A&A 386, 1129–1138 (2002)
DOI: 10.1051/0004-6361:20020268

Astronomy
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Astrophysics

Detection of free radicals in low-temperature gas-grain reactions of astrophysical interest

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Received 15 October 2001 / Accepted 20 February 2002

Abstract. For laboratory detection and investigation of free radicals which often appear in chemical reactions of astrophysical interest either as important intermediate or as final products, we pioneered the use of the electron paramagnetic resonance (EPR) technique, which is very effective in observing these substances. This has allowed both formyl (HCO and DCO) and methyl (CH_3 and CD_3) free radicals to be detected in a sequence of low-temperature gas-grain reactions of H and D atom addition in solid CO. The solid samples subjected to the EPR study were obtained by simultaneous independent deposition of CO molecules and either H or D atoms on the substrate cooled to liquid helium temperatures. The sequence of the H-atom addition gas-grain reactions in solid CO is acknowledged to be among the fundamental processes responsible for the synthesis of organic molecules in interstellar cloud dust grains. The present observation of the above free radicals confirms that the solid-state gas-grain sequence of the reactions is efficient at low temperatures; it also suggests that there should be considerable concentrations of formyl and methyl radicals in the ISM. Another study concentrated on the formation of ethyl free radicals (C_2H_5) in a low-temperature gas-grain reaction of H-atom abstraction from a C_2H_6 molecule by free H-atom in solid CH_4. These experiments were carried out by deposition onto a substrate, cooled by liquid helium, of a flow of CH_4 molecules containing a small amount of impurities such as ethane molecules (C_2H_6), free H-atoms and CH_3 radicals formed in a discharge in a pure gaseous methane. EPR spectra of CH_3 radicals, H-atoms, and C_2H_5 radicals matrix-isolated in solid CH_4 were detected. The relative concentrations of the radicals were found to depend on the experimental conditions. The abstraction reaction, $C_2H_6 + H \rightarrow C_2H_5 + H_2$, took place in CH_4-ice.

Key words. astrochemistry – molecular processes – methods: laboratory – ISM: dust, extinction – ISM: molecules – ISM: atoms

1. Introduction

In interstellar clouds, comets and the atmospheres of solar planets, a number of organic compounds have been observed. In dense interstellar clouds, starlight is largely excluded and gas-phase ion-molecule reactions become less important for the formation of interstellar molecules. This suggests that interstellar dust grains play an important role for the chemical evolution in the cold dark interstellar medium. In order to explain both the interstellar solid state reactions of the synthesis of organic molecules and their transformation and to verify the assumptions of plausible synthesis reactions, conditions were modeled, in a number of laboratories, which are similar to those in interstellar dust, cometary ices and planetary atmospheres. At these conditions, the products of the relevant low-temperature solid state reactions were studied (e.g. Gerakines et al. 1995, 1996, 2000; Ehrenfreund et al. 1996, 1997, 1999; Hiraoka et al. 1995, 1998, 1999, 2000; Bernstein et al. 1995; Pendelton et al. 1999; Sandford et al. 2000). Of special interest is a modeling of gas-grain reactions involving hydrogen atoms (Hiraoka et al. 1995, 1998, 1999, 2000) and the products formed in the cometary and interstellar ice analogs with various impurities subjected to action by UV radiation, ion bombardment and others (Gerakines et al. 1995, 1996, 2000; Ehrenfreund et al. 1996, 1997, 1999; Bernstein et al. 1995; Pendelton et al. 1999; Sandford et al. 2000). For observation and study of such low temperature reactions in the laboratory, a variety of analytical methods: IR spectroscopy, mass-spectrometry, gas chromatography, nuclear magnetic resonance (NMR) is used (Gerakines et al. 1995, 1996, 2000; Ehrenfreund et al. 1996, 1997, 1999; Hiraoka et al. 1995, 1998, 1999, 2000; Bernstein et al. 1995; Pendelton et al. 1999; Sandford et al. 2000). Though they offer a number of advantages, these methods are of limited usefulness.

