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# IR-Spectroscopy of Radiation-Stimulated Processes of Adsorption, Radiolysis, and Hydrogenation on the Surface of Metals in Contact with Hydrocarbons

*Nushaba Gadzhieva*

## Abstract

This chapter presents the results of IR spectroscopic studies of radiation-stimulated heterogeneous processes of adsorption, radiation-chemical decomposition (radiolysis) of hydrocarbons on the metal surface, and radiative hydrogenation of these surfaces under the action of gamma radiation. It deals with the spectrokinetic regularities, their features, and the mechanisms of radiation-stimulated adsorption and radiolysis of hydrocarbons in heterogeneous metal-hydrocarbon systems, in particular in heterogeneous Al (Be)-n-hexane systems, using reflection-absorption IR spectroscopy (IRRAS). The role of intermediate surface-active decomposition products in the process of heterogeneous radiolysis of hydrocarbons is discussed, as well as the influence of the surface relief of the metal in the dynamics of the change in the decomposition process on the rate of formation and the yield of final products of radiolysis.

**Keywords:** reflection-absorption IR spectroscopy, metal (Al, Be), hydrocarbons (n-hexane), gamma radiation, radiation-stimulated adsorption, radiolysis, hydrogenation

## 1. Introduction

At present, the development of radiation materials science; radiation catalysis; nuclear, space, and laser technology and nanotechnology; and technologies using radiation and high-energy particles has lead to the formation of a new promising direction—radiation-heterogeneous processes (RHP) in contact with various phases. Obtaining a package of experimental data and information on the study of RHP using complex physical-chemical methods, including spectroscopic methods, also opens up new opportunities for solving a number of problems on the surface of metals and oxides. The activated metal surface accelerates the radiation-chemical decomposition of paraffins and increases the efficiency of hydrogen production in the radiolysis of hydrocarbons. At the same time, surface adsorption of paraffins significantly influences the course of the radiation-heterogeneous decomposition

process and, therefore, the yield of radiolysis products. In the literature, there are a number of experimental and theoretical studies devoted to the study of the interaction and activation of paraffins on the surface of metals [1–4].

However, until now, the problems associated with the adsorption of hydrocarbons on the radiation-modified surface of metals have not been studied sufficiently [5–8]. In fact, there are no data on the radiation-chemical decomposition of hydrocarbons on the surface of metals and the radiation hydrogenation of these surfaces under the influence of gamma radiation. This chapter presents the results of work on IR spectroscopic studies of radiation-stimulated heterogeneous processes of adsorption, radiolysis, and hydrogenation on the surface of metals in contact with hydrocarbons [5–17].

## **2. Objects and methods of research**

### **2.1 Objects**

Metal plates of aluminum (Al) and beryllium (Be) reactor materials having a smooth polished surface with a high reflection coefficient ( $R = 0.88 + 0.05$ ) in the middle IR region ( $\lambda = 2.2\text{--}25\ \mu\text{m}$ ) were used and investigated [9, 10]. As the hydrocarbon adsorbate, the authors selected unsaturated pairs of n-hexane ( $n\text{-C}_6\text{H}_{14}$ ), the purification and adsorption of which are described in detail in [10, 11]. The formation of gaseous decomposition products—molecular hydrogen and hydrocarbons—was monitored chromatographically and spectroscopically. IR absorption spectra of gaseous hydrocarbons were obtained in a gas cuvette with an optical path length of  $\sim 1\ \text{m}$ . Radiation-chemical yields of these products have been determined [12]. The heterosystem Al (Be)/ads.n-hexane was irradiated with  $\gamma$ -quanta on an isotope  $^{60}\text{Co}$  source with dose rates  $d\Phi_\gamma/dt = 0.80$  and  $1.03\ \text{Gy/s}$  at room temperature. The absorbed dose was  $\Phi_\gamma = 0.5\text{--}120\ \text{kGy}$ .

### **2.2 Method of IR reflection-absorption spectroscopy (IRRAS)**

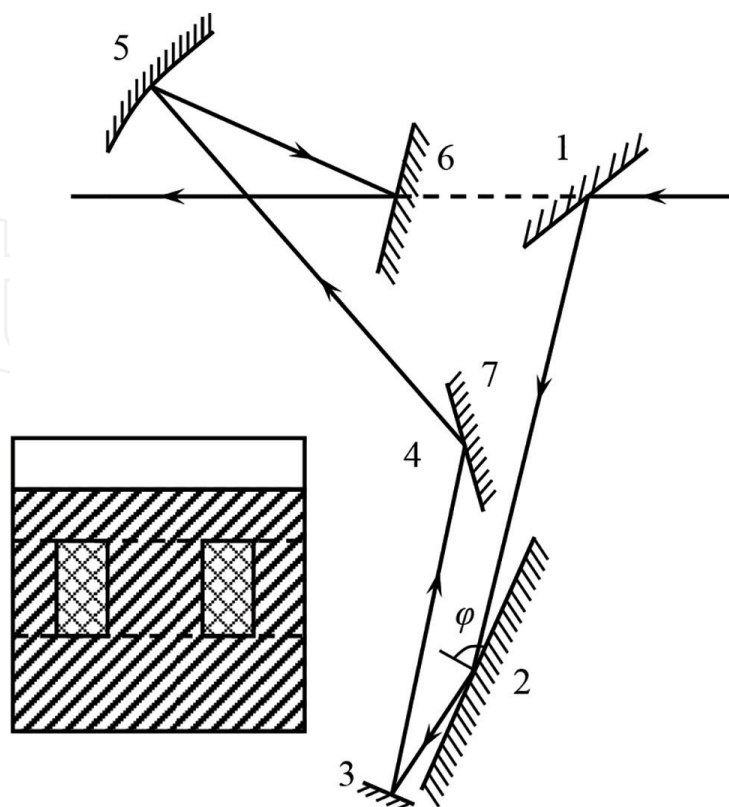
Molecular vibrational spectroscopy of substances in various aggregate states has long and firmly established itself as a method for studying their structure, properties, and all kinds of transformations in external interactions. Similar information on the adsorbed state of molecular systems would be of great value. However, it is not possible to mechanically transfer to it the whole arsenal of experimental, theoretical, and calculated methods of vibrational spectroscopy. In the experimental plan, the main difficulty is that a useful optical signal turns out to be small and, in the end, one must deal with a very poor signal-to-noise ratio, since a small number of molecules (at the level of one monomolecular layer) participate in the absorption, emission, or scattering events.

In the IR range, for measurement of the vibrational spectra of thin films on metals with a nanosized scale, the most promising are methods in which the probe electric field has a maximum intensity on a smooth surface of the metal or very close to it. This condition is satisfied when the grazing angle effect is applied to the metal in the IR reflection-absorption spectroscopy (IRRAS) method [18]. The advantage of this method is the wide range of wavelengths available for investigation. One of the most important conditions for successful application of methods of vibrational spectroscopy is a wide range of the spectrum, usually  $200\text{--}4000\ \text{cm}^{-1}$ —the area of the “fingerprint” of the overwhelming number of molecular systems, where most of the vibrational frequencies fall. In this respect, the IRRAS method seems to be the most wide-range and practical than the method of surface electromagnetic wave spectroscopy (SEW), which has high sensitivity. Therefore, in obtaining the spectra

of the reflection of oxides in the region of lattice vibrations, in studying radiation-heterogeneous adsorption processes, in the transformation of water and hydrocarbon molecules, and in studying the processes of oxidation and hydrogenation of aluminum and beryllium metals in contact with water and n-hexane. The choice of this method is due to the fact that it has already proved itself as a noncontact non-destructive optical probing method in the study of adsorbed molecules and oxide films on metal surfaces. The IRRAS method allows one to simultaneously obtain complete information about some chemical stages of radiation-heterogeneous transformations in metal-water, metal-hydrocarbon systems, the formation of adsorption—and catalytically active surface functional groups, and also to trace the formation of oxide and hydride films during oxidation and hydrogenation metal.

According to the theory of IRRAS [18], the efficiency of the interaction of infrared radiation with a smooth metal surface is achieved with incidence coal close to a sliding (i.e., close to  $90^\circ$ ) and with p-polarization. This method is sensitive to the components of the dipole moments of vibrational transitions in thin films perpendicular to the metal surface.

The IR reflection spectra at the drop of linearly polarized radiation on the sample at an angle close to the sliding angle  $\varphi = 88^\circ$  were measured at room temperature by means of a special reflecting device (Shimadzu, Japan), adapted to Specord 75 IR spectrophotometer, as well as Harrick prefixes. The optical scheme of the prefix of reflection with the coal of incidence of rays near  $88^\circ$  collected on the base of the attachment “Harrick” is shown in **Figure 1**. Mirror 1 sent a beam of radiation to the surface of sample 2 (for the axial beam  $\varphi_0 = 88^\circ \pm 0.5^\circ$ ). Narrow mirrors 3 and 4 of a special shape, as well as screen 7, provided passage through the prefix to only those rays for which the angle of incidence on the sample lay in the interval  $\varphi_0 - 1^\circ < \varphi < \varphi_0 + 1^\circ$ . The screens in front of mirror 2, which were not shown in the figure, made it possible to illuminate a part of the sample surface occupied by the film and located between two horizontal dashed lines.



