftrightarrow 1$ transition at a frequency suitable for detection, with Einstein coefficients small enough to allow the line to deviate from equilibrium with the CMB; (3) the upper and lower states

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[4] Metals will likely be dispersed into the IGM and will *not* be retained inside the shallow gravitational potential wells of the earliest galaxies (Mac Low & Ferrara 1999). Furthermore, any residual oxygen trapped inside galaxies would be either ionized or in dense, optically thick clumps and would not contribute to the signal.

should be connected via allowed transitions to another state (hereafter called state 2), so that they can be "pumped" in a two-step process; (4) a large enough background flux at the wavelength $\lambda_{02} \approx \lambda_{12}$ corresponding to the $0 \leftrightarrow 2$ and $1 \leftrightarrow 2$ transitions. In particular, the last criterion imposes the constraint $\lambda_{02} \gtrsim 1215$ Å on the wavelength of the UV pumping photons before reionization, since neutral H I depletes the background at shorter wavelengths (Haiman et al. 2000).

We selected oxygen for our study because it can be relatively abundant at high redshifts and because of the similarity of its ionization potential to that of hydrogen. The ground state of neutral oxygen is split into the three fine-structure levels of the outermost electrons in the $n = 2$ shell, hereafter denoted as 0, 1a, and 1b. We found that among the electronic states of oxygen, these are the only ones that satisfy all of the criteria above and give rise to photons observable in the CMB frequency band. The states 0–1a and 1a–1b are connected by magnetic dipolar transitions [O I] $^3P_2 \rightarrow {}^3P_1$ at 63.2 μm and $^3P_1 \rightarrow {}^3P_0$ at 145.5 μm, respectively, and the states 0–1b are connected by an electric quadrupolar transition $^3P_2 \rightarrow {}^3P_0$ at 44.1 μm. We consider only lines involving the 0 state $^3P_2$ as the lower level for the transition, since the CMB ambient field is practically unable to populate the $^3P_1$ state and the 145.5 μm line will be suppressed. Since these transitions are forbidden, the spontaneous-emission Einstein coefficients ($A_{44.1\,\mu\mathrm{m}} = 1.34 \times 10^{-10}$, $A_{63.2\,\mu\mathrm{m}} = 8.91 \times 10^{-5}$, $A_{145.5\,\mu\mathrm{m}} = 1.75 \times 10^{-5}$ s^{-1}) are much smaller than the typical values for electric dipole transitions ($\sim 10^8$ s^{-1}), a property shared by the hydrogen 21 cm line with $A_{\mathrm{H}\,21} = 2.85 \times 10^{-15}$ s^{-1}.

The states 0 and 1a, 1b are connected to the excited electronic state $^3S_1$ in the $n = 3$ shell (hereafter denoted by 2) by means of the absorption of an O I Baα photon with wavelength $\lambda_{20} \approx \lambda_{21} \approx 1300$ Å. A schematic level diagram is shown in Figure 1. In the absence of a UV field, O I is in thermal equilibrium with the CMB and, as shown in Basu et al. (2004), resonant scattering is more important than collisionally induced emission, except at extremely large overdensities. For this transition, we obtain that the collisions become important at overdensities $\gtrsim 10^7$. However, if the first stars or black holes generated a UV background at 1300 Å, then the relative populations of the fine-structure states 0 and 1 are modified by the two-step "pumping" transitions $0 \rightarrow 2 \rightarrow 1$ and $1 \rightarrow 2 \rightarrow 0$.

For simplicity we start by considering only one fine-structure transition and address the combined effect later. In what follows we use the indices i, j to denote the two levels in the fundamental state, with i referring to the lowest one. For example, for the 63.2 μm transition (i, j) corresponds to (0, 1a) (see Fig. 1). The steady state solution for the level population reads

$$\frac{n_j}{n_i} = \frac{P_{ij}^{\mathrm{UV}} + B_{ij} I_\nu}{P_{ji}^{\mathrm{UV}} + B_{ji} I_\nu + A_{ji}} \equiv \frac{g_j}{g_i} \exp\left(\frac{-T_{\star,ji}}{T_{S,ji}}\right). \quad (1)$$

