

Molecular Dynamics Simulations of the Temperature and Density Dependence of the Absorption Spectra of Hydrated Electron and Solvated Silver Atom in Water

Anne Boutin, Riccardo Spezia, François-Xavier Coudert, Mehran Mostafavi

▶ **To cite this version:**

Anne Boutin, Riccardo Spezia, François-Xavier Coudert, Mehran Mostafavi. Molecular Dynamics Simulations of the Temperature and Density Dependence of the Absorption Spectra of Hydrated Electron and Solvated Silver Atom in Water. Chemical Physics Letters, 2005, 409 (4-6), pp.219-223. 10.1016/j.cplett.2005.05.012 . hal-00199373

HAL Id: hal-00199373
https://hal.science/hal-00199373

Submitted on 18 Dec 2007

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Molecular Dynamics Simulations of the Temperature and Density Dependence of the Absorption Spectra of Hydrated Electron and Solvated Silver Atom in Water

Anne Boutin, Riccardo Spezia, François-Xavier Coudert and Mehran Mostafavi

Laboratoire de Chimie Physique, UMR 8000, CNRS, Université de Paris-Sud 11, 91405 Orsay Cedex, France. Fax : +33 1 69 15 61 88

Abstract

We report mixed quantum-classical molecular dynamics simulations of the optical absorption spectrum of the solvated silver atom and electron in liquid water. The simple one electron model is shown to be able to reproduce the strong temperature dependence of the absorption spectra of hydrated electron as well as the much weaker dependence for the silver atom. A qualitative explanation is provided for this experimental fact. When extending these simulations to very low densities corresponding to supercritical conditions the results display a progressive "desolvation" of the hydrated electron. Two other distinct theoretical models lead to results similar to those of the present QCMD simulations.

1 Introduction

Understanding the mechanism of elementary chemical events such as charge transfer in solution is one of the major challenges in chemical physics today. Owing to its importance in many domains of chemistry and biology, the hydrated electron has been the subject of numerous studies. This is also true for the radiation-induced reduction of metal ions in solution. One of the most studied elementary reactions is the reduction of a silver ion in water, following a radiolysis pulse:

$$e^-_{aq} + Ag^+ \rightleftharpoons Ag^0_{aq}$$

Article published in Chem. Phys. Lett. *409, 219 (2005)*

A full understanding of the mechanism of elementary reactions requires a precise knowledge of the nature of the reactive species. In order to better characterize short-lived species in solution, their optical spectra have been thoroughly investigated. In the case of the hydrated electron, the observation of a broad structureless absorption band centered at 715 nm dates back to the early 1960s [1–4]. Soon after, this species was detected in other solvents and the optical spectrum of the solvated electron was found to depend strongly on the nature of the solvent [5]. The maximum of the absorption band can be shifted to as high as 2200 nm in tetrahydrofuran. The temperature effect on the optical spectrum has also been studied [6–10], and it has been recently investigated in supercritical water [11,12].

The metallic silver ion/solvated atom (eq.1) is being considered as a model system for the radiolysis-induced charge transfer in solution [13–21]. The optical absorption spectra of the transient silver atom, as well as that of the charged dimer (produced by an aggregation process with an excess neighboring silver ion), have been observed by pulse radiolysis in various solvents [22]. An indication of the influence of the atom-solvent interaction is given by the solvent dependence of the optical absorption spectra in solution. In ammonia, the absorption spectra of silver atoms and dimers were observed at two different temperatures: 296 K [22] and 223 K [23]. The maximum of absorption band was found at 435 nm and 450 nm, respectively. More recently [21], the rate constant for the reduction of silver ions by hydrated electrons was measured at different temperature and is found to fit with an Arrhenius relationship (from 398 K to 573 K at 200 atm) with an apparent activation energy of 17.8 kJ.mol^{-1}. The measurement of transient absorption spectra showed that the maximum of the absorption spectrum of silver atom in water is shifted from 355 nm to 370 nm when the temperature is increased from 298 K to 473 K.