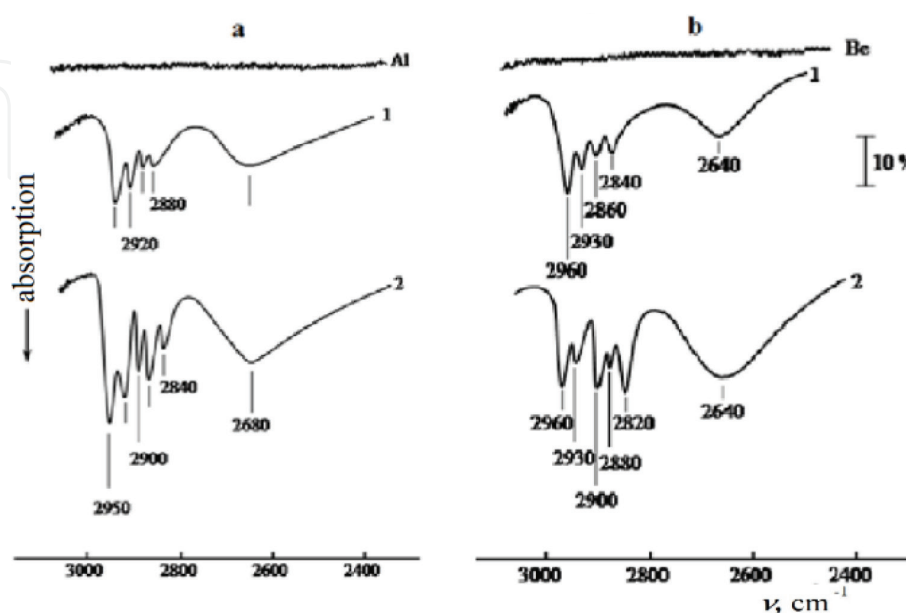
**Figure 1.** Optical scheme of the attachment of reflection: 1,4,6 - flat mirrors, 5 - concave mirror, 7 - screen,  $\varphi$  - angle of incidence of radiation on the sample. The inset shows the sample used.

After reflection from the rotary mirror 6, the radiation was directed to the detector (receiver). At  $\varphi = 88^\circ$ , the rays reflected from the entire illuminated surface of the sample were captured. When using a reflection attachment, polarizers in the form of Al gratings were placed in both channels of the spectrophotometer on plates of KRS-5 with a polarization degree of 99%, which transmitted radiation polarized parallel to the plane of incidence of radiation on the sample. Another hand-held ZnS polarizer was also used. The IR reflection spectra at the drop of linearly polarized radiation on the sample at an angle close to the sliding ( $\varphi = 88^\circ$ ) were measured in the region of wavenumbers  $\nu = 3400\text{--}650\text{ cm}^{-1}$  at room temperature. The optical densities of the absorption bands were determined from  $D = -\lg(R/R_0)$ . According to this formula, the optical densities  $D$  and  $D_0$  of the bands of stretching vibrations  $\text{C—H}$  and  $\text{Me—H}$  of adsorbed n-hexane ( $D_0$ —optical density in the initial sample,  $D$ —in the processed samples) were calculated and their ratios  $D/D_0$  were determined [18].

### 3. Radiation-stimulated adsorption of n-hexane on the surface of aluminum and beryllium

In this section, we present and discuss the results of experimental studies devoted to the spectroscopic study of radiation-stimulated adsorption of hydrocarbons, in particular n-hexane, on the surface of reactor materials-metal plates of aluminum and beryllium. To this end, the authors used the IR reflection-absorption spectroscopy method and developed a special vacuum optical cell that takes into account the specifics of conducting radiation studies. Let's consider some important aspects of this IR research, which in our opinion are the most interesting.

IR absorption spectra of n-hexane in the stretching vibration region of CH adsorbed on the dehydroxylated aluminum surface at room temperature are presented in **Figure 2a** (curve 1) [8, 10]. As can be seen from the figure, the adsorption of n-hexane on the aluminum surface is accompanied by the formation of a number of absorption bands (a.b.): narrow ones at  $\nu_{\text{max}} = 2950$  and  $2920\text{ cm}^{-1}$ , weak at  $2900$  and  $2880\text{ cm}^{-1}$  and intense wide at  $2680\text{ cm}^{-1}$ . The narrow bands are close in position to the bands characteristic of  $\nu(\text{CH})$  in the spectra of  $\text{n-C}_6\text{H}_{14}$  in the gas phase [19], which allows them to be attributed to physically adsorbed n-hexane. An



**Figure 2.** IR absorption spectra of n-hexane adsorbed on the surface of aluminum (a) and beryllium (b): 1-initial and 2- $\gamma$ -irradiated at  $\Phi_\gamma = 10\text{ kGy}$ ,  $T = 300\text{ K}$ ,  $P = 20\text{ Pa}$ .



asymmetric broad band with a maximum at  $2680\text{ cm}^{-1}$  is attributed to the vibration of one of the C—H bonds in the n-C<sub>6</sub>H<sub>14</sub> molecule perturbed by the surface centers of aluminum. The unusually low frequency of oscillations, as well as the relatively high intensity and width, indicates a strong perturbation of n-hexane molecules upon adsorption. The complex to which this a.b. object belongs is not stable and is destroyed by evacuation at room temperature. This allows us to classify this band as n-hexane adsorbed in molecular form.

The formation of a molecular complex was theoretically proved in the framework of an ab initio quantum chemical calculation of the profile of the potential energy of dissociative methane adsorption on the Ni surface and was experimentally established when studying its adsorption on metallic surfaces (Fe, Ni, Pt) [20]. Weak a.b. with maxima at  $2900$  and  $2880\text{ cm}^{-1}$  indicate a slight dissociative adsorption of n-hexane on the Al surface, which is associated with even lower concentrations of such forms than for H-bound complexes, especially at a relatively low interaction temperature.

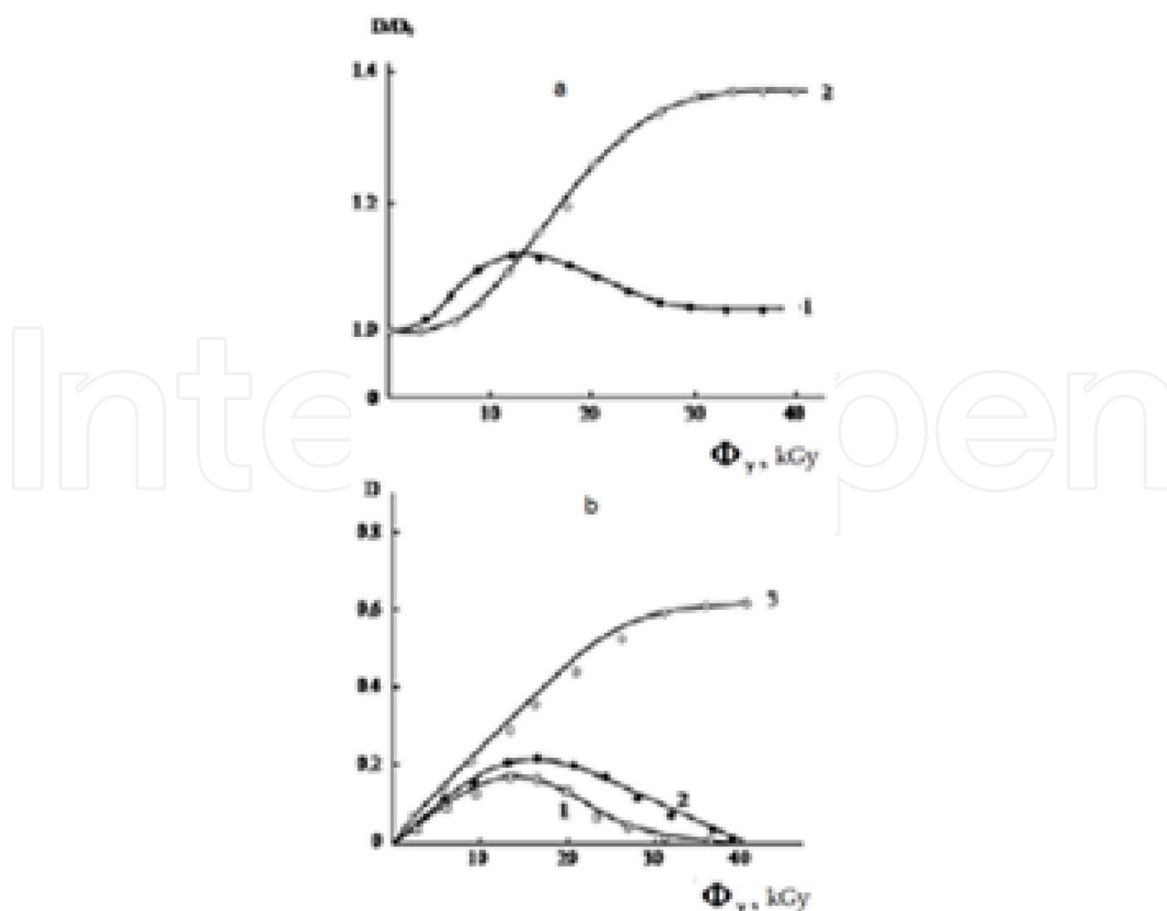
When studying the adsorption of n-hexane on preliminarily  $\gamma$ -irradiated aluminum samples, we found that starting from certain values of the irradiation dose ( $\Phi_\gamma = 10\text{ kGy}$ ) at room temperature, strong dissociative chemisorption is observed (**Figure 2a**, curve 2). It occurs as a result of the interaction of n-hexane with surface-active centers formed under the action of  $\gamma$ -quanta in aluminum. This is evidenced by the increase and redistribution of the intensities of a.b. at  $2900$  and  $2880\text{ cm}^{-1}$ , as well as the appearance in the IR spectrum of a new a.b. with a maximum at  $2840\text{ cm}^{-1}$ . The observed absorption bands apparently belong to the stretching vibrations of the CH bonds of the fragments CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, etc. bound by aluminum (aluminum alkyls) [6–8, 10].