This equation defines the spin temperature $T_{S,ji}$. Here $T_{\star,ji}$ is the equivalent temperature of the $i \leftrightarrow j$ transition [$T_{\star,ji} \equiv h\nu_{ji}/k_{\mathrm{B}} \simeq 231(63.2\ \mu\mathrm{m}/\lambda_{ji})$ K, with k_{B} the Boltzmann constant]; A_{ji}, B_{ji}, and B_{ij} are the Einstein coefficients for spontaneous emission, induced emission and absorption, respectively; P_{ji}^{UV} and P_{ij}^{UV} denote the UV de-excitation and excitation rates; I_ν denotes the specific intensity at the resonant frequency of the $i \leftrightarrow j$ transition; and $g_{1\mathrm{a}} = 3$, $g_{1\mathrm{b}} = 1$, and $g_0 = 5$ are the degeneracy factors. It is useful to define the UV color temperature

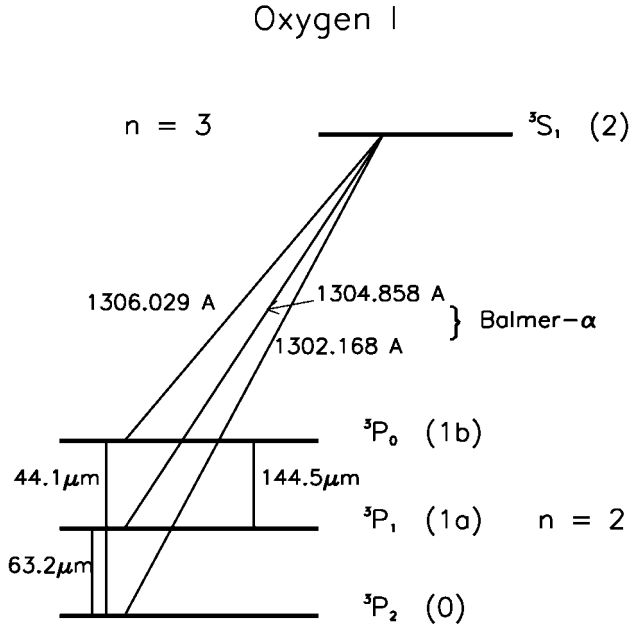

FIG. 1.—Schematic representation of the transitions of neutral oxygen considered here. Note the analogy with the 21 cm transition of H I. In the 21 cm transition the relevant line corresponds to a hyperfine transition, while for O I it corresponds to a fine-structure transition. The 21 cm line is pumped by H I Lyα photons, while the O I line is pumped by O I Baα photons.

$T_{\mathrm{UV},ji}$ in terms of the ratio of the UV de-excitation and excitation rates,

$$P_{ij}^{\mathrm{UV}}/P_{ji}^{\mathrm{UV}} \equiv (g_j/g_i) \exp(-T_{\star,ji}/T_{\mathrm{UV},ji}), \quad (2)$$

which represents the spin temperature reached in the limit of strong pumping. Following Field (1958), these pumping rates can be written as

$$P_{ji}^{\mathrm{UV}} = \left(\frac{g_2}{g_j}\right) \frac{A_{2i}}{\sum_m A_{2m}} A_{2j} \left(\frac{c^2 I_\nu}{2h\nu^3}\right)_{\nu_{2j}}, \quad (3)$$

$$P_{ij}^{\mathrm{UV}} = \left(\frac{g_2}{g_i}\right) \frac{A_{2j}}{\sum_m A_{2m}} A_{2i} \left(\frac{c^2 I_\nu}{2h\nu^3}\right)_{\nu_{2i}}. \quad (4)$$

Here $g_2 = 3$ and the subscript ν_{pq} denotes evaluation at $\nu = \nu_{pq}$, i.e., at the frequency of the transition connecting states p and q. The sum over m takes into account the five possible downward transitions from the upper state 2, obtained from the NIST data base.[5]