In this paper, we concentrate on the (P, ρ, T) dependence of the optical spectra of the hydrated electron and silver atom, rather than the solvent dependence. Until very recently [24], the red shift of the maximum of the absorption band of the hydrated electron with increasing temperature had not been investigated theoretically. Based on a mixed quantum-classical molecular dynamics simulation, Nicolas et.al. [24] reported that a "cavity picture" of the hydrated electron could qualitatively capture most of the known experimental data. It was also suggested that the red shift of the absorption spectrum could be a density, rather than a temperature effect. No such investigation exists, to our knowledge, in the case of the hydrated silver atom.

In this work, we have performed adiabatic molecular dynamics simulations of both the hydrated electron (extending our previous simulations to supercritical conditions) and hydrated silver atom species. In the ordinary liquid conditions, we show that simple one electron, mixed quantum-classical simula-

tions are able to reproduce the strong thermodynamic state point dependence of the optical spectra of the hydrated electron, as well as the weak shift of the absorption spectrum in the case of silver atom. However, this is not the case under supercritical conditions where the simulation results are found to be at variance with recent pulse radiolysis experiments [12].

2 Methods

We have performed mixed quantum classical molecular dynamics (QCMD) simulations of an excess electron in bulk water and in presence of a silver cation. The excess electron only is treated quantum mechanically, using the Born-Oppenheimer approximation. The method and the simulation details are fully described elsewhere [24,25].

For the excess electron-water interaction we used the pseudo-potential developed by Turi and Borgis [26] while for electron-silver interaction we used the form initially proposed by Durand and Barthelat [27], which we have adapted to a Gaussian grid representation of the electron [25]. Water and cations interact via classical interaction potentials made by coulombic and 6-12 Lennard Jones (LJ) terms. Water-water interactions are described by the SPC model [28].

The simulations were carried out in a box of 300 SPC water molecules, an excess electron and/or a silver cation. Standard periodic boundary conditions were used together with the Ewald summation technique for computing the electrostatic interactions. The MD time step was fixed at 0.5 fs and simulation runs lasted a few tens of picoseconds after the stabilization period.

The method used for computing the electron absorption spectrum is fully described elsewhere [24,25,29]. Different thermodynamic conditions were simulated, from ambient to supercritical conditions. Since the SPC model fails at perfectly reproducing the equation of state of liquid water in the whole thermodynamic state space, we decided to perform (N,V,T) ensemble simulations, and to fix the density of the system to the value found in the NIST WebBook [30], for each given temperature and pressure. For instance, in order to compare our hydrated silver atom simulations to experiments, we used the density values corresponding to the thermodynamic state points investigated by Mostafavi et al. [21], namely 1.00, 0.95 and 0.86 g.cm^{-3} which correspond to 298, 376 and 476 K respectively, at a pressure of 20 MPa.

3 Results and discussion

The absorption spectra of the hydrated silver atom at 20 MPa and three different temperatures are shown in Figure 1. The maximum absorption wavelengths as well as the bandwidths are fairly well reproduced by the QCMD simulations. It is interesting to mention that the absolute maximum intensity of the simulated spectra is only weakly dependent on temperature (Table 1). Experimentally, the absorption intensity is often presented as the product of G.ϵ (where G is the radiolytic yield and ϵ is the absorption extinction coefficient). As shown in Table 1, the experimental maximum intensity does not depend markedly on temperature, at constant pressure. The comparison between experiments and simulations seems to provide an indication that the change in intensity of the experimental spectra could be mainly attributed to a decrease of the radiolytic yield (since the density of the system decreases with increasing temperature), rather than a decrease of ϵ. This is also true for the hydrated electron simulations where the maximum intensity of the absorption spectrum is found to vary within less than 20% whatever the density or temperature is.

In Figure 2, we show the evolution with temperature (at constant pressure) of the maximum of the absorption spectrum of the hydrated silver atom species. As already noted above, the simulation results are in good agreement with experiments. In the same figure, we report the previously published shift in the case of the hydrated electron alone [24]. It is clear from these data that the temperature shift is much weaker in the case of silver atom that it is for the hydrated electron. In the latter case, it was suggested that the red shift of the absorption spectrum could be a density, rather than a temperature effect [24]. Here, we have carried out QCMD simulations of the hydrated silver atom at several thermodynamic state points in order to shed some light on the weak shift observed in this case. The results are given in table 2.