The dissociative adsorption is also confirmed by the appearance in the region of  $2000\text{--}1700\text{ cm}^{-1}$  of bands with frequencies of  $1920$ ,  $1830$ , and  $1760\text{ cm}^{-1}$  of Al—H bonds in the IR spectrum, which are related to surface aluminum hydrides [3, 4]. The formation of hydrides in the interaction of n-hexane with aluminum is consistent with the hydride mechanism of interaction of metals with hydrocarbons [4, 6–8].

In order to reveal the spectrokinetic regularities of radiation-stimulated adsorption of n-hexane on the aluminum surface, the kinetic adsorption curves, that is, the dependence of the changes in the relative optical densities of the D/D<sub>0</sub> bands of the molecularly and dissociatively adsorbed n-hexane forms on the absorbed dose of irradiation, were studied. The spectra are shown in **Figure 3a**. As can be seen from **Figure 3a** (curve 1), the kinetic feature of radiation-stimulated chemisorption consists of a certain initial induction period at  $\Phi_\gamma \leq 5\text{ kGy}$ , related to the healing of biographical defects, the linear region at  $2 \leq \Phi_\gamma \leq 25\text{ kGy}$ , caused by the generation of adsorption active centers and the adsorption of additional n-C<sub>6</sub>H<sub>14</sub> molecules at these centers, as well as from the stationary saturation region occurring at  $\Phi_\gamma > 25\text{ kGy}$ .

Apparently, under the action of  $\gamma$ -radiation in aluminum, new active surface states are generated, whose density increases with increasing  $\gamma$ -radiation dose in aluminum, and the probability of their interaction with adsorbed n-hexane molecules increases, which causes their dissociation. At the same time, the kinetic curve of molecularly adsorbed n-hexane is characterized by two regions: in the region  $5 \leq \Phi_\gamma \leq 10\text{ kGy}$ , formation is observed, and at  $\Phi_\gamma > 10\text{ kGy}$ , the molecular H-complex decays (**Figure 3a**, curve 2). The presence of activated dissociative chemisorption in the region  $5 \leq \Phi_\gamma \leq 25\text{ kGy}$  is also confirmed by the course of the kinetic curve obtained for surface aluminum hydrides (**Figure 3b**).

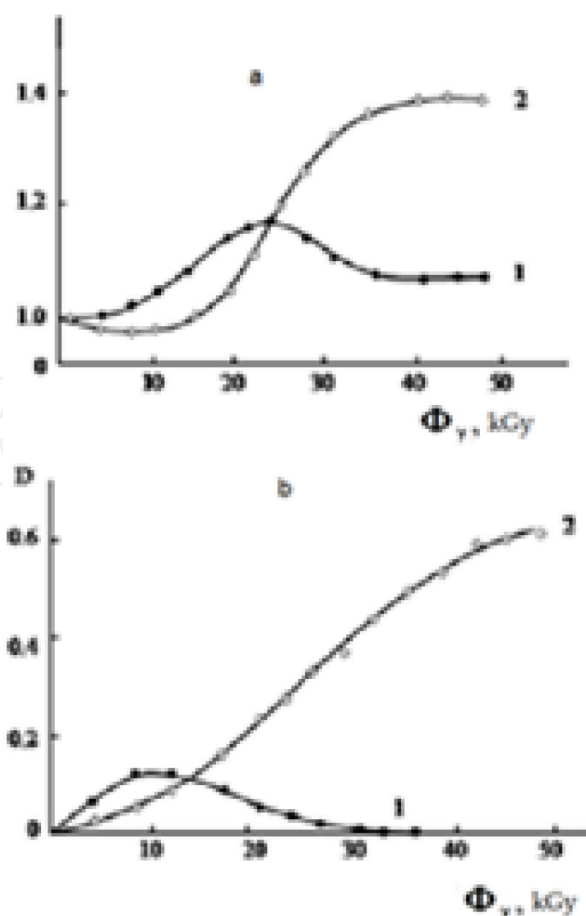
Thus, in the region of absorbed dose  $5 \leq \Phi_\gamma \leq 25\text{ kGy}$ , activated dissociative chemisorption is detected, which is explained both by an increase in the number of centers of activated adsorption due to surface-excited states of aluminum with



**Figure 3.**

(a) Dependences of the relative optical densities of the bands molecularly (1) and dissociative (2) adsorbed n-hexane from the absorbed  $\gamma$ -irradiation dose in the Al/ads.n-hexane heterosystem:  $\nu_{\max} = 2680$  (1) and  $2880 \text{ cm}^{-1}$  (2). (b) Dependences of the optical densities of the absorption bands of aluminum surface hydrides on the absorbed dose of  $\gamma$ -irradiation:  $\nu_{\max} = 1920$  (1b),  $1830$  (2b) and  $1760 \text{ cm}^{-1}$  (3b).

increasing  $\gamma$ -radiation dose and by decomposition of H-bound complexes as a result of energy transfer excitation to n-hexane molecules. Activated adsorption of n-hexane was also observed on the nickel surface [1, 20], and according to [1, 21], dissociative adsorption of methane on metals is usually activated. Similar results were also obtained in the study of the radiation-stimulated adsorption of n-hexane on the beryllium surface. The observed narrow bands refer to physically adsorbed n-hexane. The asymmetric broad band with a maximum at  $2640 \text{ cm}^{-1}$  is attributed to the vibration of one of the C—H bonds in the n-C<sub>6</sub>H<sub>14</sub> molecule perturbed by the surface centers of beryllium. The unusually low frequency of oscillations, and also the relatively high intensity and width ( $\nu_{1/2} = 50 \text{ cm}^{-1}$ ) indicate a strong perturbation of n-hexane molecules during adsorption. This band refers to n-hexane adsorbed in the molecular form. Weak a.b. with peaks at  $2860$  and  $2840 \text{ cm}^{-1}$  indicate a slight dissociative adsorption of n-hexane on the Be surface. When studying the adsorption of n-hexane on preirradiated beryllium samples, it was established that starting from certain values of the irradiation dose ( $\Phi_\gamma = 10 \text{ kGy}$ ), strong dissociative chemisorption is observed at room temperature (Figure 2b, curve 2). It occurs as a result of the interaction of n-hexane with surface-active centers formed under the action of  $\gamma$ -quanta in beryllium. This is evidenced by the appearance in the IR spectrum of new a.b. with maxima at  $2860$  and  $2820 \text{ cm}^{-1}$ . The observed absorption bands seem to refer to stretching vibrations of the C—H bonds of the fragments CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, etc., associated with beryllium (beryllium alkyls) [14, 15]. The dissociative adsorption is also



**Figure 4.**

Dependence on the absorbed dose of gamma irradiation in the Be-adsorbed n-hexane system of the relative optical densities of the bands molecularly (1) and dissociatively (2) adsorbed n-hexane (a) and optical densities of absorption bands of surface beryllium hydrides (b):  $\nu_{max} = 2640$  (1a), 2880 (2a), 1790 (1b), and 1740 cm<sup>-1</sup> (2b).

confirmed by the appearance in the IR spectrum in the 2000–1700 cm<sup>-1</sup> region of bands with frequencies of 1790 and 1740 cm<sup>-1</sup>, which relate to the Be—H bonds of surface beryllium hydrides [14, 15]. The kinetic curves of radiation-stimulated adsorption of n-hexane on the beryllium surface have also been studied in [14] (**Figure 4**). It was found that the kinetic feature of radiation-stimulated chemisorption consists of a certain initial induction period at  $\Phi_\gamma \leq 10$  kGy, a linear region at  $10 \leq \Phi_\gamma \leq 25$  kGy, and also from a stationary saturation region at  $\Phi > 25$  kGy. Apparently, the generation of new active surface states under the action of  $\gamma$ -radiation in beryllium, the density of which increases with increasing dose of  $\gamma$ -radiation in beryllium, and the probability of their interaction with adsorbed n-hexane molecules, which causes their dissociation. At the same time, the kinetic curve of molecularly adsorbed n-hexane is characterized by two regions. It is seen that the kinetic feature of radiation-stimulated adsorption in the  $5 \leq \Phi_\gamma \leq 10$  kGy region is observed, and at  $\Phi_\gamma > 10$  kGy, the molecular H-complex decays (**Figure 4a**, curve 2). The presence of activated dissociative chemisorption in the region  $5 \leq \Phi_\gamma \leq 25$  kGy is also confirmed by the kinetic curve obtained for surface beryllium hydrides (**Figure 4b**).

Thus, in the region of absorbed dose  $5 \leq \Phi_\gamma \leq 10$  kGy, activated dissociative chemisorption is detected, which is explained both by an increase in the number of centers of activated adsorption due to surface excited beryllium states with increasing dose of  $\gamma$ -radiation and by decomposition of H-bound complexes as a result of transmission excitation energy to n-hexane molecules.