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Some of them (NMR, IR spectroscopy) are not sensitive enough, while other (mass-spectrometry) do not permit studying in situ and involve thermal desorption and heating of the sample, which may lead to the observation of products different from those in the initial low-temperature reactions in the solid state sample. In the present study, we employed the electron paramagnetic resonance (EPR) method which makes it possible to observe and study, in situ and in real time, the products of low-temperature reactions at any temperature of the solid state sample. Very importantly, this method allows registration, more accurate identification and investigation of free radicals with unpaired electron spins which are frequent as intermediate products of such reactions. Moreover, the EPR method is a very sensitive one.

2. Experimental procedure

The solid samples under study are obtained by gas condensation on the thin-walled bottom of a quartz finger filled with liquid helium. Located at the center of the microwave cavity of the EPR spectrometer, the bottom is used as a substrate. Both the gas discharge and the matrix gas flow passing through a separate inlet tube to avoid the gas discharge can be cooled down to liquid nitrogen temperature. The products of radio-frequency gas discharge without intermediate feeding tubes are supplied directly onto the substrate in vacuum preventing their decay on the tube walls. Thus, the sample is obtained directly in the cavity of the EPR spectrometer, allowing an EPR observation of the sample during the condensation and a study of short-lived centres (e.g. free radicals) due to the gas discharge products.

The experimental set-up consists of a 3 cm EPR spectrometer with a microwave cavity cooled by liquid nitrogen vapor, a gas filling and purification system, a RF oscillator for exciting an electrodeless discharge, measuring instruments, and pumping facilities.

Figure 1 shows the major section of the experimental set-up: the microwave cavity of the 3 cm EPR spectrometer, the low-temperature gas discharge device and the substrate cooled by liquid helium, on which the sample is condensed.

Here, 1 is the cylindrical H_{011} – mode microwave cavity of the *X*-band EPR spectrometer, 2 is the bottom of quartz finger 3, filled with liquid helium, and 4 is a waveguide. Bottom 2 of the quartz finger is a low-temperature substrate for the gases being condensed. An electrodeless RF gas discharge is excited in glass tube 5 with outlet 6 of 0.2–0.6 mm diameter. The matrix gas can be supplied to substrate 2 by glass tube 7 and further by quartz tube 8 inserted into the cavity (channel B). The end of quartz tube 8 is located close (3 mm) to bottom 2 of the quartz finger, which facilitates effective freezing out of the matrix gas.

Whole device presented in Fig. 1 is cooled externally with liquid nitrogen vapor (LN_2) and its temperature can be varied from 77 to 300 K.

