4298 J. Phys. Chem. A **1997,** *101,* 4298−4301

Infrared Spectra and Nature of the Principal CO Trapping Sites in Amorphous and Crystalline H_2O Ice

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Received: August 13, 1996; In Final Form: March 11, 1997⊗

A detailed experimental study of the infrared characteristics of CO in H_2O ice matrixes (10−150 K) has been performed. The effects of thermal and ion irradiation processes have also been examined. H_2O:CO ice mixtures have been obtained both by co-deposition of H_2O and CO (at 10 K) and by diffusion (at ∼27 K) of CO into a preformed water ice film. It has been confirmed that CO does not diffuse into the ice at temperatures below ∼26 K. Results have been compared with previously reported diffusion experiments at 42 K. Laboratory experiments show that the profile (shape, width, and peak position) of the CO band depends on the structure of the water matrix it is embedded in and on the process (co-deposit or diffusion) by which the mixture has been obtained. This is attributed to the different amount of energy involved in the process which forms the mixture. These studies are important to understand the physical and chemical properties of ices. Furthermore information on the history of molecular ices in astrophysical environments are obtained comparing observed spectra with those taken in laboratory.

Introduction

The infrared (IR) spectrum of pure water (H_2O) ice at 10 K shows absorption bands at about 3300 cm^{-1} (3.03 μm; O−H stretching modes), 2205 cm^{-1} (4.53 μm; combination mode), 1650 cm^{-1} (6.06 μm; overtone of the libration mode and bending mode), 803 cm^{-1} (12.4 μm; libration), and a symmetrical broad band in the far-infrared at 220 cm^{-1} (45.5 μm). Laboratory experiments have shown that different forms of water ice exist, as a consequence of deposition rate of the vapor, substrate temperature, thermal, and irradiation history.[1−5] Crystalline hexagonal ice is formed at temperatures higher than 150 K and crystalline cubic ice (hereinafter $(H_2O)_{cr}$) is formed between 110 and 150 K. When vapor is deposited at temperatures lower than 100 K, the resulting ice is amorphous (hereinafter $(H_2O)_{as}$) and different amorphous forms of water ice have been reported.[1,5,6] Amorphous ice is converted to crystalline ice as the temperature increases while crystalline ice is stable when temperature decreases. Crystalline ice is converted to amorphous ice by ion irradiation.[3,4] General consequences of ion irradiation are changes in the structure of the sample, formation of other species not present in the original sample, and formation and release of radicals and volatile species.[3,4,7]

The structure of amorphous water ice is characterized by micropores where OH dangling-bond groups give rise to a narrow absorption band at about 3690 cm^{-1}.[8,9] It has also been shown that such dangling OH groups are present on the surface of large crystalline ice clusters.[10]

The profile (shape, width, and peak position) of the IR bands strongly depends on the structure of the ice and hence IR spectroscopy can be used to study structural changes due to thermal and irradiation history.

Infrared spectra of pure carbon monoxide (CO) ice at 10 K show an absorption feature at about 2140 cm^{-1} due to the fundamental vibrational mode C≡O. The spectral properties of CO strongly depend on the host molecule when it is mixed in with other species. The CO band profile in a H_2O ice matrix is very peculiar, showing a main feature at about 2138 cm^{-1} and a secondary feature at 2152 cm^{-1}.[11] This latter generally has intensity lower than that of the former.[7,11] However the relative intensity of the two bands changes in H_2O:X:CO mixtures depending on the dipole moment of species X and on the H_2O/X ratio.[7,12]

According to Sandford et al.[11] the 2138 cm^{-1} band is due to substitutional CO molecules (i.e., CO replacing H_2O molecules), while the 2152 cm^{-1} band is due to interstitial CO molecules (i.e., CO between H_2O molecules). Alternatively[8,12,13] both bands are attributed to CO molecules in the micropores. In this view the 2152 cm^{-1} band is due to CO molecules interacting with the OH dangling groups, while the 2138 cm^{-1} band has been tentatively identified with CO molecules interacting with the oxygen atoms of the pore−surface water molecules.[12]