From the definition of the UV excitation and de-excitation rates, it is easy to see that their ratio is proportional to the ratio of the quantity $c^2 I_\nu/(2h\nu^3)$ evaluated at two slightly different frequencies: ν_{2j} and ν_{2i}. It follows then that the color temperature can be approximated by

$$T_{\mathrm{UV}} \simeq \frac{T_\star}{-\partial \log n_\nu/\partial\nu|_{\nu_{2j}}} \frac{1}{\nu_{ji}} = \frac{T_{2i}}{3 + \alpha_s}, \quad (5)$$

where $n_\nu \equiv I_\nu/\nu^3$ is proportional to the number of photons with

[5] See http://physics.nist.gov/PhysRefData/ASD/lines_form.html.

frequency ν, and $\alpha_s \equiv -d \log I_\nu / d \log \nu$ is the logarithmic slope of the background spectrum near the O I Baα line. We have assumed that $\partial \log n_\nu / \partial \nu|_{\nu_{2j}} \approx \partial \log n_\nu / \partial \nu|_{\nu_{2i}}$. For a different approach, see Chuzhoy & Shapiro (2006). If $\partial \log n_\nu / \partial \nu|_{\nu_{2j}}$ is small and negative then the pumping mechanism will be more effective in the transition $i \rightarrow 2$ than in $j \rightarrow 2$, and as a result the level i will be relatively depopulated. In particular, the $j \rightarrow i$ photons will be seen in emission if $T_{\rm UV} > T_{\rm CMB}$, which will generally be the case since $T_{2i} \sim 10^5$ K $\gg T_{\rm CMB}$.

The amplitude and shape of the UV photon field at 1300 Å at the beginning of reionization is uncertain. Unlike at the H I Lyα frequency of 1215 Å, however, the high-z IGM should be optically thin at 1300 Å (see discussions of the shape of the soft UV background in Haiman et al. 1996, 2000). Therefore, the relevant background at redshift z should reflect the intrinsic spectrum of the dominant sources over the ≈27% redshift range $(1 + z) < (1 + z_{\rm source}) < (1 + z)\nu_{\rm H\,I\,Ly\beta}/\nu_{\rm O\,I\,Ba\alpha} = 1.27(1 + z)$.[6] Over the 0.2% fractional difference between ν_{2j} and ν_{2i}, we then expect a relative decrement of n_ν of ~0.2%$(3 + \alpha_s)$ throughout ν_{ji}, or a decrement of order ~1% for sources with $\alpha_s \sim 2$. For our calculations, we adopted a fiducial choice of ~1%, but in practice, our results are insensitive to this value (see below).

Given the specific intensity I_ν, the steady state solution for the level population provides the following expression for the spin temperature $T_{S,ji}$:

$$\frac{T_{\star,ji}}{T_{S,ji}} = \log\left(\frac{1 + (A_{ji}/P_{ji}^{\rm UV})\,[1 + (I_\nu c^2/2h\nu^3)_{\nu_{ji}}]}{\exp\,(-T_\star/T_{\rm UV}) + (A_{ji}/P_{ji}^{\rm UV})\,(I_\nu c^2/2h\nu^3)_{\nu_{ji}}}\right). \quad (6)$$

If at a given redshift z_s the presence of dust can be neglected, I_ν at ν_{ji} is given by the CMB, $I_\nu \equiv B_{\nu_{ji}}(T_{\rm CMB}(z_s))$. In the limit of $A_{ji} \gg P_{ji}$, in equation (6) we have $T_{S,ji} \rightarrow T_{\rm CMB}$, whereas if $A_{ji} \ll P_{ji}$ then $T_{S,ji} \rightarrow T_{\rm UV}$.

As long as the slope of the background at 1300 Å is such that $\alpha_S \sim 1$, equation (5) implies that $T_{\rm UV} > T_{\star,ji} > T_{\rm CMB}(z_s)$, so that $T_{S,ji}$ must be bracketed between $T_{\rm CMB}(z_s)$ and $T_{\rm UV}$. In the limit of $T_{\star,ji} \ll T_{\rm UV}$ [and thus $\exp\,(-T_{\star,ji}/T_{\rm UV}) \simeq 1$] and $A_{ji} \gg P_{ji}$ (both of these conditions are satisfied for the 63.2 μm line), the departure of $T_{S,ji}$ from $T_{\rm CMB}$ becomes