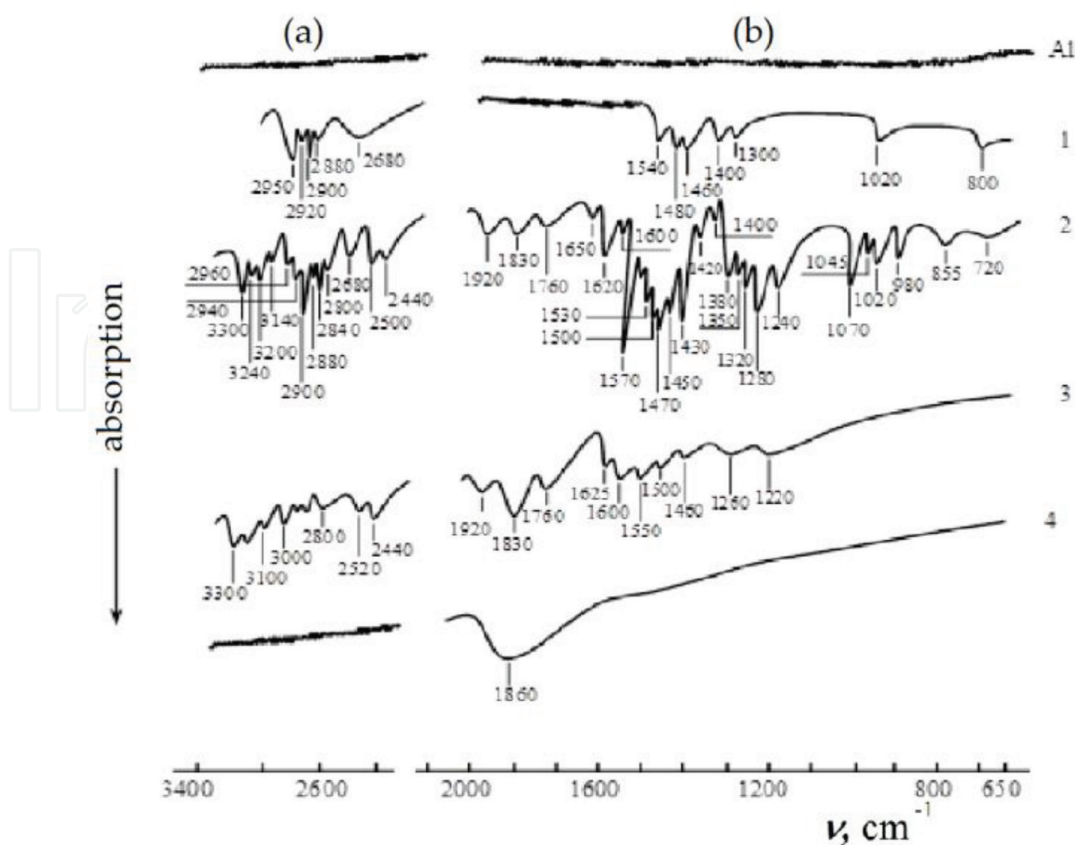


#### 4. Radiation-chemical transformation (radiolysis) of n-hexane on the surface of aluminum and beryllium

In this section, some aspects of IR spectroscopic studies of the radiation-chemical transformation of n-hexane on the surface of aluminum and beryllium at room temperature are made to determine the role of surface intermediate-active particles and their products in the dynamics of changes in the radiolysis process.

The IR spectra of the reflection of the Al/ads.n-hexane heterosystem before (curve 1) and after the action of  $\gamma$ -quanta (curves 2–4) at room temperature in the frequency range  $\nu = 3500\text{--}650\text{ cm}^{-1}$  are shown in **Figure 5**. Changes in the spectra were observed in both the region of stretching (**Figure 5a**) and deformation vibrations of C—H (**Figure 5b**). It is seen that in the unirradiated heterosystem after the adsorption of n-hexane on the aluminum surface in the stretching vibration region of CH there is an appearance of absorption bands (a.b.) indicating the occurrence of three forms of adsorption: physical adsorption (narrow bands at  $\nu_{\text{max}} = 2950$  and  $2920\text{ cm}^{-1}$ ), the molecular form of adsorption (intense broad band at  $2680\text{ cm}^{-1}$ ), and insignificant dissociative chemisorption (weak bands at  $2900$  and  $2880\text{ cm}^{-1}$ ) (**Figure 5a**, curve 1). The flow of three forms of adsorption is also confirmed by the formation of a number of bands in the region of deformation vibrations of C—H with maxima at  $\nu_{\text{max}} = 1540, 1480, 1460, 1400$ , and  $1360\text{ cm}^{-1}$  (**Figure 5b**, curve 1).

Irradiation of the Al/ads.n-hexane heterosystem by  $\gamma$ -quanta at  $\Phi_{\gamma} = 10\text{ kGy}$  leads to the formation of additional a.b. in the spectra. (**Figure 5a** and **b**, curves 2), which indicates the radiation-chemical decomposition of n-hexane on the Al surface. Radiolysis of n-hexane in the Al/ads.n-hexane system in the stretching vibration region of C—H ( $\nu_{\text{CH}}$ ) is accompanied by the disappearance of the a.b. at  $2950$  and  $2920\text{ cm}^{-1}$ , a decrease in the intensity of the broad band at  $2680\text{ cm}^{-1}$  and its narrowing and



**Figure 5.** IR absorption spectra of the Al/ads.n-hexane system: 1—initial, 2–4—after  $\gamma$ -radiolysis at  $\Phi_{\gamma} = 10$  (2), 20 (3), and 30 kGy (4).

the appearance of a series of narrow bands at 2960, 2940, 2900, 2880, 2840, and 2800  $\text{cm}^{-1}$ , and also comparatively broad at 2520 and 2440  $\text{cm}^{-1}$  bands indicating the formation of surface aluminum alkyls and molecular complexes (**Figure 5a**, curve 2). The observed new narrow a.b. at 2980–2780  $\text{cm}^{-1}$  are associated with the formation of adsorbed  $\text{C}_1$ – $\text{C}_5$  hydrocarbons, and relatively broad bands at 2500–2400  $\text{cm}^{-1}$  are possibly due to heavier than n-hexane hydrocarbons [19, 22–27]. The formation of aluminum alkyls is also confirmed by the presence in the spectrum of a.b. in the regions of planar and out-of-plane deformation vibrations of  $\delta_{\text{CH}}$  relatively narrow with maxima at 1470, 1450, 1430, 1420, 1400, 1380, and wide at 855 and 720  $\text{cm}^{-1}$  (**Figure 5b**, curve 2). A weak broad band at 720  $\text{cm}^{-1}$  refers to the pendular vibrations of the  $\text{CH}_2$  group, which are not connected with the skeleton vibrations and is characteristic of long paraffin chains of the type  $\text{—}(\text{CH}_2)_n\text{—}$  ( $n \geq 4$ ) [25–27].

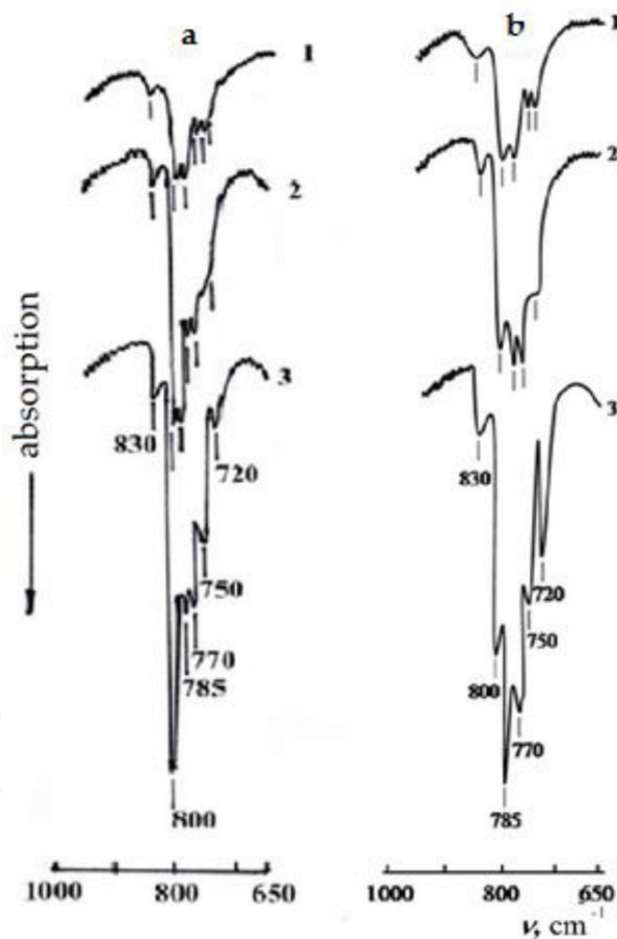
As a result of the decomposition of n-hexane in the Al/n-hexane system, various olefins, mainly trans-ethylene, propylene, butylene-1, hexene-1, and trans-hexene-3, are formed similarly to homogeneous radiolysis. This is evidenced by a.b. with maxima at 1650, 1620, 1600, 1570, and 1530  $\text{cm}^{-1}$ , characterizing the stretching vibrations  $\nu_{\text{C}=\text{C}}$  in the  $\pi$ -complexes of these adsorbed olefins with the  $\text{Al}^{3+}$  cation predominantly by the octahedral coordination of Al atoms [26–30] (**Figure 5b**, curve 2). The appearance of a number of a.b. in the regions of stretching  $\nu_{\text{CH}}$  ( $\nu \sim 3140$ – $3075 \text{ cm}^{-1}$ ), planar ( $\nu \sim 1350$ – $1200 \text{ cm}^{-1}$ ), and out-of-plane ( $\nu \sim 1100$ – $950 \text{ cm}^{-1}$ ) strain  $\delta_{\text{CH}}$  vibrations of CH containing  $=\text{CH}_2$  and  $=\text{CH—}$  groups is one of the main criteria for proving the formation of olefins on the surface of  $\pi$ -complexes [26, 27]. In this case, a.b. with peaks of 1320 and 1280  $\text{cm}^{-1}$  are attributed to the plane deformation vibrations  $\nu_1$  and  $\nu_2$  of two different symmetry classes, and a.b. with maxima of 980  $\text{cm}^{-1}$ —the out-of-plane deformation vibration of  $=\text{CH}$  disubstituted ethylene (trans) [10, 26, 27]. The formation of  $\pi$ -complexes of olefins is also confirmed by the presence of a.b. with maxima at 3300, 3240, and 3200  $\text{cm}^{-1}$  in the overtone coupling region  $\nu_{\text{C}=\text{C}}$  (**Figure 5a** and **b**, curve 2) [26, 27].