Laboratory experiments[7,11] have shown that when CO deposits on a H_2O ice layer its spectral properties are those of pure CO. On the other hand when H_2O deposits on a CO layer, this latter diffuses in water and spectral properties of a H_2O:CO ice mixture appear.[7] This different behavior has been attributed to the different bond energy of CO and H_2O molecules. Hence the energy released by water during the gas−ice transition can promote the diffusion of CO in the upper ice while the same does not happen when CO condenses on water. This experiment has been used to estimate the integrated absorbance strength, A (cm/molecule), of the CO band in water. In fact, from the spectrum due to a sample of pure CO it is possible to estimate the number of CO molecules deposited. Then assuming that no more than the CO molecules deposited can diffuse in water when this latter is deposited on the CO layer, from the profile of the CO band resulting after diffusion a lower limit for A can be estimated.[7]

The A value of pure CO has been estimated of 1.1×10^{-17} cm/molecule; for CO in H_2O it has been found that $A \geq 1.5 \times 10^{-17}$ cm/molecule. This latter value compares well with the value of 1.7×10^{-17} cm/molecule reported by Sandford et al.[11] In this paper $A(\text{pure CO}) = 1.1 \times 10^{-17}$ cm/molecule, $A(\text{CO in } H_2O) = 1.7 \times 10^{-17}$ cm/molecule and $A(\text{pure } H_2O) = 2 \times 10^{-16}$ cm/molecule will be used. This latter value refers to the 3300 cm^{-1} water ice band.

Furthermore it has been shown that when water condenses on a layer of CO irradiated with energetic ions no diffusion

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⊗ Abstract published in *Advance ACS Abstracts,* April 15, 1997.

S1089-5639(96)02462-0 CCC: $14.00

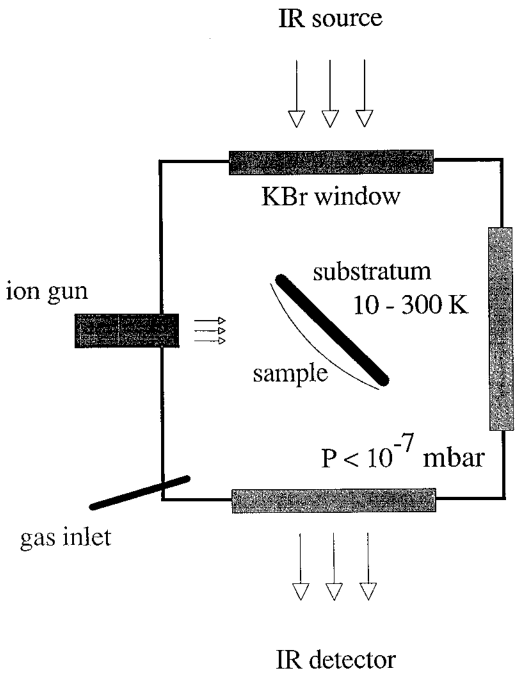

Figure 1. Schematic view of the vacuum chamber.

occurs as testified by the fact that spectral properties of irradiated CO are not influenced by water ice deposition.[7] In fact, because of irradiation, CO ice becomes more stable as a consequence of the formation of a "new" complex material made of CO, CO_2, O_2, and suboxides.[14–16]

In this paper a new detailed study of the profile of the CO band embedded in amorphous, crystalline, and ion-irradiated H_2O ice matrix is presented.

Experimental Apparatus

A detailed description of the experimental apparatus used to obtain "in situ" IR spectra of irradiated and unirradiated frozen gases can be found elsewhere.[17,18]

Frosts are accreted onto a cooled silicon crystal substrate (10–300 K). During condensation, samples can be bombarded by fast ions, here 3 keV He^+ ions (Figure 1). The beam produces a 2×2 cm^2 spot on the target (greater than the spot of the IR beam) and currents, in the range of hundreds of nA cm^{-2} to a few μA cm^{-2} in order to avoid a macroscopic heating of the target. The substrate plane forms an angle of 45° with the IR beam and the ion beam. Thus before, during, and after irradiation, spectra can be taken without tilting the sample.

The penetration depth of 3 keV He^+ ions in frozen gases (mixtures), here studied, is only about 0.05 μm, and such thin samples would show very weak IR features, thus targets have been irradiated during deposition in order to obtain samples thick enough to exhibit a good spectrum. The energy released to the sample by impinging ions (dose) will be given in eV per small molecule (16 amu) because this is a convenient way to characterize chemical changes and compare the results obtained by irradiating different samples.