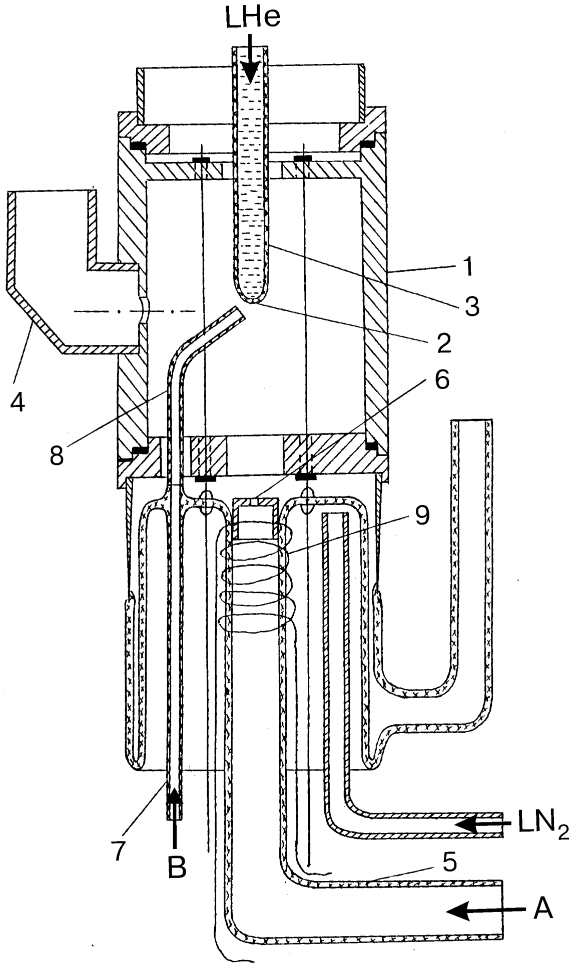

Fig. 1. The main part of the experimental set-up including the microwave cavity of the EPR spectrometer, the gas discharge system, the second gas inlet tube avoiding gas discharge, and the quartz finger cooled by liquid helium (LHe) with the sample condensed onto the bottom of the quartz finger as on a substrate (for notations see the text).

A RF (14-MHz) oscillator is used to sustain the discharge. The RF power is fed through a coaxial cable to coil 9 wound over the gas discharge tube 5.

The experimental procedure is as follows. The gas in channel A is passed through the liquid-nitrogen-vapor-cooled gas discharge tube 5, in which an electrodeless RF discharge is excited. Ground-state gas atoms or molecules, together with the gas discharge products pass through outlet 6 of discharge tube 5 into the evacuated cavity and reach bottom 2 of quartz finger 3 filled with liquid helium at 1.2–4.2 K. Pure additional matrix gas, also cooled by liquid nitrogen vapor (LN_2), may be passed through tubes 7–8 (channel B), avoiding the gas discharge, onto the substrate. The gas from channel A is condensed together with discharge products onto substrate 2 at a temperature of 1.2–4.2 K either with or without the gas flux passing through channel B. In the present study, the sample deposition usually takes about 30–60 min. Upon completion of the deposition, the fluxes from channels A and B are switched off, and EPR spectra of the sample