At a constant density of 1.0 g.cm^{-3}, a temperature effect (red shift) is obtained. On the other hand, at a constant temperature of 573 K, a density effect (blue shift) is observed. At constant pressure, these two effects compensate each other and this leads to the weak temperature effect seen in Figure 2.

In a previous QCMD work, we have shown that the hydrated silver atom behaves as a dipolar excitonic state [29]. This is to say that the active electron and the silver cation act as a strong, fluctuating, dipole. The average distance between the electron and the cation can be computed from the QCMD simulations. It is shown, in Table 2, that a strong correlation exists between the change in the maximum of the absorption spectrum and the electron-cation distance.

From these findings, we suggest that the behavior of the active electron in the hydrated silver atom species is mainly governed by the presence of the neighboring silver cation. The thermodynamics state point slightly affects the electron-cation distance, and this has an effect on the absorption spectrum. Two distinct temperature and density effects are observed, but these effects are weak.

This is in clear contrast with the behavior of the hydrated electron, for which the thermodynamic state point effect was shown to be much stronger. It was suggested to be more or less related to the size of the cavity in which the electron was sitting, and in turn to the density of the system.

We have reinvestigated the density effect on the optical spectra of the hydrated electron, in order to compare the QCMD data to other simulation results of the literature. Our aim was also to extend our simulations to the supercritical conditions, for which some new experimental data became available recently [12,31]. In Figure 3, we report the QCMD computed evolution of the maximum of the absorption spectrum of the hydrated electron as a function of density, and compare our data with the results obtained using other methods, namely Path Integral MD (PIMD [32]) and Car-Parrinello MD (CPMD [33]). Interestingly enough, the PIMD and CPMD simulations are in rather good agreement with the present QCMD data and were performed at different temperatures. This seems to confirm the existence of a strong density effect, the maximum of the absorption spectrum decreasing linearly with the density of the system, to as low as 0.1 g.cm^{-3}. It is worth mentioning that PIMD, CPMD and Adiabatic (this work) simulations rely on rather different methods and approximations.

In a recent experimental work, however, Bartels and coworkers [12] clearly observe a "levelling off" of the density effect. At densities lower than 0.5 g.cm^{-3} (supercritical conditions), the maximum of the absorption spectra is near 1 eV, and does not change anymore with decreasing densities. An analysis of their data leads Bartels and coworkers to suggest that the inner solvation shell of the electron remains constant in this density region [12]. This is in contrast with the QCMD results which display a progressive and continuous "desolvation" of the electron as the density decreases. This is shown in the radial distribution functions reported in Figure 4. The structure of the solvation shell is progressively lost when the density decreases and the first peak of the radial distribution functions is shifted to larger distances. According to the unpublished results of the Katsumura group [31], even in the supercritical domain a slight decrease of the maximum of absorption is observed from 1.04 eV to 0.97 eV, corresponding to densities from 0.5 to 0.2 g.cm^{-3}. Such a slight shift has also been observed by Bartels and coworkers [12]. However, our calculations show a marked decrease of $E_{\max}$ from 1.15 to 0.87 eV for the same range of density.

4 Conclusions

We have shown that QCMD simulations are able to capture most of the important features of the optical spectrum of the silver atom and electron species solvated in ordinary liquid water. The strong thermodynamic state point dependence of the absorption spectra of hydrated electron as well as the much weaker dependence for the silver atom are well reproduced, and a qualitative explanation is provided for this experimental evidence. When extending the QCMD calculations to very low densities corresponding to supercritical conditions the simulation results display a progressive "desolvation" of the hydrated electron. This is at variance with recent pulse radiolysis experiments [12] in which the solvation shell is suggested to "level off". The reason for this discrepancy is not clear, since two other distinct theoretical models lead to results similar to those of the QCMD simulations.

5 Acknowledgements

We are most grateful to David Bartels and Yosuke Katsumura for fruitful discussions, and for providing us with recent supercritical water results (ref. [12,31]) prior to publication.

References

[1] E. J. Hart, J. W. Boag, J. Am. Chem. Soc. 84 (1962) 4090.

[2] J. W. Boag, E. J. Hart, Nature 197 (1963) 45.

[3] J. P. Keene, Nature 197 (1963) 47.

[4] E. Hart, M. Anbar, The Hydrated Electron, Wiley, New York, 1970.