With an increase in the  $\gamma$ -radiation dose  $\Phi_\gamma$  up to 20 kGy, the spectra are transformed: the intensities of some a.b. associated with adsorbed hydrocarbons and olefins decrease, indicating that they are partially decomposed (**Figure 5a** and **b**, curve 3). Partial decomposition of olefins is accompanied by their dissociative adsorption and the formation of  $\pi$ -allyl complexes on the aluminum surface [26]. A further increase in the value of  $\Phi_\gamma$  to 30 kGy leads to a complete decomposition of hydrocarbons and olefins (curve 4). In addition, an interesting fact was discovered, consisting in an increase in the intensities of a.b. associated with the formation of surface hydrides. At irradiation doses up to 10 kGy, bands with frequencies of 1920, 1830 and 1760  $\text{cm}^{-1}$  appear in the IR spectrum in the region 2000–1700  $\text{cm}^{-1}$ , which refer to  $\text{Al—H}$  [2–4]. With an increase in the dose of  $\gamma$ -irradiation up to 20 kGy, the intensities of these a.b. increase, which indicates the accumulation of hydrogen in the form of its hydrides (**Figure 5b**, curves 2, 3). A further increase in the value of  $\Phi_\gamma$  to 40 kGy is accompanied by the formation of aluminum hydride  $\text{Al—H}_3$  stable at room temperature (a.b. with a maximum at 1830  $\text{cm}^{-1}$ ) (**Figure 5b**, curve 4) [10]. As follows from IR spectroscopy, the radiolysis of n-hexane in the  $\gamma$ -irradiated Al-n-hexane heterosystem is accompanied by the formation of intermediate decomposition products—surface aluminum alkyls,  $\pi$ -complexes of olefins and aluminum hydrides (**Table 1**).

The main end products of decomposition are gaseous hydrocarbons and molecular hydrogen, the formation of which was monitored by spectroscopic and chromatographic methods. IR absorption spectra of gaseous hydrocarbon products of n-hexane radiolysis in the region of out-of-plane deformation vibrations of  $\text{C—H}$  are shown in **Figure 6a**. It can be seen that for small values of the absorbed dose of  $\gamma$ -irradiation ( $\Phi_\gamma = 10 \text{ kGy}$ ) in the Al/n-hexane system, a.b. with maxima at 830, 800, 785, 770, 750, and 720  $\text{cm}^{-1}$  (**Figure 6a**, curve 1), whose location and

Sample	Surface aluminum alkyls ( $\nu$ $\text{cm}^{-1}$ )	Surface $\pi$ -complexes of olefins ( $\nu$ , $\text{cm}^{-1}$ )	Surface hydrides ( $\nu$ , $\text{cm}^{-1}$ )
Al/ads.n-hexane	2960, 2940, 2900, 2880, 2840, and 2800 (region of stretching vibrations C—H), 2520 and 2440 Narrow bands 1470, 1450, 1430, 1420, 1380 (region of planar and nonplanar deformation of the vibrations $\delta_{\text{CH}}$ ), broad 855 and 720	1650, 1620, 1600, 1570, and 1530 (C = C bond) 3300, 3240, and 3200 (overtone coupling region C = C) $\nu \sim 3140\text{--}3075$ (the stretching vibration region $\nu_{\text{CH}}$ ) $\nu \sim 1350\text{--}1200$ and $\nu \sim 1100\text{--}950$ (the region of planar and out-of-plane deformation $\delta_{\text{CH}}$ vibrations of C—H containing $=\text{CH}_2$ and $=\text{CH—}$ groups)	1920, 1830 (stable form $\text{AlH}_3$ ), 1760

**Table 1.**  
*Spectroscopic assignment of intermediate products of radiolysis of n-hexane on the aluminum surface.*



**Figure 6.**  
*IR spectra of the absorption of gaseous hydrocarbon products of n-hexane radiolysis on the surface of Al (a) and Be (b) in the region of out-of-plane deformation vibrations of CH at doses of gamma irradiation  $\Phi_\gamma = 10$  (1), 20 (2), and 30 kGy (3).*

half-width allows them to be assigned to  $\text{C}_1\text{--C}_5$  hydrocarbons in the gas phase [19]. With an increase in the absorbed dose of  $\Phi_\gamma$  to 30 kGy, the intensities of these bands are redistributed and increased (curves 2–3), and a further increase in  $\Phi_\gamma$  to 40 kGy does not lead to appreciable changes in the spectrum. Comparison of dose changes in the absorption spectra of intermediate and final hydrocarbon products of the

decomposition of n-hexane in the  $\gamma$ -irradiated Al/ads.n-hexane system, which occur as a function of the absorbed dose of  $\gamma$ -irradiation, shows that they have an antibatic character. According to the chromatographic analysis, the total radiation-chemical yield of hydrocarbons  $\Sigma G(C_1-C_5)$  is 0.36 molecule/100 eV. The kinetic regularity of the accumulation of molecular hydrogen in the radiolysis of n-hexane in the Al/ads.n- $C_6H_{14}$  system was studied in [10]. Based on the kinetic curve of  $H_2$  accumulation, the rate of the radiative formation of  $H_2$  is determined and the radiation-chemical yield of molecular hydrogen  $G_{ads}(H_2)$  in the Al/ads.n-hexane heterosystem is calculated, taking into account the total absorbed radiation dose of gamma quanta, which is  $G_{ads}(H_2) = 29.6$  molecule/100 eV. It should be noted that the yield of hydrogen for a homogeneous phase (in the absence of aluminum) is  $G(H_2) = 5.2$  molecule/100 eV [29–31].

A comparison of  $G_{ads}(H_2)$  and  $G(H_2)$  under identical conditions indicates the radiation-catalytic activity of aluminum during the decomposition of n-hexane. Similar results were obtained with the radiation-chemical transformation of n-hexane on the surface of beryllium at room temperature. Radiolysis of n-hexane in the presence of beryllium is accompanied by the formation of intermediate decomposition products-surface beryllium hydrides, beryllium alkyls, and  $\pi$ -olefin complexes (**Table 2**).

The variety of products of n-hexane radiolysis is a consequence of the formation of highly reactive radicals upon irradiation of hydrocarbons. Thus, the formation of higher hydrocarbons in the radiolysis of n- $C_6H_{14}$  is due to the appearance of a number of alkyl radicals that combine with each other to form  $C_7H_{16}$ , or n-hexane or  $C_7H_{16}$ , and give products of more complex composition. The main end products of decomposition are gaseous hydrocarbons and molecular hydrogen. IR absorption spectra of gaseous hydrocarbon products of n-hexane radiolysis on the beryllium surface in the region of extraplane deformation vibrations of  $C-H$  are presented in **Figure 6b**.

According to the chromatographic analysis, the total radiation-chemical yield of hydrocarbons  $\Sigma G(C_1-C_5)$  is 0.28 molecule/100 eV. The kinetic regularity of the accumulation of molecular hydrogen in the radiolysis of n-hexane in the system Be/ads.n- $C_6H_{14}$  [14, 15] has been studied. Based on the kinetic curve of  $H_2$  accumulation, the rate of the radiative formation of  $H_2$  is determined and its activation energy is calculated, which is  $E_a \approx 4.5$  kC/mol. According to the calculation, the radiation-chemical yield of molecular hydrogen is  $G_{ads}(H_2)$  in the heterosystem Be/ads.n- $C_6H_{14}$ , taking into account the total absorbed radiation dose of  $\gamma$ -quanta, is  $G_{ads}(H_2) = 24.8$  molecule/100 eV. It should be noted that the yield of hydrogen for a homogeneous

Sample	Surface beryllium alkyls ( $\nu$ , $cm^{-1}$ )	Surface $\pi$ -complexes of olefins ( $\nu$ , $cm^{-1}$ )	Surface hydrides ( $\nu$ , $cm^{-1}$ )
Be/ads. n-hexane	2960, 2930, 2900, 2880, 2840, 2820 (region of stretching vibrations $C-H$ ), 2520 and 2420 narrow bands 1468, 1450, 1430, 1415, 1400, 1370 (region of planar, out-of-plane deformation vibrations $\delta_{CH}$ ), broad bands 855 and 720 $cm^{-1}$	1660, 1610, 1580, 1565, 1550, 1530 ( $C=C$ bond) 3300, 3840, 3200 and 3140 (overtone region $C=C$ ) $\nu(3140-3050)$ (region stretching vibrations $\nu_{CH}$ ) $\nu(2140-3050)$ $\nu(1060-950)$ (region of planar, out-of-plane deformation vibrations of $C-H$ containing $=CH_2$ and $=CH$ groups)	1790, 1740 (stable form $BeH_2$ )

**Table 2.**  
*Spectroscopic assignment of intermediate products of radiolysis of n-hexane on the surface of beryllium.*



phase (in the absence of beryllium) is  $G(\text{H}_2) = 5.2$  molecule/100 eV. A comparison of  $G_{\text{ads}}(\text{H}_2)$  and  $G(\text{H}_2)$  under identical conditions indicates the radiation-catalytic activity of beryllium and aluminum during the decomposition of n-hexane.

