Nonlinear dependence of continuous extinction of visible and IR optical radiation on absolute humidity of air

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Based on the experimental data obtained along extended paths under field conditions and in a laboratory cell, it is shown that the minimum values of the extinction coefficient in the spectral region of 0.44–11.5 μm nonlinearly depend on the absolute humidity of air. It is proposed that the physical nature of this effect is absorption of radiation by weakly bound molecular complexes of water vapor. The obtained absorption coefficients have a neutral behavior in the visible and near IR spectral regions and increase toward longer waves. In terms of the square dependence on the absolute humidity, their values are about 0.000 090–0.000 145 $km^{-1} g^{-2} m^6$.

Introduction

To study the nature of anomalous (excess) absorption of shortwave radiation in clouds is one of important problems of modern climatology. The excess absorption manifests itself in the fact that the absorption obtained in field measurements of net solar fluxes under and above clouds often exceeds the absorption calculated by radiative models taking into account contributions of all gases. Obviously, revealing the nature of the observed absorption is very important for quantitative estimation of the principal factors affecting the Earth albedo and determining the Earth's radiation budget both in the presence of clouds and in the cloudless atmosphere.

Currently there exist several hypotheses that explain this phenomenon.[1–6] Rozenberg[1,2] supposes that the principal reason of the anomalous absorption of shortwave radiation is the presence of a fine aerosol fraction in the inter-droplet space of a cloud. This fraction mostly consists of soot and does not show itself in scattering. In Ref. 3, the excess absorption of radiation in clouds is thought connected with water vapor continuum absorption in the shortwave spectral region.

In Ref. 4, it is assumed that, along with the absorbing aerosol, the increase of the contribution of molecular scattering due to the increase of the photon mean free path at multiple scattering plays a noticeable role in the anomalous absorption of shortwave radiation in clouds. In Ref. 5, it is stated that the excess absorption observed in clouds is only seeming and caused by horizontal transfer of radiation in a stochastically inhomogeneous cloud. Finally, in Ref. 6, based on the model of a multilayer concentrically inhomogeneous water droplet, it was shown that the anomalous absorption of shortwave radiation in clouds can be explained by non-additive absorption of light by particles of atmospheric haze that form a part of liquid-droplet clouds. However, the nature of the excess absorption is still debatable.

We have undertaken an attempt to relate the excess absorption to the experimentally observed continuous extinction of visible and IR radiation. This extinction depends on the absolute humidity of air. It should be noted that separation of the continuous extinction from the data on spectral transmittance of the atmosphere under field conditions is, generally, a very complicated problem, because continuous extinction is very low and in most cases fully hidden by extinction of radiation by submicron and coarse aerosol particles. To minimize this factor, data on atmospheric transmittance obtained under conditions of high atmospheric transparency should be corrected for aerosol extinction, and the continuous extinction should be estimated using minimum points.

1. Conditions of the experiment

To solve the formulated problem, we have formed a set of data on spectral coefficients of total extinction in the wavelength region $\lambda = 0.44–11.5$ μm. The data were obtained from measurements of the atmospheric transmittance along a 4630 m long path in the region of the Lake Balkhash (Kazakhstan). This region is characterized by very long meteorological range.[7]

The spectral transparency was measured by means of an instrumentation described in Ref. 8 at the following wavelengths: 0.44, 0.48, 0.55, 0.69, 0.87, 1.06, 1.22, 1.60, 2.17, 3.97, 9.2, 10.6, and 11.5 μm. Interference ($\lambda = 0.44–2.2$ μm) and combined ($\lambda > 3$ μm) filters were used for selecting a needed wavelength. The filter pass band was about 0.010 μm in the visible region, 0.015–0.020 μm in the region from 0.8 to 2.2 μm, and 0.15–0.30 μm in the region from 3.97 to 11.5 μm. A random rms error in calculating the total extinction coefficients did not exceed 0.007 km^{-1} in the region from 0.44 to 1.06 μm and 0.010 km^{-1} in

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the region from 1.06 to 11.5 μm. To extend the variability range of the absolute humidity, data obtained in different seasons (spring, summer, fall) were included in the data set.