[5] F. Y. Jou, L. M. Dorfman, J. Chem. Phys. 58 (1973) 4715.

[6] W. C. Gottschall, E. J. Hart, J. Phys. Chem. 71 (1967) 2102.

[7] R. S. Dixon, V. J. Lopata, Rad. Phys. Chem. 11 (1978) 135.

[8] F. Y. Jou, G. R. Freeman, J. Phys. Chem. 83 (1979) 2383.

[9] H. Christensen, K. Sehested, J. Phys. Chem.-US 90 (1986) 186.

[10] H. Shiraishi, Y. Katsumura, D. Hiroishi, K. Ishigure, M. Washio, J. Phys. Chem. 92 (1988) 3011.

[11] G. Wu, Y. Katsumura, Y. Muroya, X. Li, Y. Terada, Chem. Phys. Lett. 325 (2000) 531.

[12] D. M. Bartels, K. Takahashi, J. A. Cline, T. W. Marin, C. D. Jonah, J. Phys. Chem. A 109 (2005) 1299.

[13] J. H. Baxendale, E. M. Fielden, J. P. Keene, M. Ebert, in Pulse Radiolysis, J. P. Keene, A. Swallow, J. H. Baxendale, Eds. Acad. Press, London, 1965.

[14] R. Tausch-Treml, A. Henglein, J. Lilie, Ber. Bunsenges. Phys. Chem. 82 (1978) 1343.

[15] J. Von Pukies, W. Roebke, A. Henglein, Ber. Bunsenges. Phys. Chem. 72 (1968) 842.

[16] M. Mostafavi, J. L. Marignier, J. Amblard, J. Belloni, Radiat. Phys. Chem. 34 (1989) 605.

[17] E. Janata, A. Henglein, B. G. Ershov, J. Phys. Chem. 98 (1994) 10888.

[18] E. Janata, J. Lilie, M. Martin, Radiat. Phys. Chem. 43 (1994) 353.

[19] E. Janata, Radiat. Phys. Chem. 44 (1994) 449.

[20] S. Kappoor, D. Lawless, P. Kennepohl, D. Meisel, N. Serpone, Langmuir 10 (1994) 3018.

[21] M. Mostafavi, M. Lin, G. Wu, Y. Katsumura, Y. Muroya, J. Phys. Chem. A 106 (2002) 3123.

[22] J. Belloni, M. O. Delcourt, J. L. Marignier, J. Amblard, in Radiation Chemistry, P. Hedwig, L. Nyikos and R. Shiller Eds., Akademiai Kiado, Budapest, 1987.

[23] Farhataziz, P. Cordier, L. M. Perkey, Radiat. Res. 68 (1976) 23.

[24] C. Nicolas, A. Boutin, B. Lévy, D. Borgis, J. Chem. Phys. 118 (2003) 9689.

[25] R. Spezia, C. Nicolas, P. Archirel, A. Boutin, J. Chem. Phys. 120 (2004) 5261.

[26] L. Turi, D. Borgis, J. Chem. Phys. 117 (2002) 6186.

[27] P. Durand, J. C. Barthelat, Theoret. Chim. Acta 38 (1975) 283.

[28] H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, J. Hermans, In: Interaction models for water in relation to protein hydratation, Dordrecht: Reidel, 1981.

[29] R. Spezia, C. Nicolas, A. Boutin, R. Vuilleumier, Phys. Rev. Lett. 91 (2003) 208304.

[30] P. Linsstrom, W. Mallard, NIST Chemistry WebBook, Gaithersburg MD (http://webbook.nist.gov), 2001.

[31] Y. Katsumura, private communication.

[32] D. Laria, M. Skaf, J. Phys. Chem. A 106 (2002) 8066.

[33] M. Boero, M. Parrinello, K. Terakura, T. Ikeshoji, C. Liew, Phys. Rev. Lett. 90 (2003) 226403.

Table 1
Relative intensity of the maximum of the absorption spectrum of the hydrated silver atom at three temperatures (at 298 K, $\epsilon_{360\ \mathrm{nm}}$ =16000 $\mathrm{mol^{-1}cm^{-1}}$). The experimental and simulation data are normalized with respect to the ambient thermodynamic conditions data.

