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Potential microwave probes of the proton-to-electron mass ratio at very high redshifts

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ABSTRACT
Recently a stringent constraint on the change in the proton-to-electron mass ratio at a redshift of 0.89 has been established using theoretical predictions and radio observations of the methanol molecule. To get an insight at deeper look-back times, accurate determinations of variations of the proton-to-electron mass ratio at higher redshifts are needed. We propose a microwave probe of the proton-to-electron mass ratio employing the primordial molecular ions H_2^+, D_2^+, and He_2^+ considering redshifts from 0 to 70. Microwave rovibronic transitions of these ions, which are presented here, crucially exhibit high or very high sensitivities to a variation of the proton-to-electron mass ratio and could in principle be detected by the Atacama Large Millimeter/submillimiter Array.

Key words: molecular processes – molecular data

1 INTRODUCTION

Critical investigations of the possibility that fundamental constants of nature could depend on time and space in the evolving Universe become more possible with the fast developing current experimental techniques (Uzan 2003). Attempts were made recently to establish constraints on the change of the proton-to-electron mass ratio $\mu = m_p/m_e$. Earlier strict constraints (Flambaum & Kozlov 2007; Murphy et al. 2008; Henkel et al. 2009; Kanekar 2011), obtained from inversion spectra of ammonia, were improved very recently by Bagdonaite et al. (2013a,b) to $\Delta\mu/\mu = (0.0 \pm 1.0) \times 10^{-7}$ (at the redshift $z = 0.89$) using theoretical predictions (Jansen et al. 2011; Levshakov et al. 2011) and new PKS 1830-211 radio observations for the methanol molecule.

The limit obtained there allows for a cosmological look-back time of roughly half of the age (7 billion years) of the Universe. In order to get an insight at deeper look-back times accurate determinations of μ at higher redshifts are needed. Apparently, information from the deepest look-back times can be expected using signals from the primordial molecules or molecular ions consisting of hydrogen, helium, and possibly lithium. So far all such monitorings were performed exclusively for the hydrogen molecule (see Bagdonaite et al. 2012, and references therein). However, as the pertinent spectra are not recorded with adequate accuracy, it appears worthwhile to probe also other molecular systems. The prospects of such monitorings seem to be improved dramatically after launching the ALMA (Atacama Large Millimeter/submillimeter Array) project.

It turns out that the ALMA facilities can largely cover the frequency region of the microwave components of the H_2^+ and D_2^+ ($A^2\Sigma_u^+ \leftrightarrow X^2\Sigma_g^+$) and He_2^+ ($A^2\Sigma_g^+ \leftrightarrow X^2\Sigma_u^+$) rovibronic spectra measured by Carrington et al. (1995a,b); Carrington (1996), and also the forbidden electric dipole spectrum of the H_2^+ ($X^2\Sigma_g^+ \rightarrow X^2\Sigma_g^+$) predicted by Bunker & Moss (2000). Therefore at least in principle, H_2^+, D_2^+, and He_2^+ appear as fairly suitable probes of the early expansion of the Universe. The use of H_2^+, D_2^+, and He_2^+ in astronomical searches is facilitated by the fact that these molecules can be studied theoretically at a very high accuracy level and that the corresponding highly accurate experimental data are available allowing a critical comparison and eventually adjustment of the theoretical findings.

The purpose of this study is to generate accurate estimates, so far unavailable, of the mass sensitivities of all the H_2^+, D_2^+, and He_2^+ $A \leftrightarrow X$ transitions, which may be of astronomical relevance and could be detected by the ALMA facility. So far the most distant galaxies were detected at redshifts of $z = 8.6$ (Lehnert et al. 2010) and $z = 9.6$ (Zheng et al. 2012). Because the first observable star was most likely formed 30 million years after the Big Bang (at redshift $z \sim 65$ (see Naoz et al. 2006)), the calculations presented here are performed for the redshift range of $0 < z < 70$.