The data set formed in such a way consisted of 48 spectra of the total extinction coefficient and the corresponding values of the absolute air humidity measured by an optical method in the water vapor absorption band at $\lambda = 0.94$ μm. To increase the accuracy, the absolute humidity was measured intergally on the path. The relative humidity of air during the period of measurements varied from 40 to 93%, the air temperature ranged from −10 to +35°C, the absolute humidity was from 1.23 to 18.7 g/m^3, and the wind speed varied from 1.6 to 8.8 m/s.

2. Results

In Refs. 9 and 10, we have found the dependences of the continuous extinction in the region from 0.44 to 3.97 μm on the absolute humidity of air within the framework of the linear dependence $\alpha_{cont} = k_{abs}\, a$, where α_{cont} is the coefficient of continuous extinction, k_{abs} is the absorption coefficient, a is the absolute humidity of air. The absorption coefficients were obtained in Ref. 9 using minimum points, and in Ref. 10 they were determined by the method of least squares with extrapolation to zero. The obtained values proved to be from 0.012 to 0.018 and from 0.020 to 0.028 g^{-1}cm^2, respectively.

This paper presents the results of study of the continuous extinction. In this case, the extinction was considered in the whole wavelength region from 0.44 to 11.5 μm in the framework of not only linear but also nonlinear dependence on the absolute humidity. The extinction by submicron aerosol particles[11] was excluded from the total extinction together with continuum absorption by water vapor and selective absorption by atmospheric gases. The difference between the total extinction and the excluded components is residual extinction that consists of extinction by coarse aerosol particles and continuous extinction.

The dependences of the coefficients of residual extinction on the absolute humidity at several wavelengths in the visible and IR spectral regions are shown in Fig. 1. Here, dots are for experimental data. It is seen that the coefficients of residual extinction nonlinearly depend on the absolute humidity. This conclusion is confirmed by curves *1* obtained by the method of least squares. Curves *2* are the dependences of the coefficients of continuous extinction on the absolute humidity obtained using minimum points in the framework of the square dependence $\alpha_{cont} = k_{abs}\, a^2$.

To substantiate the use of the square function to describe the relation between the coefficients of continuous extinction and the absolute humidity, this kind of dependence was studied. The dependences of the residual extinction coefficients on the absolute humidity were set in the form $\alpha_{res} = K_0 + K_1\, a^n$, where α_{res} is the residual extinction coefficient; K_0, K_1, and n are fitting parameters that were determined by the method of least squares.

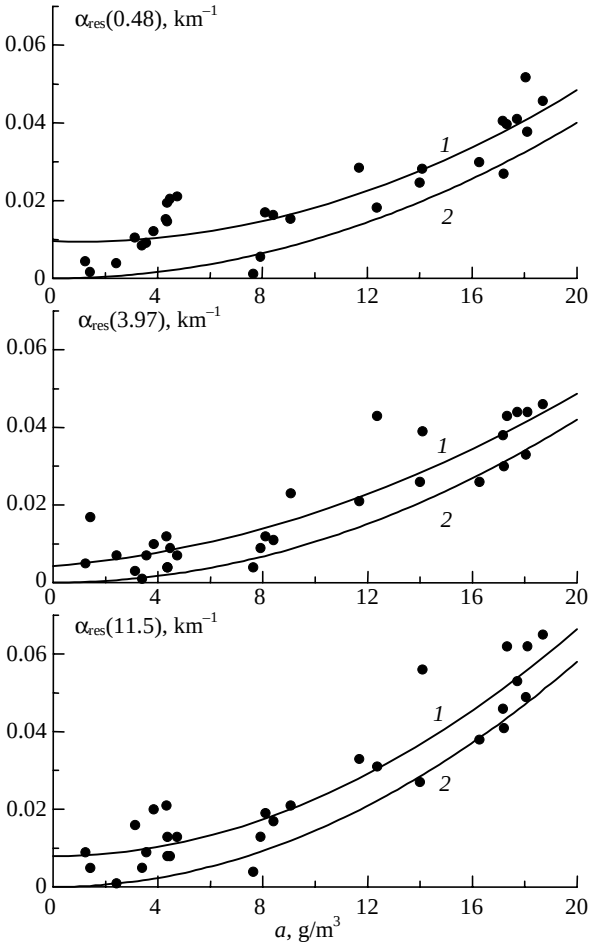

Fig. 1. Dependences of coefficients of residual extinction on absolute humidity of air at wavelengths of 0.48, 3.97, and 11.5 μm.