$$\frac{T_{S,ji} - T_{\rm CMB}}{T_{\rm CMB}} \simeq \frac{T_{\rm CMB}}{T_{\star,ji}}\frac{g_2}{g_j}\frac{A_{2j}}{A_{ji}}\frac{A_{2i}}{\sum_m A_{2m}}\left(\frac{2h\nu^3}{c^2 I_\nu}\right)_{ji}\left(\frac{I_\nu c^2}{2h\nu^3}\right)_{2j}, \quad (7)$$

i.e., it depends linearly on the UV flux at 1300 Å, and the dependence on $T_{\rm UV}$ is negligible.

The solid lines in Figure 2 show the deviation of T_S with respect to $T_{\rm CMB}$ as a function of the UV flux for $z_s = 10$ (*thin line*) and $z_s = 7$ (*thick line*) for the case of the 63.2 μm (0 → 1a) line. While this relative deviation is small (~10^{-3} to 10^{-5}), it nevertheless modifies the populations of levels 0 and 1.

The distortion in the CMB spectrum can be parameterized by the y-parameter, $y \equiv \Delta I_\nu / B_\nu(T_{\rm CMB})$, where ΔI_ν is the deviation in surface brightness from the Planck spectrum with the unmodified CMB temperature. Before computing the distortion using the spin temperature above, it is useful to obtain an order-of-magnitude estimate. Because the optical depth of the IGM for the UV photons in our case is small (we find $\tau_{20} = 7.3 \times 10^{-2}$ at redshift 10 for $Z/Z_\odot = 10^{-3}$), multiple scatterings will be rare. (Note that this is different from the case of the H I 21 cm line, where the Lyα photons responsible for the pumping have a large optical depth and scatter multiple times.) In this case, roughly a fraction τ_{20} of every 1300 Å photon produced by stars will scatter off an O I atom and produce an "excess" $\nu_{ji} \equiv \nu_{j0}$ photon. Just prior to reionization, assuming that a few UV photons have been produced per H atom (corresponding to a background flux of J_ν = a few × 10^{-21} ergs s^{-1} cm^{-2} sr^{-1} Hz^{-1}), the distortion should be roughly $y \sim f_{\Delta z}^{-1}\tau_{20}\eta \sim 10^{-10}$, where $\eta \sim 6 \times 10^{-10}$ is the baryon-to-photon ratio and $f_{\Delta z}$ represents the fraction of CMB photon in the frequency band corresponding to the redshift range Δz.

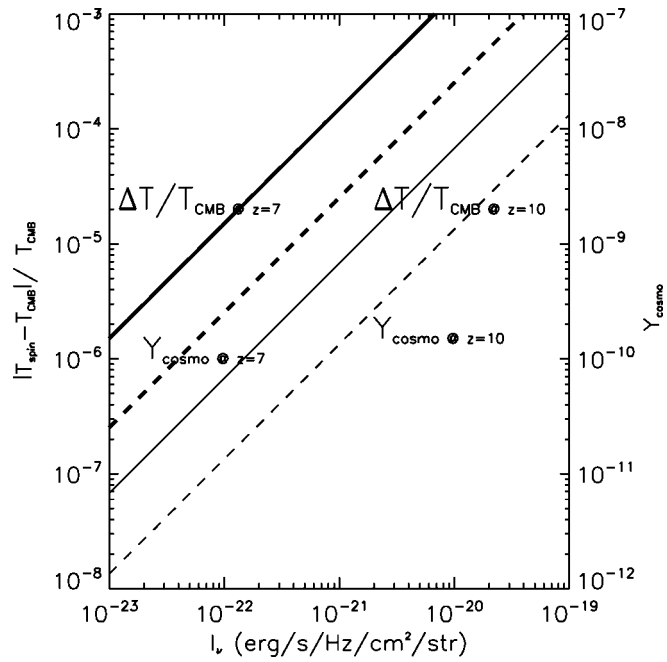

FIG. 2.—*Solid lines*: Relative departure of the spin temperature T_S from the CMB temperature as a function of the background intensity at the Baα frequency of O I. Note that these intensities are within the range of amplitudes required for reionization (~10 photons per H atom; Haiman et al. 2000). *Dashed lines*: CMB distortion parameter $y \equiv \Delta I_\nu^{63.2\,\mu\rm m}/B_\nu(T_{\rm CMB})$. In both cases, thick lines refer to $z = 7$, thin lines to $z = 10$.