H_2O:CO mixtures have been obtained both co-depositing the two species and by diffusion of CO into a preformed amorphous, crystalline or ion-irradiated water ice film as schematically shown in Figure 2. Figure 2a,b depict co-deposit and irradiation of the mixture during co-deposit, respectively. Figure 2c–e describe diffusion in amorphous, irradiated and crystalline water ice samples, respectively. Diffusion has been obtained by depositing CO on the water ice layer and warming the sample up to about 30 K. Crystalline films have been obtained depositing water vapor at 150 K and cooling the sample to 10 K (Figure 2e). The effects of ion irradiation have been studied both irradiating the mixture during co-deposition (Figure 2b) and by diffusion of CO into a preformed irradiated water ice film (Figure 2d). When ions impinge on an ice sample, they release their energy. Laboratory experiments[3,19] have shown that this energy strongly modifies the structure of the water matrix. In Figure 2b,d, ion irradiation is described by crosses and the sample modified by ion irradiation is described by open circles and crosses.

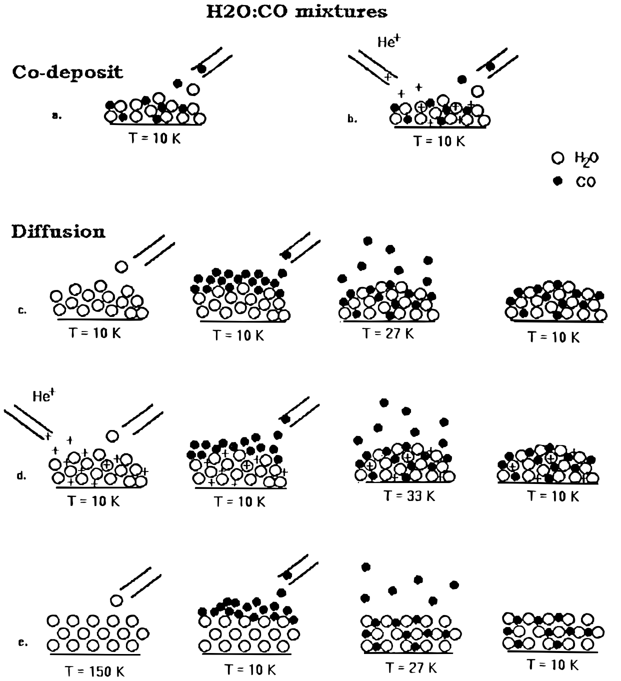

Figure 2. Schematic depiction (not to scale) of H_2O:CO mixtures obtained after co-deposit and diffusion. Open circles refer to H_2O molecules, solid circles to CO molecules; crosses (+) among molecules indicate that the matrix has been modified by ion irradiation. Co-deposit: both species are deposited simultaneously (a) at 10 K and effects of ion irradiation are studied by bombarding the sample during deposition (b). Diffusion: CO molecules can diffuse in amorphous (c), ion irradiated (d) and crystalline (e) water ice. (c) Amorphous water is obtained at 10 K, CO is deposited on this ice layer, the sample is warmed to 27 K and CO molecules partially sublimate and partially diffuse underneath, the sample is cooled to 10 K and the spectrum is taken. (d) Water is irradiated during deposition at 10 K, CO is deposited on the irradiated layer, the sample is warmed to ~30 K and CO molecules partially sublimate and partially diffuse underneath, spectra are taken after the sample is cooled to 10 K. (e) Crystalline water ice is obtained at 150 K, the sample is cooled to 10 K and CO is deposited on it, the sample is warmed to 27 K and CO molecules partially sublimate and partially diffuse underneath, spectra are taken after the sample is cooled to 10 K.

Spectra presented in the following section have been taken at resolution of 2 cm^{-1} with sample temperature of 10 K.

Results and Discussions

As discussed above, when CO deposits on a H_2O ice layer its spectral properties are those of a pure CO layer. However, if this double-layered sample (Figure 2) is warmed to a temperature greater than 26 K, CO molecules partially sublimate and partially diffuse in the water ice underneath. Diffusion both in amorphous and in crystalline films is clearly evidenced by the changes in the CO band profile. Furthermore after heating the sample the CO feature is still present up to about 120 K in both cases. If it were a pure CO film on the top of the water ice film, all CO molecules would have sublimated at much lower temperatures.