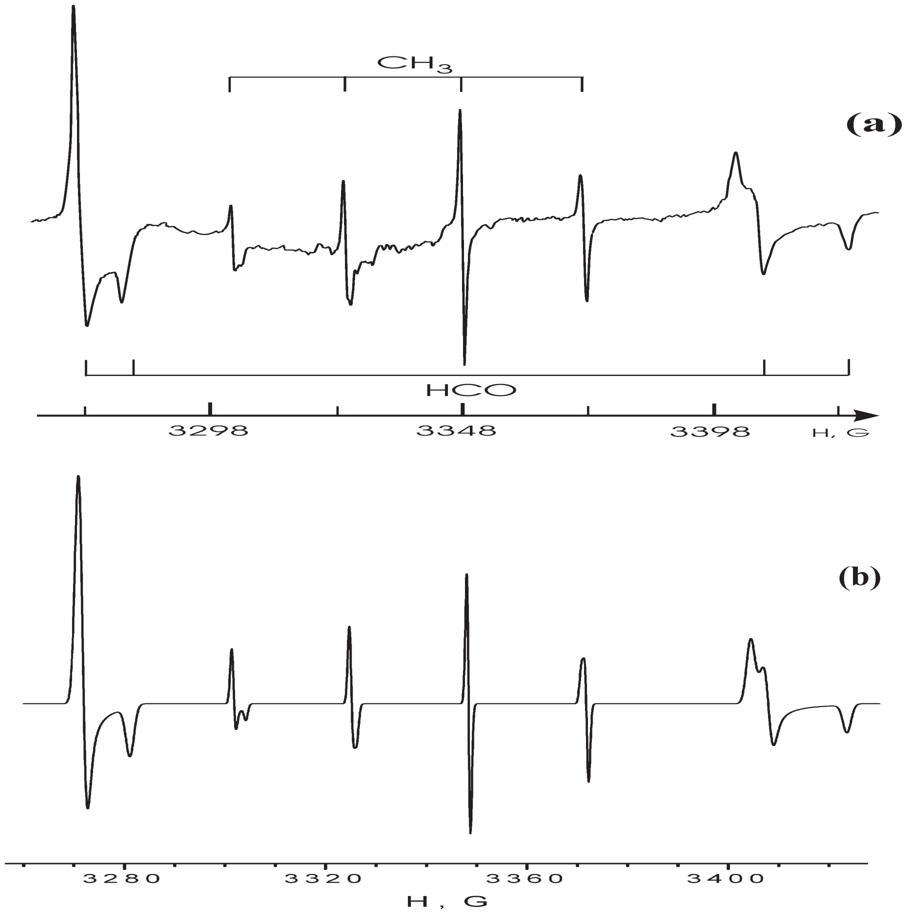

Fig. 2. a) The EPR spectrum of HCO and CH_3 free radicals formed in a sequence of gas-grain H-atom addition reactions in solid CO at 4.2 K. The EPR resonance frequency $f_{\mathrm{res}} =$ 9353.04 MHz. **b)** The simulated EPR spectrum for HCO and CH_3 free radicals in solid CO. $f_{\mathrm{res}} =$ 9353.0 MHz. (For details, see text).

are taken. While the sample was obtained and the spectra were recorded, the substrate temperature could be set to 1.2–4.2 K by pumping out the helium vapor from bath 3.

The experimental procedure and set-up have been described in papers by Zhitnikov & Dmitriev (1994, 1995).

3. Gas-grain consecutive H-atom addition reactions in solid CO

Stepwise low-temperature hydrogenation reactions taking place on and in interstellar dust grains are known to be among the fundamental processes responsible for the synthesis of organic molecules in interstellar clouds. In particular, the low-temperature consecutive gas-grain H-atom addition reactions in solid CO are considered in (Hiraoka et al. 1998). Of these, the sequence of reactions of H atoms with CO is an important case:

$$\begin{array}{rcl} \mathrm{CH_4} \leftarrow \mathrm{CH_3} & + & \mathrm{OH} \rightarrow \mathrm{H_2O} \\ & \uparrow & \\ \mathrm{CO} \rightarrow \mathrm{HCO} \rightarrow \mathrm{H_2CO} \rightarrow & \mathrm{CH_2OH} & \rightarrow \mathrm{CH_3OH} \\ & \downarrow & \\ \mathrm{CH_4} \leftarrow \mathrm{CH_3} \leftarrow \mathrm{CH_2} & + & \mathrm{H_2O}. \end{array} \tag{1}$$

It is known that an exothermic reaction of the H atom with CO in spite of the energy barrier is liable to proceed even at low temperatures due to tunneling. This sequence of reactions of H atoms with solid CO was previously investigated in laboratory conditions by mass spectrometry (Hiraoka et al. 1998) which could record only closed-shell and stable molecules such as methane (CH_4), methanol (CH_3OH), and formaldehyde (H_2CO) among the reaction products. However, the observation of free radicals: CH_2OH, formyl (HCO), methyl (CH_3), hydroxyl (OH), and methylene (CH_2), which appear as intermediate products is of great importance for the confirmation and detailed investigation of this solid-phase process. Intermediate reaction products, such as free radicals, cannot be detected by mass spectrometry, but by electron paramagnetic resonance (EPR) they can be detected.

The present section is devoted to the detection and study of free radicals in the above sequence of low-temperature reactions of H atoms with solid CO using EPR. The experimental procedure involved co-deposition of gaseous CO supplied through channel B (see Fig. 1) and a flow of molecular hydrogen gas-discharge products containing abundant H atoms from channel A onto a quartz substrate at 1.3–4.2 K. Normally, the deposition took 30 min; after this *X*-band EPR spectra of the sample were recorded. Thus a process was simulated which is similar to the one what takes place in interstellar dust grains.