A comparative analysis of the studies shows that gamma irradiation of aluminum (beryllium)/ads.n-hexane heterosystems with  $\gamma$ -quanta in the region of absorbed dose of  $5 < \Phi_\gamma \leq 50$  kGy leads to a radiation-chemical decomposition of n-C<sub>6</sub>H<sub>14</sub>. In contrast to the homogeneous phase, the radiolysis of n-hexane in the presence of aluminum and beryllium is accompanied by the formation of intermediate products of decomposition of surface aluminum and beryllium hydrides, aluminum (beryllium) alkyls, and  $\pi$ -complexes of olefins. The authors revealed the limits of doses of complete radiolysis of n-hexane, below which its partial decomposition occurs, and at higher levels, a stationary saturation region sets in. The kinetics of the accumulation of molecular hydrogen has been studied and its radiation-chemical yields, which constitute the are determined  $G_{\text{ads}}(\text{H}_2) = 24.8$  (in the presence of Be) and 29.6 molecule/100 eV (in the presence of Al), respectively.

In the heterogeneous radiolysis of n-hexane in contact with a metal,  $\gamma$ -quanta are exposed to both n-hexane and metal [28–30]. Since metals are a core of positive ions immersed in an electron gas, excitation and ionization produced by radiation in them create only defects that arise during elastic collisions [28, 29]. Such defective centers are the radiation-induced active states  $S^*$  (ions, localized charges, etc.), whose density on the surface of metals with thin oxide films is much larger compared to the surface of metals (Al, Be) with continuous oxide layers. The interaction of the active surface states of  $S^*$  and the release of secondary electrons from the metal under the action of  $\gamma$ -radiation ( $Me \xrightarrow{\gamma} S^*, e_s$ ) with n-hexane lead to the excitation of its molecules by n-C<sub>6</sub>H<sub>14</sub><sup>\*</sup> (ads). In the surface-active states of  $S^*$ , the excitation of n-hexane molecules is carried out through complexation stages with further transfer of excitation energy to the molecules of n-C<sub>6</sub>H<sub>14</sub>.

## 5. Radiation-stimulated hydrogenation of the surface of aluminum and beryllium in contact with n-hexane

The study of radiation-stimulated hydrogenation of the surface of metals in contact with hydrocarbons is of interest from the point of view of the development of radiation-heterogeneous catalysis processes [29, 30]. The identification of the mechanisms and kinetic regularities of the formation of hydride layers at the initial stage of the process is necessary to solve the problems of radiation embrittlement of metals and alloys, as well as the production of molecular hydrogen by its accumulation in the form of hydrides [23, 24, 29, 30].

In this section, the features of the radiation-stimulated hydrogenation of the surface of aluminum and beryllium contacting with n-hexane are exposed under the action of gamma irradiation at room temperature.

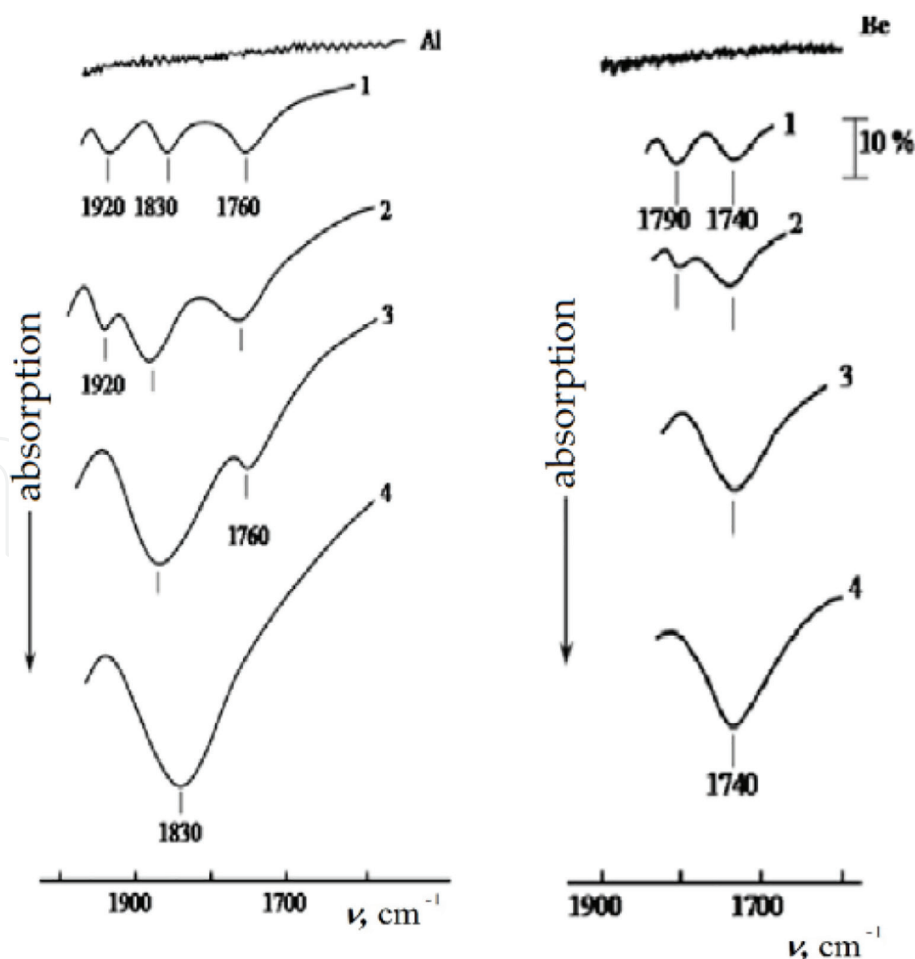
Radiation-chemical conversion of n-hexane in the Al-n-hexane heterosystem takes place at an absorbed dose of  $\Phi_\gamma > 0.5$  kGy and is accompanied by the formation of aluminum hydrides, which is confirmed by the appearance and IR reflection spectra in the bands  $\nu = 2000\text{--}1500$  cm<sup>−1</sup> of the absorption bands 1920, 1830, and 1760 cm<sup>−1</sup>, related to the Al—H bonds (**Figure 7a**, curve 1). The formation of hydrides in the interaction of n-hexane with aluminum occurs via the hydride mechanism of interaction of metals with hydrocarbons [3, 4] according to which in the first stage of the reaction after orientation of n-hexane molecules on the aluminum surface and mutual polarization of molecular and atomic layers at the aluminum/ads.n-hexane interface, a new metal-hydrogen bond is formed, and a new chemical compound, the hydride, appears on the surface of the metal. The formation



of various types of hydrides is associated with different coordination numbers of a coordinative unsaturated aluminum atom [2–4]. **Figure 6a** shows the change in the bands of Al—H stretching vibrations as a function of the contact time  $\tau$  of aluminum with n-hexane under radiation exposure ( $T = 300\text{ K}$ ,  $d\Phi_\gamma/dt = 0.80\text{ Gy/s}$ ). Increasing the contact time from 10 min to 40 h (absorbed dose of 0.5 and 120 kGy, respectively) leads to the transformation of spectra accompanied by the redistribution of the intensities of these bands and their fusion and the formation of aluminum hydride in a more stable form of Al-H<sub>3</sub> ( $\nu = 1830\text{ cm}^{-1}$ ) at room temperature (curves 2–4). According to [2–4], the frequencies of stretching vibrations of Al—H<sub>3</sub> are in the region of  $1850\text{--}1770\text{ cm}^{-1}$ , while the intensity increases by almost an order of magnitude and the half-width  $\nu_{1/2}$  by 3.6 times (from 50 to 180  $\text{cm}^{-1}$ ).

A similar picture is also observed when the bands of stretching vibrations of Be—H are varied as a function of the contact time  $\tau$  of beryllium with n-hexane under radiation action ( $T = 300\text{ K}$ ,  $d\Phi_\gamma/dt = 0.80\text{ Gy s}$ ). Increase in the contact time from 10 min to 40 h is accompanied by the transformation of hydride bands and the formation of beryllium hydride in the stable form of Be—H<sub>2</sub> ( $\nu = 1740\text{ cm}^{-1}$ ) (**Figure 7b**, curves 2–4). In this case, the intensity increases almost by  $\sim 4$ , and the half-width  $\nu_{1/2}$  by  $\sim 2.2$  times. The observed increase in  $\nu_{1/2}$  for the vibration bands of Al—H and Be—H in hydride layers is due to the inhomogeneous broadening caused by the effect of  $\gamma$ -irradiation.