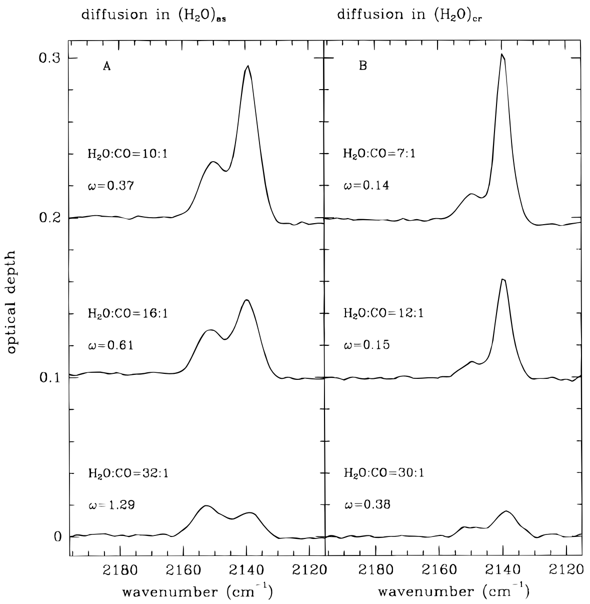

Figure 3. IR spectra (at 10 K) of the 2140 cm^{-1} (4.67 μm) band of CO after diffusion (at ~27 K) in amorphous (A) and crystalline (B) water ice for different H_2O/CO ratios. From bottom to top, spectra refer to same water ice sample (~0.2 μm thick); different H_2O/CO ratios have been obtained repeating the diffusion process. The ω value (τ(2152)/τ(2139)) has been reported for each spectrum. Spectra, in real units, have been shifted upward by 0.1 in the optical depth scale, for clarity.

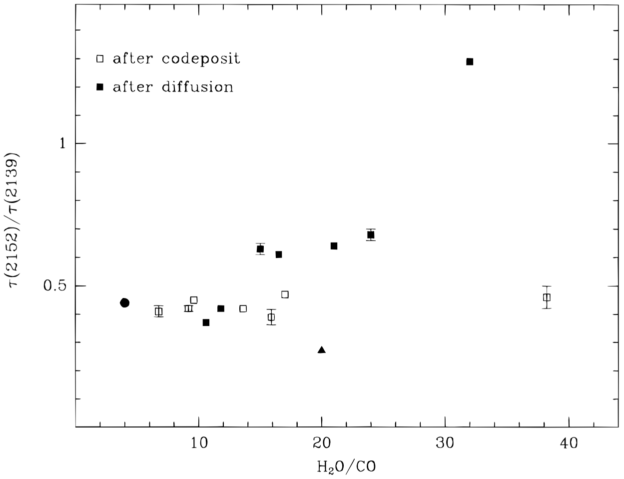

Figure 4. Comparison of the optical depth ratio, $\omega = \tau(2152)/\tau(2139)$, versus H_2O/CO ratio, in H_2O:CO mixtures obtained after co-deposit (at 10 K) and diffusion (at 27 K; square points). The triangle from Sandford et al.;[11] the circle from Schmitt et al.[13]

Figure 3 shows the profile, on an optical depth (τ) scale, of the CO band after diffusion in amorphous and crystalline water ice for different H_2O/CO ratios estimated after diffusion. Spectra have been taken at 10 K cooling the sample after diffusion at 27 K. The band due to CO in mixtures with H_2O is obtained after subtraction of the contribution of the water band at about 2200 cm^{-1}.