The experiments yielded the spectra shown in Fig. 2a. These spectra are due to HCO and CH_3 radicals matrix-isolated in solid CO. The HCO spectrum is a doublet with a separation between the hyperfine components of 140 G and $g = 2.00$. The CH_3 spectrum is a quartet with $g = 2.00$ and an average separation between the adjacent lines of 23.5 G. The numbers and positions of the lines very closely match the known values of HCO (Adrian et al. 1962) and CH_3 (Adrian et al. 1985), which strongly substantiates that they have been formed in the present experiments. This is the first occasion of the detection of free radicals in a process of gas-solid type where organic substances are synthesized. The observed HCO and CH_3 EPR spectra indicate an anisotropy of these paramagnetic centers (trapped radicals) in solid CO. Figure 2b shows a simulated EPR spectrum for HCO and CH_3 free radicals trapped in a polycrystalline solid CO. The EPR spectra for formyl and methyl radicals were simulated from the following parameters for the hyperfine structure, A, tensors and g-factor tensors: for HCO, $A_{xx} = 132.89$ G, $A_{yy} = 136.32$ G, $A_{zz} = 142.11$ G, $A_{yz} = 5.79$ G, $g_x = 2.0011$, $g_y = 1.9997$, $g_z = 1.9930$, a linewidth of 1.6 G and Gaussian line shape were assumed (see also Adrian et al. 1962); for CH_3, $A_{xx} = A_{yy} = A_\perp = 23.50$ G, $A_{zz} = A_\parallel = 22.20$ G, $g_x = g_y = g_\perp = 2.0026$, $g_{zz} = g_\parallel = 2.0022$ and a linewidth of 0.75 G and the Gaussian line shape were assumed. The simulated spectrum in Fig. 2b shows the concentration of CH_3 radicals to be about 2% of the HCO concentration. This gives new information on the concentrations of the intermediate products in the Seq. (1).

The results lend support to the validity of the above sequence of hydrogenation reactions in solid CO which are likely to occur in the interstellar medium. After H_2, CO is the most abundant molecule in dense interstellar clouds. The other free radicals, expected to be formed in this process, were not observed reliably in the present experimental conditions. These conditions are currently being changed (by increasing the substrate temperature and varying the condensation procedure) in order to be able to record these radicals. The radicals are hard to observe, probably because of a great difference in rate constants between reactions (tunneling for the most part) in Seq. (1). Such a difference would have the effect of decreasing the concentration of those intermediate products that are result of a reaction with a low rate constant and (or) hydrogenated with a high rate constant and vice versa.

In many studies it was experimentally confirmed (Hiraoka et al. 1995), that hydrogen atoms diffuse over long distances in solid matrices and take part in tunneling reactions in the temperature region of 4–20 K. In contrast to mobile H atoms, the diffusion of atoms other than H and of molecules at cryogenic temperatures has not been reported so far. The high mobility of H atoms on solids suggests that hydrogen plays a major role in the solid state chemical evolution of dense clouds, i.e. they diffuse long distances on grain surfaces and in mantles and react with trapped and immobilized atoms and molecules to form hydrogenated products in the mantles. In the work by Hiraoka et al. (1995), the reactions between atomic hydrogen and nitrogen atoms trapped in an N_2 matrix in the temperature range of 10–30 K were studied to check the possibility of ammonia synthesis in the grain mantles. It was concluded that H atoms migrated into the N_2 matrix to a depth of at least 200 N_2 monolayers and hydrogenated N atoms trapped in the N_2 matrix (Hiraoka et al. 1995). A CO matrix is isoelectronic and very similar to a N_2 matrix (their melting points $T_m(CO) = 68$ K, $T_m(N_2) = 63$ K).

The available data suggest that the Seq. (1) with the formation of HCO and CH_3 radicals (Fig. 2a) may occur in our experiments as follows. The CO molecules from channel B as well as H_2 molecules and H atoms from channel A, Fig. 1, simultaneously enter the sample surface. The CO flow is estimated to be an order of magnitude greater than that of H_2 molecules, while H atoms constitute a portion of the H_2 quantity; the temperature of all particles incident on the sample being in the range of 80 to 100 K. For this reason there exists a steadily growing solid CO layer which traps hydrogen atoms. On and under the surface, all products of reactions (1) are immobilized, while the light hydrogen atoms trapped there are highly mobile and diffuse long distances taking part in the Seq. (1) of the H-atom addition to the intermediate products. This is the reason why the Seq. (1) yields not only the first intermediate product, HCO, but also the CH_3 radical as an intermediate product which is also observed in our experiments. This model is also supported by the fact that no EPR spectra of matrix-isolated H-atoms were observed, which testifies that nearly all trapped hydrogen atoms disappear through the Seq. (1), except for atoms which have escaped the surface or taken part in the recombination reaction to form the H_2 molecule.