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2 METHODS

It should be noted that the H_2^+, HD^+, and D_2^+ cations were considered as potential probes for temporal variations of the proton-to-electron mass ratio already by Hilico et al. (2000, 2001); Karr & Hilico (2006). Treating these cations as three body Coulomb systems, these authors have evaluated extremely accurate energies and pertinent mass sensitivities of the $N = 0$, 1, and 2 ro-vibrational states of the ground electronic states. To get these characteristics for the excited states, apparently, one can perform similar calculations and get the desired results with even higher accuracy (Ishikawa et al. 2012). These calculations, however, are not feasible in the case of He_2^+. Therefore, we have decided to adopt an indirect approach, in which we rely on less quantitative *ab initio* potential energy functions and their morphing by fitting to extremely accurate experimental data. Namely, we rely on the following ro-vibrational Hamiltonian (Herman & Asgharian 1966; Bunker & Moss 1977)

$$H_{\rm eff} = T_{\rm kin} + V_{\rm rot}(R) + V_{\rm ad}(R) + V'(R), \qquad (1)$$

where

$$T_{\rm kin} = -\frac{\hbar^2}{2M_{\rm red}}\frac{\rm d}{{\rm d}R}\, f_v(R)\, \frac{\rm d}{{\rm d}R} \qquad (2)$$

$$V_{\rm rot}(R) = \frac{\hbar^2}{2M_{\rm red}}\, f_r(R)\, \frac{N(N+1)}{R^2}, \qquad (3)$$

$$f_x(R) = 1 + \mu\, g_x(R) \qquad (x = v, r), \qquad (4)$$

$M_{\rm red}$ is the appropriate atomic reduced mass, $V_{\rm ad}$ is the 'adiabatic' part of the molecular potential energy curve (assumed to include the Born-Oppenheimer, adiabatic, relativistic, QED and residual retardation terms) and the terms $V'(R)$, $g_r(R)$ and $g_v(R)$ account for nonadiabatic effects. The so-called vibrational, $g_v(R)$, and rotational, $g_r(R)$, g-factors are assumed to acquire their *ab initio* values and the effective potential energy function $V_{\rm eff}(R) = V_{\rm ad}(R) + V'(R)$ is assumed to be determinable by fitting to the available experimental data. As the nonadiabatic functions $g_v(R)$ and $g_r(R)$ are not available for all the studied states, and also because the spectral data pertaining the excited states are too limited to allow for their detailed fitting, we have decided to simplify the above Hamiltonian by assuming that these functions can be approximated in the following way

$$g_x(R) \doteq g_x^0\, M_{\rm red}\, \frac{(R - R_e)}{R^2} \qquad (x = v, r), \qquad (5)$$

where the constants g_x^0 are fitting parameters.

To respect the fact that the available experimental data are rather scarce, especially for the excited electronic states, we have decided to perform our fittings in the framework of the Jenč's Reduced Potential Curve approach (Jenč 1983; Jenč et al. 1993), which appears as a suitable tool for a quantitative morphing of accurate *ab initio* potential energy curves in terms of only very few morphing parameters (Patkowski et al. 2009).

In the case of H_2^+, the reduced potential curves were constructed using the Born-Oppenheimer potential curves of Bishop & Wetmore (1973) and Peek (1965) and the adiabatic corrections of Bishop & Wetmore (1973) and Fabri et al. (2009). The potentials were interpolated using the cubic splines and extrapolated in the same way as in Schwenke (2001). In the case of He_2^+, the reduced potential curves were constructed using the Born-Oppenheimer potential curves V_4 of Carrington et al. (1995b) and the adiabatic corrections of Xie et al. (2005). The potentials were interpolated using the cubic splines and extrapolated using the expressions given in Xie et al. (2005). The corresponding transition dipole moments published very recently by Augustovičová et al. (2013) were used.

3 RESULTS AND DISCUSSION

In order to get an insight on the effects induced by the approximation defined by Eq. (5), we have first performed test calculations for HD, for which there are all needed data available in the literature (Ulivi et al. 1991; Piszczatowski et al. 2009; Pachucki & Komasa 2010; Kassi & Campargue 2011; Dickenson et al. 2013). The results show practically quantitative agreement between the experimental data and their fitted counterparts (see online supplementary information).

The first step of the actual calculations consisted in the fitting of the theoretical ro-vibrational energies of Hilico et al. (2000) and Moss (1993), the experimental microwave data of Carrington et al. (1995b), and vibronic data of Raunhardt et al. (2008) for H_2^+ (D_2^+) and He_2^+, respectively. The resulting potentials were in turn used to evaluate the sought sensitivities K_μ defined via

$$\frac{\Delta\nu}{\nu} = K_\mu\, \frac{\Delta\mu}{\mu}, \qquad (6)$$

where $\Delta\nu$ is the frequency shift of the probed transition induced by the variation of μ.