Figure 3A shows diffusion in amorphous water. From bottom to top the spectra refer to the same water ice sample, about 0.2 μm thick. Different H_2O/CO ratios have been obtained by repeating the diffusion process three times as follows: in the first step a layer of CO was deposited on the water ice film, the sample was warmed to about 27 K in order to obtain diffusion and then cooled to 10 K, and the spectrum was taken (shown in the bottom panel of Figure 3A); in the second step a layer of CO was deposited on the previous sample, which was warmed to 27 K in order to obtain diffusion and then cooled to 10 K, and the spectrum was taken (shown in the middle panel of Figure 3A); in the third step, again, a layer of CO was deposited on the previous sample, which was warmed to 27 K in order to obtain diffusion and then cooled to 10 K, and the spectrum was taken (shown in the top panel of Figure 3A). As is the case for a co-deposited mixture, the CO profile is characterized by two peaks at 2139 and 2152 cm^{-1}. However the relative intensity of these two features depends on the H_2O/CO ratio. If we define ω as the peak optical depth ratio (τ(2152)/τ(2139)), Figure 3A shows that it decreases as the H_2O/CO ratio decreases. It is evident that, as the H_2O/CO ratio decreases, the optical depth of the 2152 cm^{-1} band only slightly increases while the 2139 cm^{-1} band increases. This indicates that CO molecules first occupy most of the sites which give rise to the 2152 cm^{-1} band and then the other sites which give rise to the 2139 cm^{-1} band.

Figure 3B shows diffusion in crystalline water. The crystalline ice film has been obtained depositing water vapor at 150 K and cooling the sample to 10 K (Figure 2e). From bottom to top the spectra refer to the same water ice sample, about 0.2 μm thick. Different H_2O/CO ratios have been obtained repeating the diffusion process three times as described above. Figure 3B shows that the CO band profile has the intensity of the 2152 cm^{-1} band much lower than that obtained for CO in amorphous water at the same H_2O/CO ratio. Water ice at 150 K is characterized by large crystalline clusters and only few substitutional sites, while many interstitial sites would be available to CO molecules. Then, according to Sandford et al.[11] we would expect an intense band at 2152 cm^{-1} (due to interstitial CO) and a weak band at 2138 cm^{-1} (due to substitutional CO). This is not the case and the result obtained favors the hypothesis that the weak 2152 cm^{-1} band is due to CO molecules bonded to OH dangling groups present, in minor quantity, on the surface of crystalline ice clusters.[9] Thus Figure 3 shows that CO molecules first bond with OH dangling groups available and then occupy the other sites.

Figure 4 shows ω (τ(2152)/τ(2139)) as a function of the H_2O/CO ratio for mixtures obtained after co-deposit at 10 K and diffusion in amorphous ice. Several H_2O:CO (4:1 to 100:1) co-deposited mixtures have been studied which give $\omega \sim 0.4$ independently of the mixture.[7,13] Also, the same ω value, independent of the mixture, is obtained when diffusion of CO in H_2O matrix occurs at 42 K.[12] This latter experiment has been here repeated and the result is confirmed. On the other hand ω depends on the H_2O/CO ratio when the mixture is obtained after diffusion at 27 K. The apparent discrepancy between the ω values obtained after co-deposit and diffusion is here attributed to the different amount of energy involved in the different processes which form the mixture (i.e., co-deposit at 10 K, diffusion at 42 K, and diffusion at 27 K). In fact, when a mixture is obtained by co-deposition or by diffusion at 42 K the energy released during the water vapor−ice transition or by the warmup, at so high a temperature, causes a rearrangement of CO molecules which gives $\omega \sim 0.4$. When this energy is not available (i.e., diffusion at 27 K, lowest temperature at which diffusion occurs) CO molecules bond first with dangling OH groups giving rise to $\omega > 1$ for high H_2O/CO ratios.

Figure 5 shows a comparison of the profile of the CO band in a water matrix obtained after co-deposit and diffusion for H_2O:CO = 10:1 mixtures. The CO band in a co-deposited mixture has peak position ($\tilde{\nu}$) at 2138 cm^{-1} and full width half-maximum (fwhm) equal to 11 cm^{-1}. It is similar to the CO band profile obtained diffusing CO in H_2O at 27 K ($\tilde{\nu}$) = 2139 cm^{-1}, fwhm = 7.5 cm^{-1}). However in the latter case the profile is sharper. Perhaps this occurs because CO molecules occupy more uniquely defined positions when they have diffused to