To compute the distortion of the CMB at the redshifted ν_{ji} frequency more precisely, we use the radiative transfer equation $dI_\nu/ds = h\nu\Psi(\nu)[n_j(A_{ji} + B_{ji}I_\nu) - n_i B_{ij} I_\nu]/(4\pi)$, with ds the cosmological line element along the line of sight. Since the line profile $\Psi(\nu)$ is narrow, we have ignored the effect of cosmological expansion. For $Z_{\rm O\,I}/Z_\odot = 10^3$, we find the optical depth for the 0 → 1a and 0 → 1b transitions

$$\tau_{j0} = \frac{c^3}{8\pi\nu_{j0}^3}\frac{A_{j0}}{H(z_s)}\frac{g_j}{g_0}\frac{1 - \exp\,(-T_{\star,j0}/T_{S,j0})}{\chi(z_s)}\,n_{\rm O\,I}(z_s) \quad (8)$$

to be very small ($\tau_{1a\,0} = 2.1 \times 10^{-7}$, $\tau_{1b\,0} \sim 3 \times 10^{-13}$). In this equation we have approximated the line profile function $\Psi(\nu)$ by a Dirac delta, and χ^{-1} is the fraction of oxygen atoms in the $^3P_2$ level to the ground level ($\chi = 1$ to a good approximation). Assuming a constant UV background (justified by the fact that $\tau_{20} \ll 1$), the net change to the CMB due to the

[6] Lyα scattering for these sources should be negligible (Chen & Miralda-Escudé 2004; Furlanetto & Pritchard 2006), while the contribution from yet more distant sources will be blocked, because the photons redshifting down to 1300 Å by redshift z will have passed through the H I Lyβ resonance (or higher lines), and they will have been broken down into lower energy photons.

presence of O I can be written as an integral along the line of sight of the emissivity, resulting in

$$\Delta I_\nu^{j0}(z_s) = \frac{h\nu_{j0}}{4\pi}\frac{c}{H(z_s)}\frac{A_{j0}}{\nu_{j0}}n_{\mathrm{O\,I}}(z_s)\frac{g_j}{g_0}\frac{\exp(-T_{\star,j0}/T_{S,j0})}{\chi(z_s)} \times\left[1-\frac{\exp(T_{\star,j0}/T_{S,j0})-1}{2h\nu^3/(c^2 I_\nu)_{\nu_{j0}}}\right]. \quad (9)$$

The corresponding CMB distortion at the observed frequency $\nu = \nu_{j0}/(1+z_s)$ is given by $y \equiv \Delta I_\nu^{j0}/B_\nu(T_{\mathrm{CMB}}(z_s))$. In our case $\tau_{j0} \ll 1$, and the distortion parameter can be written in the simple form $y \simeq \tau_{j0}\{(\exp x - 1)/[\exp(T_{\star,j0}/T_{S,j0}) - 1] - 1\}$, with $x \equiv T_{\star,j0}/T_{\mathrm{CMB}}(z_s)$.

For the 63.2 μm line, $T_{\star,63.2\,\mu\mathrm{m}}/T_{\mathrm{CMB}} \sim 10$ but $T_{\star,63.2\,\mu\mathrm{m}}/T_{\mathrm{CMB}}(T_{S,63.2\,\mu\mathrm{m}}/T_{\mathrm{CMB}} - 1) \ll 1$; thus

$$y \simeq \tau_{63.2\,\mu\mathrm{m}}\frac{T_{\star,63.2\,\mu\mathrm{m}}}{T_{S,63.2\,\mu\mathrm{m}}}\left(\frac{T_{S,63.2\,\mu\mathrm{m}}}{T_{\mathrm{CMB}}} - 1\right). \quad (10)$$

In this case, the distortion parameter y is simply the relative deviation of $T_{S,63.2\,\mu\mathrm{m}}$ with respect to T_{CMB} multiplied by the optical depth times the ratio $T_{\star,63.2\,\mu\mathrm{m}}/T_{S,63.2\,\mu\mathrm{m}} \sim 10$.