Temperature / K	298	373	473
Density / $\mathrm{g.cm^{-3}}$	1.00	0.95	0.86
Exp [21]	1.0	0.97	0.87
QCMD	1.0	0.97	0.92

Table 2
Maximum of the absorption spectrum of hydrated silver atom (in eV) as a function of temperature and density, from QCMD simulations. The corresponding average electron-silver cation distance (in Å) is given in parenthesis.

Temperature	Density / $\mathrm{g.cm^{-3}}$				
/ K	1.00	0.95	0.86	0.73	0.50
298	3.59 (0.52)	—	—	—	—
373	3.52 (0.61)	3.49 (0.59)	—	—	—
473	3.49 (0.63)	—	3.47 (0.59)	—	—
573	3.47 (0.66)	—	—	3.47 (0.52)	3.57 (0.47)

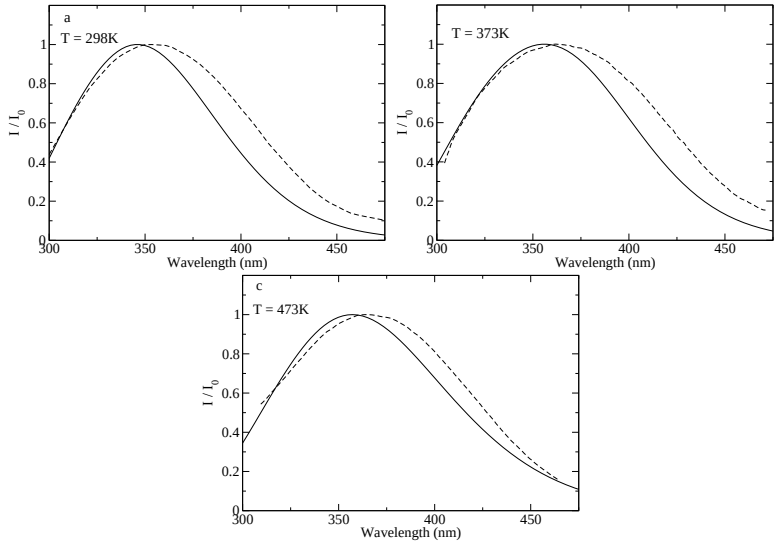


Fig. 1. Experimental (dashed lines [21]) and simulated (full lines) normalized absorption spectrum of hydrated silver atom at 20 MPa and 298 K (a), 373 K (b) and 473 K (c).

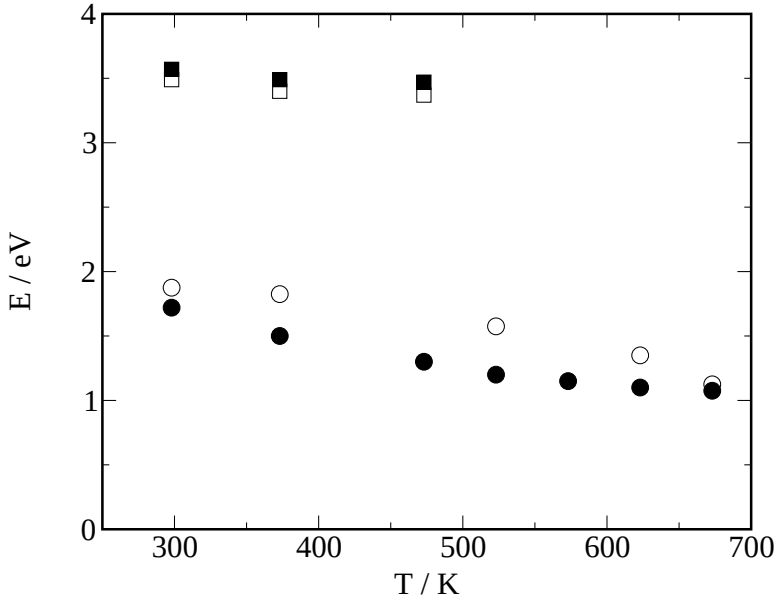


Fig. 2. Temperature dependence (at constant pressure) of the maximum of the absorption spectrum of hydrated silver atom. Full squares: experiments [21], open squares: simulations (this work). Also shown are the data for the hydrated electron. Full circles: experiments [11], open circles: simulations [24].