It is known that irradiation leads to the nucleation and growth of defects such as dislocation loops and pores and stimulates diffusion processes, initiating the effect



**Figure 7.**  
 The change of the bands of stretching vibrations of Al—H and Be—H on the dependence of contact time  $\tau$  of aluminum (a) and beryllium (b) with n-hexane under radiation action  $\tau$ : 10 min (1), 5 h (2), 20 h (3), and 40 h (4). ( $T = 300\text{ K}$ ,  $d\Phi_\gamma/dt = 0.80\text{ Gy/s}$ ).

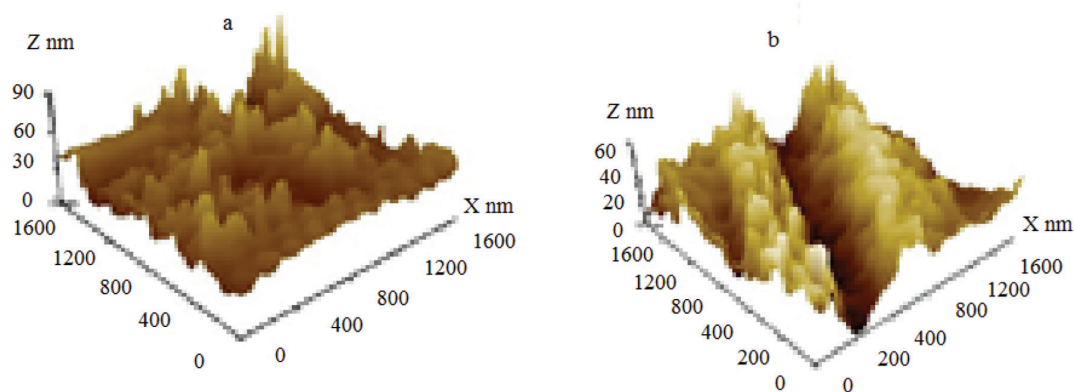
of segregation of impurities and/or the appearance of new phases, the formation of which in conventional thermal conditions is impossible. Thus, it can be argued that in the general case, irradiation initiates the creation of microstructural inhomogeneities in the metal [32], which possibly lead to broadening of the Al—H and Be—H vibration bands of the hydride layers obtained by radiation hydrogenation of Al and Be in contact with n-hexane.

It should be noted that the probability of formation of MeC precipitates on the surface of Al and Be plates contacting with n-hexane in the region of the absorbed dose  $\Phi_\gamma \leq 120$  kGy is small. Therefore, in the IR reflection spectra, it was not possible to detect the absorption bands of the skeleton vibration of Al (Be)—C bonds [33]. With the purpose of experimental confirmation of the role of hydrogen nanoclusters (accumulations) during defect formation on the metal surface during their interaction by substances under the action of gamma radiation, a microscopic study of the aluminum surface after radiative hydrogenation was carried out.

**Figure 8a** and **b** shows 3D AFM images of surfaces of aluminum plates up to (a) and after hydrogenation at an absorbed dose of  $\Phi_\gamma = 120$  kGy. The surface of the original Al plate with a thin natural oxide film ( $d = 3.6$  nm) is characterized by a high degree of density defect (a). Hydrogenation of aluminum leads to the formation of hydride phase islands on its surface and the formation of a continuous hydride layer with a thickness  $d \sim 450$  nm as a result of the introduction of  $H^+$  ions and their migration into the volume either from a defective surface or from internal traps along the grain boundaries. In the 3D images of hydrogenated aluminum, the areas indicating carbon nanotube-like formations are clearly distinguished [7, 21].

The yields of hydrogen accumulated in the form of aluminum and beryllium hydrides have also been determined. To this end, the kinetics of hydrogen desorption by aluminum and beryllium at a temperature of  $T = 423$  K was studied by the method of [6, 7]. The yields of  $H_2$  are found to be 0.12 molecule/100 eV for aluminum and 0.07 molecule/100 eV for beryllium. The experimental results obtained once again testify to the high ability of aluminum to accumulate hydrogen in the form of its hydride. It should be noted that the development of systems related to storage and generation of hydrogen for autonomous power plants based on oxygen-hydrogen fuel cells in efficiency (27 g components per 1 g of hydrogen) is inferior to aluminum only to systems with lithium hydride and lithium metal. This shows that one of the promising methods is the radiation-chemical reduction of hydrogen from water by metallic aluminum.

IR spectroscopic studies revealed that hydrogen was partially accumulated in the form of Al (Be) hydride [6, 7, 16] upon radiolysis of n-hexane on the surface of aluminum and beryllium metals. The dynamics of formation of the hydride layer shows that the process of radiation-stimulated hydrogenation at room temperature



**Figure 8.**  
3D images of the surface of the initial (a) and hydrogenated (b) aluminum samples.

on the surface of these metals, contacting with n-hexane, with  $\gamma$ -irradiation in the absorbed dose range of 0.5–120 kGy has a multistage nature. IR spectroscopic data are in good agreement with the results of electrophysical measurements [11, 12]. In works on electrophysical measurements, it was shown that the transition from the first stage to the latter is accompanied by a decrease in the electrical conductivity of aluminum and beryllium by several times and by an order of magnitude increase in the thickness of the resulting hydride layer. The growth of the electrical resistivity of metals at the last stage is explained by the formation of a subsurface layer of dissolved hydrogen that dissipates the conduction electrons and the formation of defects in the structure of metals.

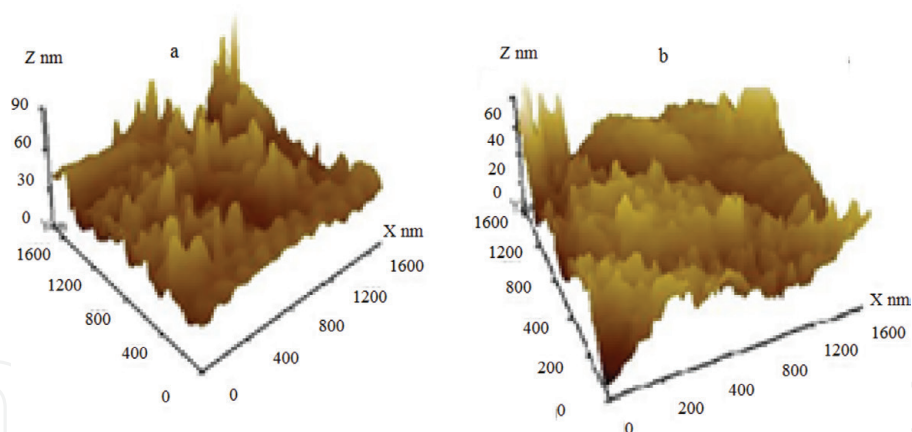
## **6. The influence of the surface relief of aluminum on the processes of radiolysis of n-hexane**

As noted above, the problems associated with the occurrence of radiation processes in a heterogeneous metal-hydrocarbon system have not been studied sufficiently; there are also no experimental data on the effect of the state of the metal surface on the course of radiation-heterogeneous processes of paraffin decomposition. Most metals are usually characterized by the presence of thin protective oxide films on their surface, the passivation of which is disturbed under the condition of increased radiation. This leads to a change in the surface state of metals and significantly affects the course of radiation-heterogeneous processes of paraffin decomposition [5–17]. In the nanostructured surface of metals, the mechanisms and rates of radiation-chemical transformations change-local charges and their distribution, ionization energies and electron affinity, conformations and reactivity; new “forced” reactions appear; and many other anomalies are found [34–35]. The process of radiolysis of n-hexane on the surface of previously radiation-oxidized aluminum plates containing thin oxide films of various thickness to reveal the role of Al nanostructured surface in the dynamics of the decomposition process and its influence on the rate of formation and on the yield of final products of radiolysis is considered in [9, 11]. The kinetics of the accumulation of molecular hydrogen during the decomposition of n-hexane on the surface of Al in a relationship with the growth of oxide films was studied.

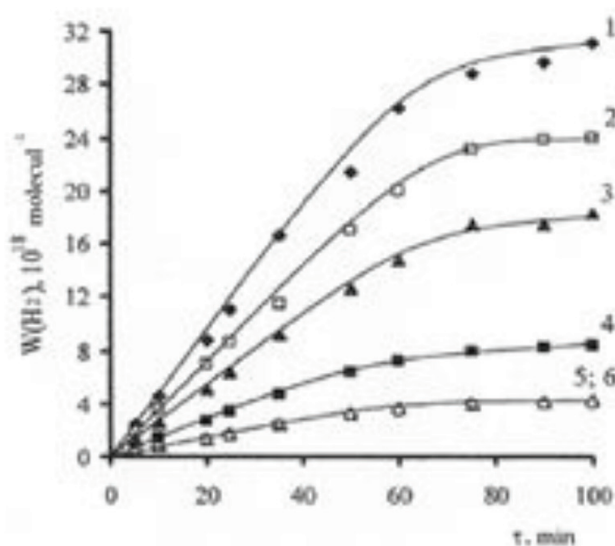
Nanostructuring of the Al surface was created by preliminary oxidation of aluminum plates in contact with water under the action of  $\gamma$ -radiation at room temperature by the method of [17]. This involved the modification of the metal surface and the formation of a nanostructured oxide coating with an unusual property. 3D AFM-images of these surfaces are shown in **Figure 9**. Radiation-oxidized plates of Al contained oxide films with a thickness of 8–600 nm on the surface [5].