The dashed lines in Figure 2 show the amplitude of the distortion introduced by the O I 63.2 μm transition at $z_s = 7$ (*thick line*) and 10 (*thin line*) as a function of the UV background intensity, over a range expected to be relevant for the epoch just prior to reionization. Note that apart from the $T_{\star,63.2\,\mu\mathrm{m}}/T_{S,63.2\,\mu\mathrm{m}}$ factor, equation (10) is identical to that found for the H I 21 cm spin temperature. Since in our case for $Z_{\mathrm{O\,I}}/Z_\odot \sim 10^{-3}$ the relative deviations of $T_{S,63.2\,\mu\mathrm{m}}$ with respect to T_{CMB} are typically $\sim 10^2$–10^3 smaller than in the H I 21 cm scenario, and since $\tau_{21\,\mathrm{cm}} \approx 10^{-4}$, our y-distortion is $\sim(10^2$–$10^3)(Z/10^{-3}\,Z_\odot)^{-1}$ smaller than in the 21 cm case. For the 44.1 μm ($0 \rightarrow 1$b) transition, the amplitudes of y are a factor $\sim$5 larger, but the relevant frequencies are more contaminated by dust and thus more difficult to detect, as we discuss next.

Our basic result is that the O I 63.2 μm (and 44.1 μm) transition could be seen as a deviation in the present-day CMB blackbody spectrum of the order of up to 10^{-8} at around 160–500 GHz (481 GHz corresponds to $z = 10$ and 160 GHz to $z = 30$, for the 63.2 μm transition).

The FIRAS experiment has already obtained constraints on the deviation of the CMB spectrum from a blackbody. We find that in the range of frequencies corresponding to $10 < z_s < 20$ for the 63.2 μm line, the FIRAS data (Fixsen et al. 1996) constrain $y < 10^{-5}$ at the 1 σ level (4×10^{-5} at the 3 σ level). Considering the expected background UV flux at these redshifts, we obtain a FIRAS constraint of 5 (40) $Z_\odot$ at $z_s > 10$. Although this constraint is far bigger than existing measurements at $3 \lesssim z \lesssim 5$ (e.g., Schaye et al. 2003; Aguirre et al. 2004), it is the first *direct* constraint on the $Z_{\mathrm{O\,I}}$ of the IGM in the universe at $z \approx 10$. Since y scales linearly with $Z_{\mathrm{O\,I}}$, by comparing different, accurately calibrated *Planck* HFI channels, constraints of $y < 5 \times 10^{-7}$ could be imposed. An experiment able to reduce the FIRAS y uncertainty (e.g., Fixsen & Mather 2002) by 2–3 orders of magnitude could impose interesting constraints.

The main limitation to the measurement is foreground dust emission from the Galaxy and from IR galaxies; however, high Galactic latitude patches of the sky and observations at higher frequencies (to remove the IR galaxies) could be used for this purpose. Of course, there could be other cosmological effects (such as decaying particles; see Fixsen & Mather 2002 for a discussion) producing distortion at the feeble $y \sim 10^{-8}$ level. It remains to be seen whether the O I distortion can be disentangled from these. One further consideration is that clustering of the sources will make it more easily detectable. The signal should trace the clustering properties of the (enriched) fossil H II regions during reionization and should dominate over the primary CMB angular power spectrum in the damping tail, showing a similar angular pattern to that of the Ostriker-Vishniac effect. In this case the spectral dependence will be different, since this signal is restricted to frequencies probing the O I 63.2 μm transition at redshifts where $Z_{\mathrm{O\,I}}$ and the UV background are not negligible (C. Hernández-Monteagudo et al. 2007, in preparation). Our technique complements future experiments that will detect the H 21 cm hyperfine transition in absorption because it is sensitive to different systematics and operates at different wavelengths. This would be highly valuable, since H I 21 cm + O I measurements in combination can probe the spatial distribution of metallicity directly.

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