Figure 2 shows the spectral behavior of the exponent n. The straight line in Fig. 2 was obtained by the method of least squares. It is seen that n increases slightly as the radiation wavelength increases. In the visible wavelength region $n = 1.45$–1.9, and in the far IR region (9–12 μm) $n = 1.96$–2.56. The values of n obtained in the visible region under field conditions are in good agreement with the value $n = 1.63$ obtained in Ref. 12 on the basis of laboratory data[13] for Ar laser at the wavelength $\lambda = 0.44$ μm. Thus, the dependences of the coefficients of continuous extinction on the absolute humidity proved to be close to the square ones.

The spectral behavior of the absorption coefficient is shown in Fig. 3. In contrast to Refs. 9 and 10, where k_{abs} decreases as the wavelength increases in the visible region, it has the neutral behavior in the visible and near IR regions and increases toward longer waves. In the studied wavelength region, it ranges from 0.000 090 to 0.000 145 km^{-1}·g^{-2}·m^6. The error in determining the

coefficients k_{abs} is approximately 0.000 010 $km^{-1}·g^{-2}·m^6$. The curve shown in Fig. 3 was obtained by the method of least squares supposing that the spectral behavior of k_{abs} is described by the exponential dependence of the form $k_{abs}(\text{range}) = A + B\exp(\lambda/C)$, where A = 0.000 024 $km^{-1}·g^{-2}·m^6$, B = 0.000 067 $km^{-1}·g^{-2}·m^6$, and C = 18.6 μm.

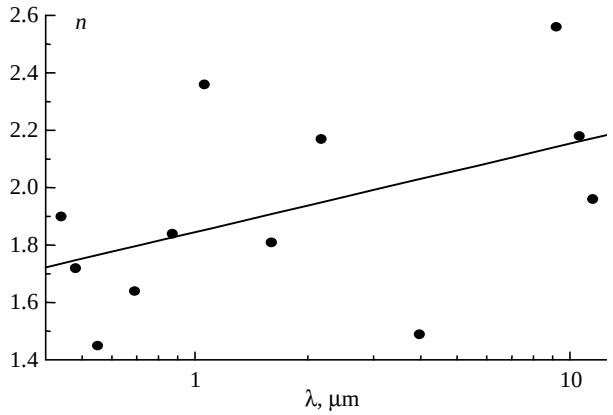

Fig. 2. Spectral behavior of the exponent n.

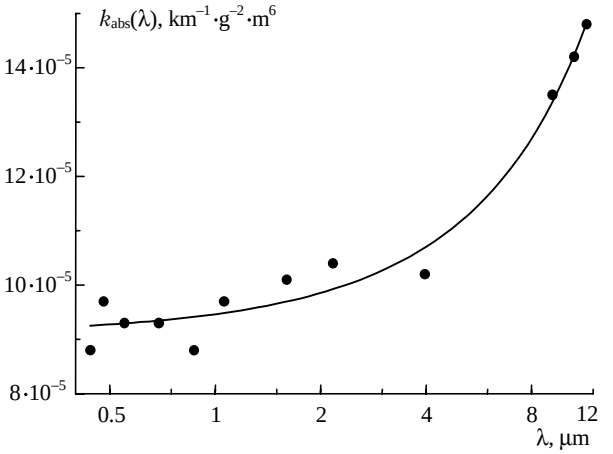

Fig. 3. Spectral dependence of the absorption coefficient in the spectral region from 0.44 to 11.5 μm.

From the analysis of the data shown in Fig. 1 it follows that the absorption coefficients are overestimated in Refs. 9 and 10. This is caused by two reasons. First, the neglect of extinction by the submicron fraction in Refs. 9 and 10 has led to overestimation of the absorption coefficients in the visible region and their spectral dependence. Second, application of the method of least squares with extrapolation to zero to the experimental data set with a wide scatter of points has led to additional overestimation of the absorption coefficients[10] in the whole spectral region. Taking these factors into account, we have obtained new data. Since the dependences of the continuum absorption coefficients on the absolute humidity are nonlinear, new estimates of the absorption coefficients obtained in the framework of the linear dependence on the absolute humidity are somewhat overestimated at $a < 12–15$ g/m^3 and underestimated at $a > 12–15$ g/m^3. The values of the absorption coefficients in the spectral region of 0.44–3.97 μm obtained by different authors are given in the Table.