The kinetics of the accumulation of molecular hydrogen in the radiolysis of n-hexane in radiation-oxidized Al/ads.n-hexane systems at room temperature has been studied. Based on the kinetic curves of  $H_2$  accumulation shown in **Figure 10**, the rates of formation and radiation-chemical yields of molecular hydrogen are determined. The radiation-chemical yields of  $H_2$  are calculated in two ways [31].

For comparison with the homogeneous phase and the characteristics of the radiation-catalytic activity, the values of the radiation-chemical yield of  $H_2$ - $G_{ads}(H_2)$  are calculated, taking into account the energy absorbed by the substance subjected to radiolysis (n-hexane) and the entire system of  $G_{total}(H_2)$ . Comparison of the values of  $G_{ads}(H_2) = 21.4\text{--}127.2$  molecule/100 eV in the heterogeneous radiolysis of n- $C_6H_{14}$  with a value of  $G(H_2) = 5.2$  molecule/100 eV for the homogeneous phase (in the absence of aluminum) under identical conditions of our experiments indicates radiation-catalytic activity of aluminum during the decomposition of



**Figure 9.** 3D images of radiation-oxidized surfaces of aluminum with thickness  $d = 8$  (a) and 600 nm (b).



**Figure 10.** Kinetics of accumulation of molecular hydrogen on radiation-oxidized aluminum surfaces containing oxide films with a thickness of 8 (1), 40 (2), 80 (3), 200 (4), 400 (5), and 600 nm (6).

n-hexane. The energy efficiency of converting the energy of ionizing radiation to the energy of molecular hydrogen is characterized with the aid of  $G_{\text{total}}(\text{H}_2)$ , and therefore, in the future, their values are used in the discussion.

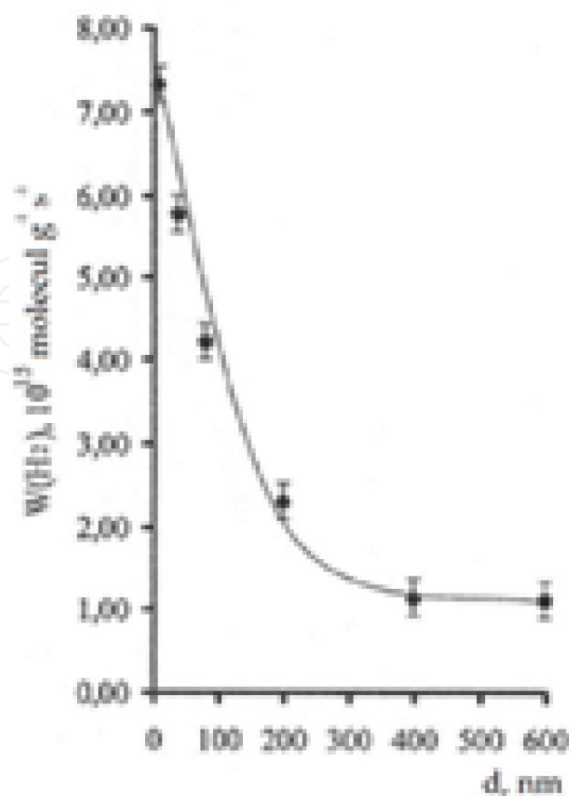
The dependence of the rate of formation of molecular hydrogen  $W(\text{H}_2)$  in the radiolysis of n- $\text{C}_6\text{H}_{14}$  in radiation-oxidized Al/ads.n-hexane systems on the thickness of oxide films on the aluminum surface is shown in **Figure 11**. As can be seen from **Figure 11**, this dependence has an exponential character. The decrease in the thickness ( $d$ ) of oxide films by  $\sim 2$  orders of magnitude (from 600 to 8 nm) is accompanied by an increase in the rate of formation of molecular hydrogen  $W(\text{H}_2)$  by  $\sim 7$  times (from  $1.1$  to  $7.6 \cdot 10^{15} \text{ g}^{-1} \text{ s}^{-1}$ ). In this case, the value of the yield of molecular hydrogen  $G_{\text{total}}(\text{H}_2)$  increases from 4.3 to 8.2 molecule/100 eV. An abrupt increase in the value of the rate of formation of  $\text{H}_2$  is observed in the region of small thicknesses ( $d = 8\text{--}80 \text{ nm}$ ), where the surface of aluminum shows comparatively high catalytic activity. A further increase in the thickness of oxide films from 80 to 600 nm leads to a monotonic decrease in the rate of formation of molecular hydrogen.

The effect of the topography of the powder surface on the rate of its oxidation and on the yield of molecular hydrogen was also found by the authors of [36, 37] in the oxidation of compact and porous beryllium and beryllium powder by steam. It was found that the interaction of compact and porous beryllium with water vapor



under certain conditions of experiments and oxidation states, the growth of the rate constant acquires the character of a jump and the yield of molecular hydrogen increases by an order of magnitude. The results obtained are explained with the dynamic instability of the oxide layer structure on the surface of compact and porous beryllium and the change in the relief surface area of the “recess-protrusion” type [36]. A direct evidence of the role of the nanostructured surface of Al containing oxide films of various thicknesses in the process of n-hexane decomposition in the heterogeneous system of radiation-oxidized Al/ads.n-hexane is the AFM data. **Figure 9** shows the AFM images of surfaces of radiation-oxidized aluminum containing oxide films of different thicknesses (a, b). Comparison of the images shows that the surface of Al containing thin oxide films ( $d = 8 \text{ nm}$ ) is characterized by its high defectiveness (**Figure 9a**).

It is known that at room temperature, the interaction of oxygen with aluminum produces clusters with a small number of atoms [38, 39] and there are more than 10 complexes on the surface of Al, differing not only in localization sites but also in structure and electronic structure. As a rule, such complexes coexist even at sufficiently high degrees of filling of the surface and interact with each other. Complexes with the greatest reactivity play the role of active centers in heterogeneous catalysis [35]. The presence of such complexes on the surface of Al in the initial stages of its oxidation is confirmed by the registration of multiquantum vibrational transitions of oxygen clusters using scanning tunneling microscopy and topographic images [35], as well as the results of RTL studies [15, 17]. Depending on the size and shape of the oxygen nanoclusters, the specific surface energy of aluminum also changes [38]. The presence of a hydroxyl cover also contributes to an increase in the adsorption of n-hexane on the oxidized aluminum surface, since OH groups are active adsorption centers [39]. Further oxidation of aluminum leads to the formation of oxide islands on its surface and the formation of a continuous intrinsic oxide layer



**Figure 11.**  
 Dependence of the rate of formation of molecular hydrogen upon the radiolysis of n-hexane in systems of radiation-oxidized aluminum/ads.n-hexane from the thickness of oxide films on the Al surface.



( $d \sim 80\text{--}600\text{ nm}$ ) as a result of introduction of oxygen atoms and migration of oxygen hole centers to the volume either from a defective surface or from internal traps along grain boundaries (**Figure 9b**). Depending on the degree of oxidation of the aluminum surface, its adsorption capacity with respect to n-hexane will vary.

The surface of Al containing thin oxide films in comparison with the surface with continuous oxide layers is characterized by a greater adsorption capacity. These processes are most effective if the thicknesses of oxide films are commensurable with the values of the mean free path of charge carriers (electrons and holes) in the metal and oxide, and the total energy transfer absorbed by the adsorbent (Al–Al<sub>2</sub>O<sub>3</sub>) to surface adsorbed n-hexane molecules is determined, which causes its decomposition by the recombination mechanism [27, 29].

## 7. Conclusion

This chapter presents the results of IR spectroscopic studies (IR reflection-absorption spectroscopy) of radiation-stimulated heterogeneous processes of adsorption, radiation-chemical decomposition (radiolysis) of hydrocarbons on the metal surface, and the radiation hydrogenation of these surfaces under the action of gamma radiation. The role of intermediate surface-active decomposition products in the process of heterogeneous radiolysis of hydrocarbons is discussed, as well as the influence of the surface relief of the metal in the dynamics of the change in the decomposition process on the rate of formation and the yield of final products of radiolysis. The chapter deals with the spectrokinetic regularities, their features, and the mechanisms of radiation-stimulated adsorption and radiolysis of hydrocarbons in heterogeneous metal-hydrocarbon systems, in particular in heterogeneous Al (Be)-n-hexane systems first time. It is shown that n-hexane absorption in Al (Be) surface happens by the molecular and dissociative mechanisms. It has been found that the decomposition of excited n-hexane molecules upon their radiolysis on the surface of aluminum and beryllium metals is accompanied by the formation of active intermediate decomposition products that can interact with the surface-active states of metals and form their hydrides, alkyls, and  $\pi$ -complexes of olefins. The final decomposition products are hydrocarbons and molecular hydrogen (H<sub>2</sub>). It is shown that during the radiolysis of n-hexane on the surface of Al and Be metals, hydrogens are partially accumulated in the form of their hydrides.

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### **Author details**

Nushaba Gadzhieva

Institute of Radiation Problems of the National Academy of Sciences of Azerbaijan,  
Baku, Azerbaijan

\*Address all correspondence to: [nushaba6@mail.ru](mailto:nushaba6@mail.ru)

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