For a transition with frequency $\nu = (E_{v'N'} - E_{v''N''})/h$ we also calculated its line strength

$$S_{v'N',\,v''N''} = \mathscr{S}_{N',N''}\, |\langle\psi_{v'N'}|d_z|\psi_{v''N''}\rangle|^2 \qquad (7)$$

and the corresponding Einstein coefficient

$$A_{v'N',\,v''N''} = \frac{64\,\pi^4\,\nu^3_{v'N',\,v''N''}\,S_{v'N',\,v''N''}}{(4\pi\varepsilon_0)\,3h\,c^3\,(2N'+1)}, \qquad (8)$$

where the only non-zero Hönl-London coefficients are $\mathscr{S}_{N',N'+1} = N'+1$ and $\mathscr{S}_{N',N'-1} = N'$ and c is the speed of light in vacuum. For these calculations we used our radiative-association code (Augustovičová et al. 2012) modified to accommodate bound-bound transitions.

Not surprisingly, as it can be surmised from the theoretical analysis of DeMille et al. (2008), the calculated sensitivities acquire magnitudes, which are comparable with their 'record-breaking-methanol' counterparts (see Tables 1-4 and their complete versions in the online supplementary information). Interestingly, the largest sensitivity constant evaluated in this study, $K = -407$, was obtained for the ($v_A = 0, N_A = 3 \leftarrow v_X = 26, N_X = 4$) transition of D_2^+.

4 CONCLUSION

The predicted sensitivities are obtained here with positive or negative values which allows single molecular analyses without any reference molecules. Since the corresponding transitions have also fairly large line strengths, they could be promising candidates for astrophysical observations. On the other hand, although the H_2^+, D_2^+, and He_2^+ cations are assumed to play central roles in the primordial chemistry (Lepp et al. 2002), they have not yet been detected in extraterrestrial environments and it has actually been argued that their detection would be a very difficult task (Shuter et al. 1986; Howells & Kennedy 1991). However, the radiative lifetimes

Table 1. The $A \leftrightarrow X$ microwave transitions of H_2^+.

v', N'	v'', N''	$\nu_{\rm fit}$	$\nu_{\rm exp}$	S	A	K_μ
			$A \rightarrow X$			
0, 0	18, 1	514956.6		3.073	2.038×10^{-1}	31.669
0, 1	18, 0	645722.3		2.484	1.083×10^{-1}	26.982
0, 1	18, 2	352014.8		7.493	5.293×10^{-2}	39.683
0, 2	18, 1	593778.1		4.452	9.055×10^{-2}	27.400
0, 2	18, 3	156614.7	156633	15.406	5.751×10^{-3}	65.568
			$X \rightarrow A$			
19, 0	0, 1	52907.5	52895	8.884	6.400×10^{-4}	-17.594
19, 1	0, 0	96431.6	96432	5.268	7.659×10^{-4}	-5.739
19, 1	0, 2	17610.2	17610	24.113	2.135×10^{-5}	-29.230

Note. Frequencies ν are in MHz, line strengths S in D^2, and Einstein coefficients A in s^{-1}; the $\nu_{\rm exp}$ column contains data from Carrington et al. (1995a).

Table 2. Forbidden electric dipole $X \rightarrow X$ microwave transitions of H_2^+.

v', N'	v'', N''	$\nu_{\rm fit}$	$\nu_{\rm theor}$	S	A	K_μ
19, 1	19, 0	15664.4	15679.0	4.80×10^{-3}	0.3×10^{-8}	25.220
19, 1	18, 2	420586.7	420536.4	3.90×10^{-4}	4.7×10^{-6}	31.939
19, 0	18, 1	595723.9	595616.8	1.12×10^{-4}	1.15×10^{-5}	25.783
19, 1	18, 0	714294.2	714183.7	1.63×10^{-4}	9.6×10^{-6}	23.642

Note. Frequencies ν are in MHz, line strengths S in D^2, and Einstein coefficients A in s^{-1}; the $\nu_{\rm theor}$, S, and A columns contain data from Bunker & Moss (2000).

of the H_2^+ states involved in the microwave transitions (with an upper radiative lifetime limit of 1000 s) are shorter than the timescale estimated for the destructions of H_2^+ by collisional reactions with H_2 or H (Shuter et al. 1986; Howells & Kennedy 1991). H_2^+ ions formed in the upper levels of the discussed transitions may thus be expected to undergo spontaneous emission before being destroyed by chemical reactions, especially in low density plasmas. It has further been reported that the Cassini-Huygens facility provided a strong evidence that H_2^+ is present in the Saturn's magnetosphere (Thomsen et al. 2010). Besides these arguments the unprecedented detection potential of the ALMA installation is finally decisive for the observation of the proposed microwave transitions.