Table. Coefficients of continuum absorption $k_{abs}(\lambda)$, in $g^{-1}·cm^2$, obtained along horizontal and slant paths

λ, μm	Data			
	Ref. 9	Ref. 10	Ref. 14	new
0.44	0.018	0.028	–	0.012
0.48	0.017	0.028	–	0.012
0.55	0.016	0.025	–	0.012
0.69	0.015	0.024	0.037	0.012
0.87	0.014	0.021	0.018	0.012
1.06	0.012	0.021	0.016	0.012
1.6	0.012	0.020	0.015	0.012
2.12	–	–	0.019	–
2.17	0.014	0.021	–	0.014
2.27	–	–	0.008	–
3.97	0.016	0.021	–	0.016

The data of Ref. 14 were obtained along slant paths and corrected in Ref. 15 for continuum and selective absorption by water vapor.

Comparison of these data shows that the absolute values of the coefficients of continuum absorption obtained in the framework of the linear dependence on the absolute humidity are in a good agreement with the results[14] obtained along slant paths. The closeness of the absorption coefficients on near-ground and slant paths points to the validity of the obtained results.

3. Comparison of the field and laboratory data

To confirm the validity of the nonlinear dependence of continuum absorption on the absolute humidity, the results obtained under field conditions and in a multipath laboratory cell[13] in the visible region were compared. Let us recall that Ref. 13 presents the results of measuring the extinction of radiation of Ar (λ = 0.44 μm), He–Ne (λ = 0.63 μm), and CO_2 (λ = 10.59 μm) lasers by water vapor on a 2.98 km long path at different temperature and humidity. It proved that the minimum values of the extinction coefficients in the visible region increase with the increase of the absolute humidity both in the laboratory cell and under field conditions. Such a dependence obtained for the Ar laser (open and close circles correspond to the experimental data) is shown in Fig. 4.

It is seen from Fig. 4 that the dependence of the extinction coefficient on the absolute humidity is nonlinear. Curve *1* obtained by the method of least squares confirms this conclusion. Curve *2* is drawn by minimum points. It describes the dependence of continuum absorption on the absolute humidity in the framework of the square dependence. The absorption coefficient here is 0.000 080 $km^{-1}·g^{-2}·m^6$, whereas, according to our data, it is equal to 0.000 092 $km^{-1}·g^{-2}·m^6$ in this spectral region. This difference is within the random

error of experimental data, though, it is possibly an evidence of a negative temperature dependence (0.7% deg^{-1}) of this kind of absorption, because the laboratory data were obtained at T = 323 K and the field data were obtained at 303 K.

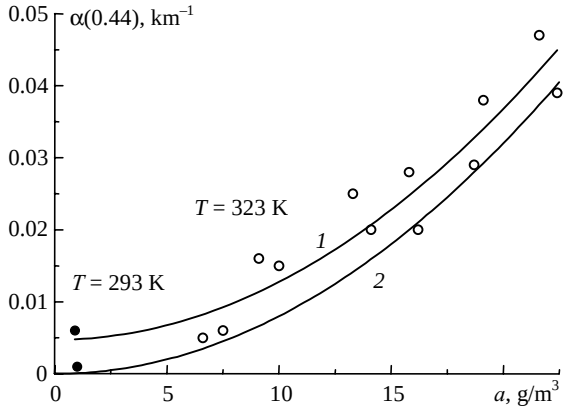

Fig. 4. Dependence of the coefficient of extinction of Ar laser radiation on the absolute air humidity at T = 293 K (close circles) and T = 323 K as judged from on the data of Ref. 16.

One more confirmation of the obtained dependences is the result of comparison of the continuous extinction and continuum absorption[16] obtained under field conditions in the region of 10.6 μm with the data of laboratory measurement of the continuum absorption.[17] Figure 5 shows the data of different authors on the water vapor continuum absorption at T = 296 K and continuous extinction at 10.6 μm.