The fact that the HCO and CH_3 spectra are really due to the Seq. (1) in solid CO (and not from, for example, the possible small CH_4 impurity in the gaseous H_2 discharge) was checked in additional experiments, where D_2 was passed through the discharge zone instead of H_2. Simultaneously, pure CO was fed through channel B. The spectra obtained in these runs, (Fig. 3a), are composed of only DCO and CD_3 free radical spectra. No HCO or CH_3 radicals are seen in Fig. 3a. When divided into two parts, these spectra coincide, respectively, with those of DCO obtained by Adrian et al. (1962) in photolysis experiments and of CD_3 by Toriyama et al. (1979). Figure 3b shows a simulated EPR composite spectrum of the mixture of DCO and CD_3 radicals trapped in a polycrystalline solid CO. The spectrum is a sum of two neat spectra for DCO and CD_3 radicals in CO matrix shown in Figs. 3c and d, respectively. The EPR spectra for formyl and methyl radicals were simulated from the following parameters for the hyperfine structure, A, tensors and g-factor tensors: for DCO, $A_{xx} = 20.45$ G, $A_{yy} = 20.97$ G, $A_{zz} = 21.86$ G, $A_{yz} = 0.89$ G, $g_x = 2.0033$, $g_y = 2.0019$, $g_z = 1.9952$, a linewidth of 0.9 G and a mixture of 1:1 Gaussian to Lorentzian lines were assumed (see also Adrian et al. 1962); for CD_3, $A_{xx} = A_{yy} = A_\perp = 3.62$ G, $A_{zz} = A_\parallel = 3.42$ G, $g_x = g_y = g_\perp = 2.0026$, $g_{zz} = g_\parallel = 2.0022$