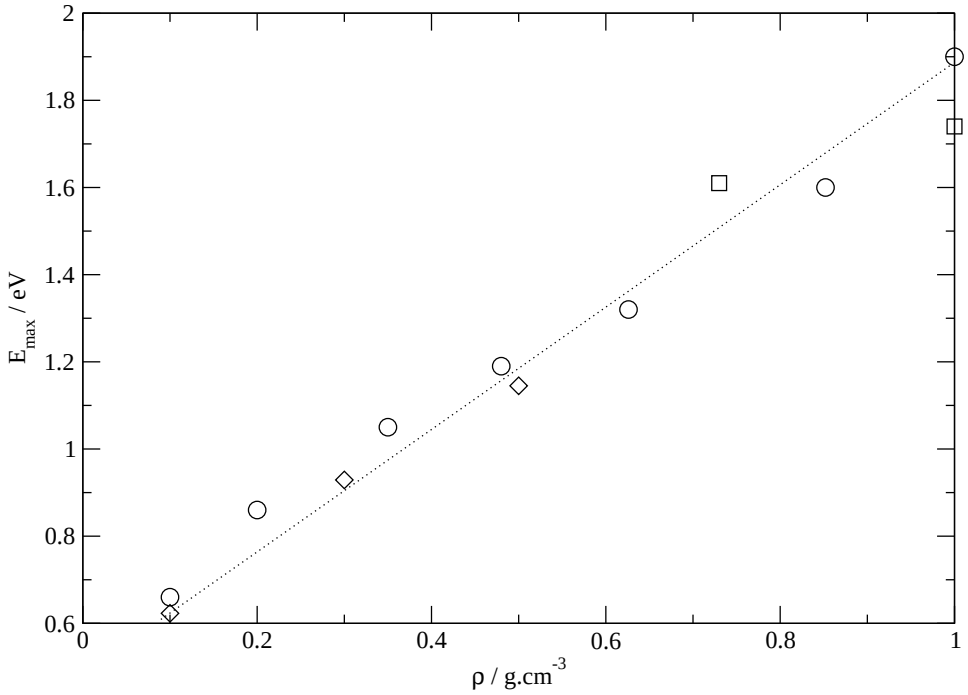


Fig. 3. Evolution of the computed maximum of the absorption spectrum of the hydrated electron as a function of density. Circles: QCMD (this work); diamonds: Path-Integral MD [32]; Squares: Car-Parrinello MD [33].

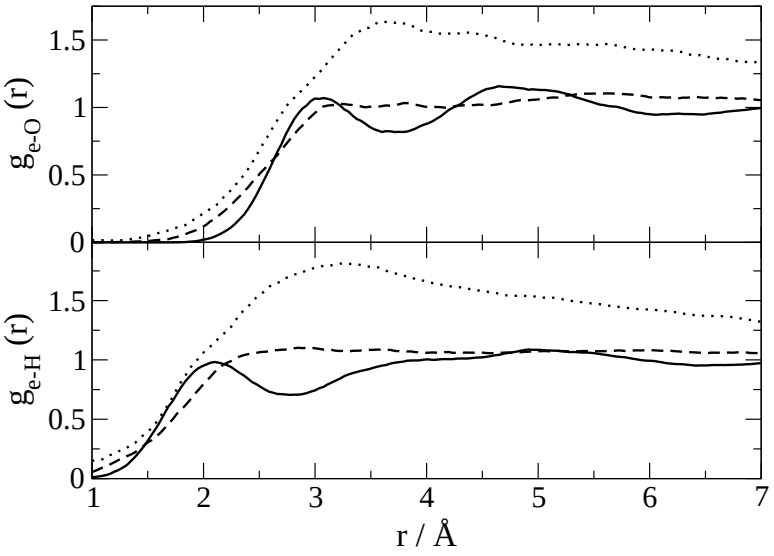


Fig. 4. Radial distribution functions for the electron-oxygen (upper panel), and electron-hydrogen (lower panel) distances at different densities. Solid lines: 1.0 g.cm^{-3}. Dashed lines: 0.48 g.cm^{-3}. Dotted lines: 0.20 g.cm^{-3}.