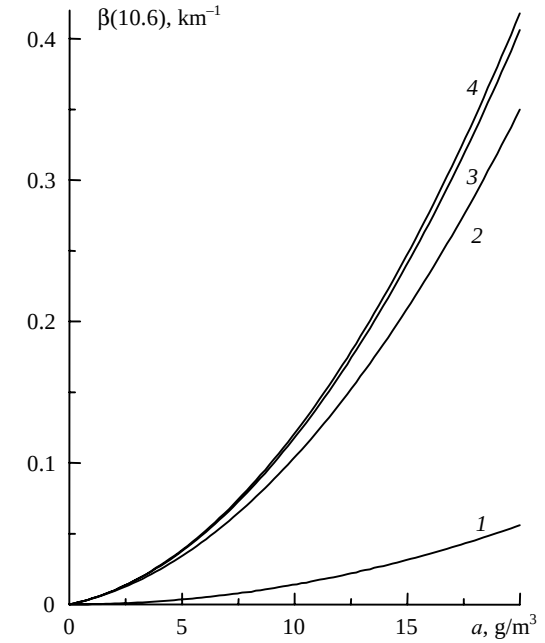

Fig. 5. Comparison of the data of different authors on water vapor continuum absorption at T = 296 K and continuous extinction at 10.6 μm: continuous extinction (*1*), continuum absorption obtained in Ref. 16 (*2*), sum of curves *1* and *2* (*3*), and continuum absorption obtained in Ref. 17 (*4*).

When comparing the results on continuum absorption, it turned out that the sum of the coefficients of continuous extinction and continuum absorption[16] obtained under field conditions is close to the value of continuum absorption obtained in the laboratory.[17] The difference in the coefficients of continuum absorption obtained under field and laboratory conditions is explained by different techniques used for their determination. Thus, in Ref. 16 the continuous extinction was excluded using the values of the extinction coefficient in the region of 1–4 μm, but in Ref. 17 it remained. So the continuum absorption coefficients in Ref. 16 proved to be less by the value of the continuous extinction in the region of 1–4 μm.

4. Mechanisms of continuous extinction

The increase of the minimum values of the extinction coefficients with the increase of the absolute humidity in both the field and laboratory experiments may be caused by the following factors: (i) extinction by submicron and coarse aerosol and (ii) absorption by water vapor and weakly bound molecular complexes of water vapor. Let us consider these factors in detail.

4.1. Extinction by submicron aerosol

The independence of the continuous extinction on the wavelength in the visible spectral region casts some doubts on explanation of the studied effect by absorption due to submicron aerosol,[9,10] because in this case its value should be inversely proportional to the radiation wavelength. To estimate the influence of this factor, we have drawn the dependences of the coefficients of aerosol extinction, extinction by the submicron fraction of atmospheric aerosol α_{sm}, and residual extinction α_{res} on the absolute humidity in the visible and near IR spectral regions. The aerosol extinction coefficients have been divided into components in Ref. 11. Such dependences at the wavelength of 0.48 μm are shown in Fig. 6. It is seen that α and α_{res} increase and α_{sm} decreases as the absolute humidity increases. This indicates that the dependence under discussion cannot be explained by extinction due to submicron aerosol.

4.2. Extinction due to coarse aerosol

The increase of α_{res} with the increase of the absolute humidity (see Fig. 6) indicates that the dependence under study may be caused by synchronous carry-over of water vapor and coarse aerosol from the surface into upper atmospheric layers. To exclude this relation, studies should be conducted in a laboratory, where this effect is absent. For this purpose, we used the experimental data obtained in a multipath laboratory cell.[13] It turned out that the minimum

values of the extinction coefficients increase in the visible spectral region with the increase of the absolute humidity under both laboratory and field conditions (see Fig. 4). Calculations of the sedimentation rate of water droplets in Ref. 13 show that all large droplets with the radius larger than 0.2 μm under steady-state conditions deposit on the cell walls. In the laboratory cell, there is no synchronous carry-over of water vapor and coarse aerosol from the surface that leads to the dependence of the extinction coefficient on the absolute humidity. Thus, the dependence under discussion cannot be explained by extinction due to coarse aerosol.