Apart from the homonuclear diatomics H_2^+, D_2^+, and He_2^+ other primordial species could in principle also been chosen for the purpose of this study. For instance the deuterated species HD, H_2D^+, or HD_2^+ could be promising candidates for astronomical observations due to the fact that they have actually been detected in extraterrestrial sources (see Caselli et al. 2003). Also HeH^+, which has recently tentatively been identified in one of the highest redshift quasars with $z = 6.4$ (Zinchenko et al. 2011) and which has always been expected to be abundant in interstellar environments, could be thought of in this context. It has to be stressed however that the corresponding sensitivity coefficients K_μ of the ro-vibrational transitions between low-lying vibrational levels of a single electronic state (e.g. $X \rightarrow X$) of these ions are by orders of magnitude smaller than the sensitivity coefficients of the ro-vibronic $A \leftrightarrow X$ transitions, which are accessible for the homonuclear diatomics selected here.

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Table 3. The $A \leftrightarrow X$ microwave transitions of D_2^+.

v', N'	v'', N''	$\nu_{\rm fit}$	$\nu_{\rm exp}$	S	A	K_μ
			$A \rightarrow X$			
0, 0	26, 1	162124.4	162165.2	5.918	1.225×10^{-2}	59.209
0, 1	26, 0	215438.7	215484	5.595	9.060×10^{-3}	46.855
0, 1	26, 2	109628.6	109672.8	12.859	2.744×10^{-3}	78.142
0, 2	26, 1	211802.5	211847	11.477	1.060×10^{-2}	45.139
0, 2	26, 3	48013.2	48064.3	21.876	2.353×10^{-4}	145.883
0, 3	26, 2	189639.2	189681	18.329	8.676×10^{-3}	44.871
0, 4	26, 3	152839.8	152896.5	26.819	5.169×10^{-3}	45.453
1, 0	27, 1	11117.9	11138.1	22.896	1.529×10^{-5}	97.619
1, 1	27, 0	25783.0	25755.4	16.676	4.629×10^{-5}	50.245
			$X \rightarrow A$			
26, 4	0, 3	11978.9	11928.0	35.183	3.265×10^{-6}	-406.966
27, 0	0, 1	118294.6	118296.7	2.291	1.843×10^{-3}	-10.337
27, 1	0, 2	95215.2	95222.5	4.826	6.746×10^{-4}	-10.400

Note. Frequencies ν are in MHz, line strengths S in D^2, and Einstein coefficients A in s^{-1}; the $\nu_{\rm exp}$ column contains data from Carrington et al. (1995a).

Table 4. The $A \leftrightarrow X$ microwave transitions of He_2^+.

v', N'	v'', N''	$\nu_{\rm fit}$	$\nu_{\rm exp}$	S	A	K_μ
			$A \rightarrow X$			
0, 0	22, 1	384695.5		2.083	5.761×10^{-2}	33.071
0, 2	22, 1	438939.4		3.984	3.271×10^{-2}	28.883
0, 2	22, 3	264152.2		7.020	1.255×10^{-2}	42.473
0, 4	22, 3	382670.8		8.177	2.473×10^{-2}	29.102
0, 4	22, 5	101406.5	101460	14.770	8.275×10^{-4}	81.484
1, 0	22, 1	603065.1		0.095	1.016×10^{-2}	21.176
1, 0	23, 1	49649.4	49646	4.689	2.765×10^{-4}	44.371
1, 2	22, 1	622318.2		0.142	3.309×10^{-3}	20.528
1, 2	22, 3	447531.0		0.164	1.421×10^{-3}	25.287
1, 2	23, 1	68902.5	68924	6.261	1.946×10^{-4}	32.036
1, 2	23, 3	8926.8	8949	25.107	1.577×10^{-6}	144.214
			$X \rightarrow A$			
23, 1	0, 0	168720.1	168709	1.628	1.265×10^{-3}	-12.770
23, 1	0, 2	114476.3	114539	3.932	9.562×10^{-4}	-18.432
23, 3	0, 2	174452.0		3.577	1.314×10^{-3}	-6.822
23, 3	0, 4	55933.4	55880	9.287	1.108×10^{-4}	-19.792

Note. Frequencies ν are in MHz, line strengths S in D^2, and Einstein coefficients A in s^{-1}; the $\nu_{\rm exp}$ column contains data from Carrington et al. (1995b).

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