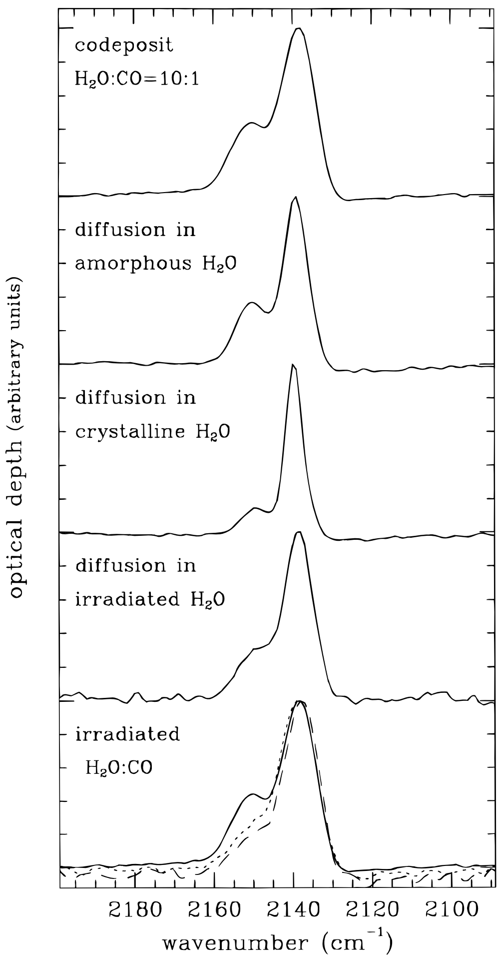

Figure 5. IR spectra of the 2140 cm^{-1} (4.67 μm) band of CO ice in a water matrix at 10 K for H_2O:CO = 10:1. Mixtures have been obtained by a co-deposit (at 10 K) of the two species and by diffusion (at ~27 K) of CO into a preformed H_2O ice film. The next to lowest panel shows the profile of the CO band after diffusion (at ~27 K) into a H_2O film deposited and irradiated with 70 eV/16 amu at 10 K. The lowest panel shows a comparison of a H_2O:CO = 10:1 mixture with two similar mixtures irradiated with 8 eV/16 amu (dotted line) and 18 eV/16 amu (dashed line).

reach them rather than being randomly assigned during co-deposition.[19] The profile changes when CO diffuses in crystalline water ice ($\tilde{\nu} = 2139$ cm^{-1}, fwhm = 5 cm^{-1}).

The bottom panel in Figure 5 shows a comparison of a H_2O:CO mixture with two mixtures irradiated during deposition with 8 eV/16 amu ($\tilde{\nu} = 2138$ cm^{-1}, fwhm = 11 cm^{-1}) and 18 eV/16 amu ($\tilde{\nu} = 2138$ cm^{-1}, fwhm = 10.5 cm^{-1}), respectively. It is evident that after ion irradiation the intensity of the 2152 cm^{-1} band decreases giving rise to a shoulder on the higher wavenumber side of the main band. If CO is diffused into a film of irradiated H_2O at 10 K (in the next to bottom panel, dose = 70 eV/16 amu) the band profile ($\tilde{\nu} = 2138$ cm^{-1}, fwhm = 8.5 cm^{-1}) is very similar to that obtained after ion irradiation of a H_2O:CO mixture. This indicates that the different profile in irradiated and unirradiated mixtures is due to a different structure of the water sample which, in fact, is indicated by a different profile of the 3 μm H_2O band.[19]

Conclusions

Infrared spectra of solid CO (10 K) in amorphous, ion-irradiated and crystalline H_2O ice have been studied. H_2O:CO mixtures have been obtained both after co-deposit and diffusion. Laboratory experiments have shown that the profile of the CO band strongly depends on the structure of ice matrix it is embedded in. These results are consistent with the hypothesis that both the 2152 and the 2138 cm^{-1} bands are due to CO molecules in micropores[12] with the 2152 cm^{-1} due to CO molecules interacting with the OH dangling groups of the pore surface. Furthermore it has been shown that the profile of the CO band in water ice matrix depends on the amount of energy involved in the process by which the H_2O:CO mixture has been obtained.

Icy grain mantles have been detected in dense molecular clouds in the interstellar medium along the line of sight of several IR sources.[20-22] Solid H_2O:CO mixtures have been identified. This identification is based on comparison of observed and laboratory spectra. The results here presented could give important information on the physicochemical and evolutionary properties of interstellar icy mantles.

Acknowledgment. I wish to thank Maddalena Palumbo and Giovanni Strazzulla for helpful discussions about this work. This research has been supported by the Italian Space Agency (ASI) and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST).

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