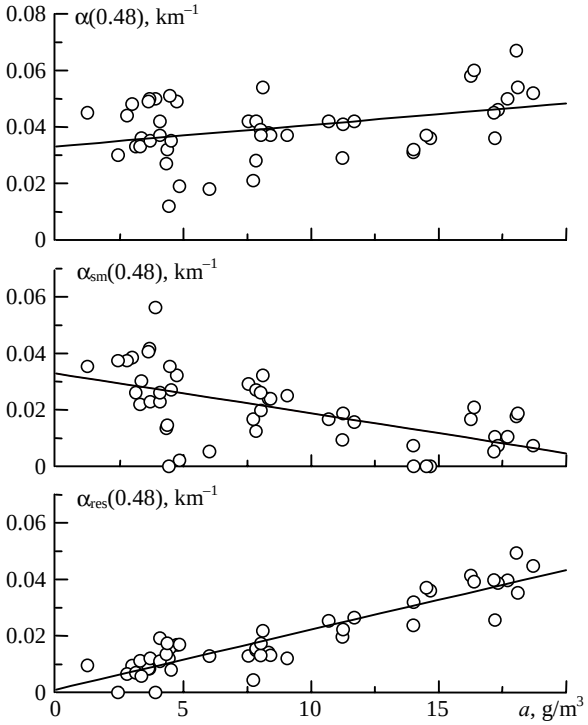

Fig. 6. Dependences of the coefficients of aerosol extinction α, residual extinction α_{res}, and extinction due to submicron aerosol α_{sm} at 0.48 μm on the absolute humidity of air.

4.3. Absorption by water vapor

To clear up the physical nature of continuous extinction, in Ref. 15 the contribution of the continuum absorption by water vapor in the shortwave spectral region was calculated. The obtained values of the continuum absorption coefficient proved to be one to two orders of magnitude less than those measured in Ref. 10. The calculations performed in Ref. 18 showed that the absorption by weak spectral lines of water vapor also cannot explain the value of continuous extinction.

4.4. Absorption by weakly bound molecular complexes of water vapor

Weakly bound molecular complexes of water vapor may have neutral absorbing properties in the visible spectral region. According to Ref. 19, they "can be termed minor gaseous constituents of the second kind, since they are derivatives of the standard gaseous components of the atmosphere and they exist only in the gas-phase environment of the parent molecules."

The dependences of the continuous extinction in the visible region on the absolute humidity with the exponents $1 < n < 2$ indicate that the physical nature of this effect can be absorption by two types of weakly bound molecular complexes. Each of these types of complexes contributes markedly to the total absorption. The first type is absorption by weakly bound molecular complexes consisting of water vapor molecules and other molecules of air. This absorption linearly depends on the absolute humidity, because its value is proportional to the concentration of water vapor molecules. The second type is absorption by weakly bound molecular complexes consisting of water vapor clusters (dimers, trimers, etc.) and molecules of air. The dependence of this type of absorption on the absolute humidity is described by a square function, because dimers dominate among water vapor clusters and their concentration is proportional to the squared absolute humidity of air.[20]

Conclusion

Based on the analysis of the minimum values of the optical radiation extinction coefficients obtained on long paths under field conditions and in a laboratory cell, it is shown that continuum absorption in the spectral region from 0.44 to 11.5 μm nonlinearly depends on the absolute humidity of air. Unlikely Refs. 9 and 10, in which the extinction coefficient decreases as the wavelength increases in the visible spectral region, here it has the neutral behavior in the visible and near IR spectral regions and increases toward longer waves. The value of this coefficient is $0.000\,090–0.000\,145\ km^{-1}\cdot g^{-2}\cdot m^6$ in the framework of the square dependence on the absolute humidity.

The dependences of the minimum values of the extinction coefficients in the visible region on the absolute humidity are nonlinear under both laboratory and field conditions and close to each other. When comparing the results on continuous extinction and continuum absorption[16] in the region of 10.6 μm, it turned out that the sum of the coefficients of continuous extinction and continuum absorption obtained under field conditions is close to the value of the continuum absorption obtained in the laboratory cell.[17] This points to the validity of the results on continuous extinction of optical radiation in the visible and IR regions depending on the absolute humidity of air.

The new data on the absorption coefficient in the region from 0.44 to 3.97 μm were obtained in the framework of the linear dependence on the absolute humidity.

It is supposed that the revealed effect is caused by absorption by weakly bound molecular complexes of water vapor.

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