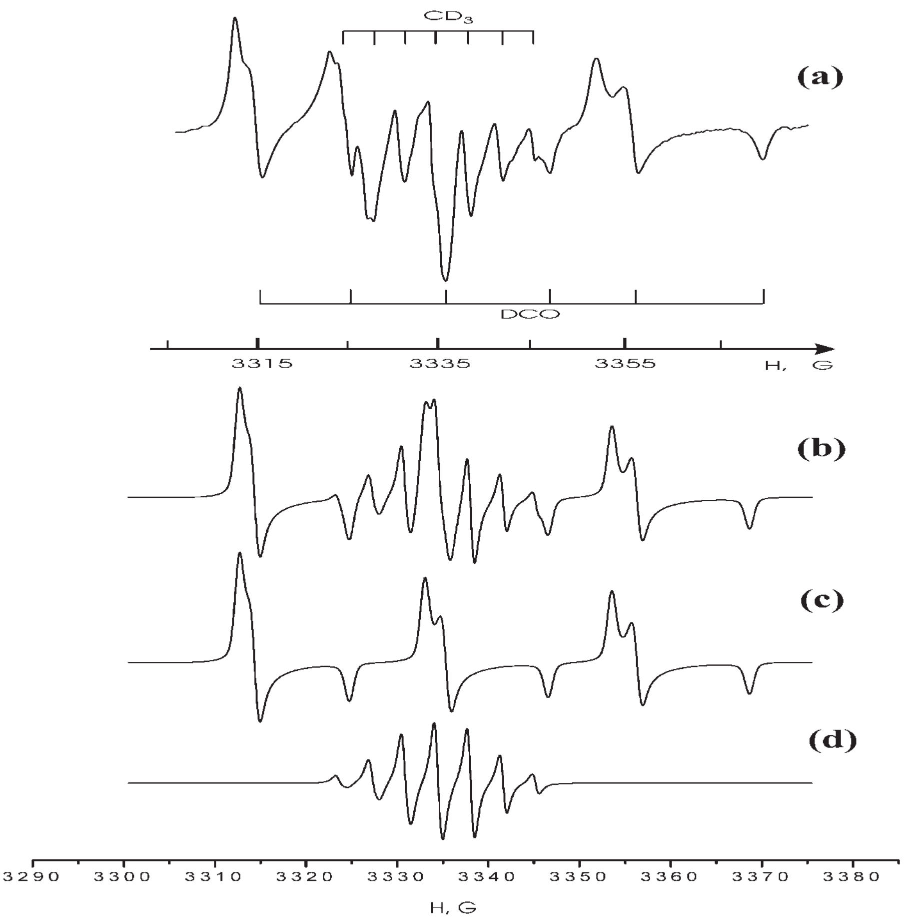

Fig. 3. a) The EPR spectrum of DCO and CD_3 free radicals formed in a sequence of gas-grain D-atom addition reactions in solid CO at 4.2 K. The EPR resonance frequency f_{res} = 9345.66 MHz. **b)** The simulated EPR spectrum of the free radical mixture of DCO and CD_3 trapped in solid CO. **c)** The simulated EPR spectrum of DCO radical trapped in solid CO, which is one component to contribute to the composite two-component spectrum **b)**. **d)** The simulated EPR spectrum of CD_3 radical trapped in solid CO which is the second component of the spectrum **b)**. In the simulation EPR resonance frequency was taken equal 9345.7 MHz. The simulation parameters are given in the text.

and a linewidth of 0.75 G and Lorentzian line shape were assumed. The best fit of the simulated curve (b) is obtained from a concentration of CD_3 radical of about 1% of the DCO concentration in solid CO. After the sample condensation was completed, repeated registration of the EPR spectra of samples at fixed temperatures 1.5–4.2 K showed no changes in the spectra like those depicted in Figs. 2a and 3a for several hours. Thus, no reactions of type (1) occur in the sample in the above temperature range with no flow of CO molecules and H or D atoms from the gas phase. In that case, the concentrations of methyl and ethyl radicals in the sample did not change noticeably for hours at least.

Thus, the present results provide further direct support for the gas-grain Seq. (1).

The above results allow the suggestion to be made that HCO and CH_3 radicals may accumulate in large concentrations in interstellar gas grains, cometary ices and planetary atmospheres. The optical spectra of the free radicals HCO and CH_3 are well know (Bernstein et al. 1995; Gerakines et al. 1996). It may be beneficial to study in the laboratory the optical spectra of these radicals together with the EPR spectra in various matrices of astrophysical interest. Observation of these radicals and an estimate of their concentration in the interstellar medium will provide important information on the transformation of inorganic molecules to organic ones in space conditions.

4. Low-temperature reactions between the CH_4 gaseous discharge products trapped in the solid CH_4 matrix

Methane (CH_4) and ethane (C_2H_6) have been found in comets and in the atmospheres of several solar planets. The observation of saturated hydrocarbons either frozen on grains or as gases, provides strong evidence that the reactions on dust grains play an important role in the interstellar chemical evolution. To explain the high (>0.5) C_2H_6/CH_4 ratio in comets, a mechanism was proposed of CH_4 conversion into C_2H_6 through the production of C_2H_6 in icy grain mantles in the clouds of origin either by photolysis of CH_4-rich ice (Gerakines et al. 1996; Hiraoka et al. 1999) or by hydrogen-addition reaction to C_2H_2 condensed from the gas phase (Hiraoka et al. 1999; Sandford et al. 2000). Other pathways of the formation of C_2H_6 molecules trapped in the solid CH_4 matrix through the gas-grain processes are discussed here. Using the EPR technique, we studied low-temperature reactions in the solid CH_4 of the products of gaseous discharge in CH_4.

Figure 4 shows an EPR spectrum of the sample obtained by 30 min condensation of CH_4 gas from channel A onto a substrate at 4.2 K together with the discharge products formed in the channel (Fig. 1). During this process, no gas flow was fed through channel B. In turn, the gas flux from channel A was set at minimum so as to make

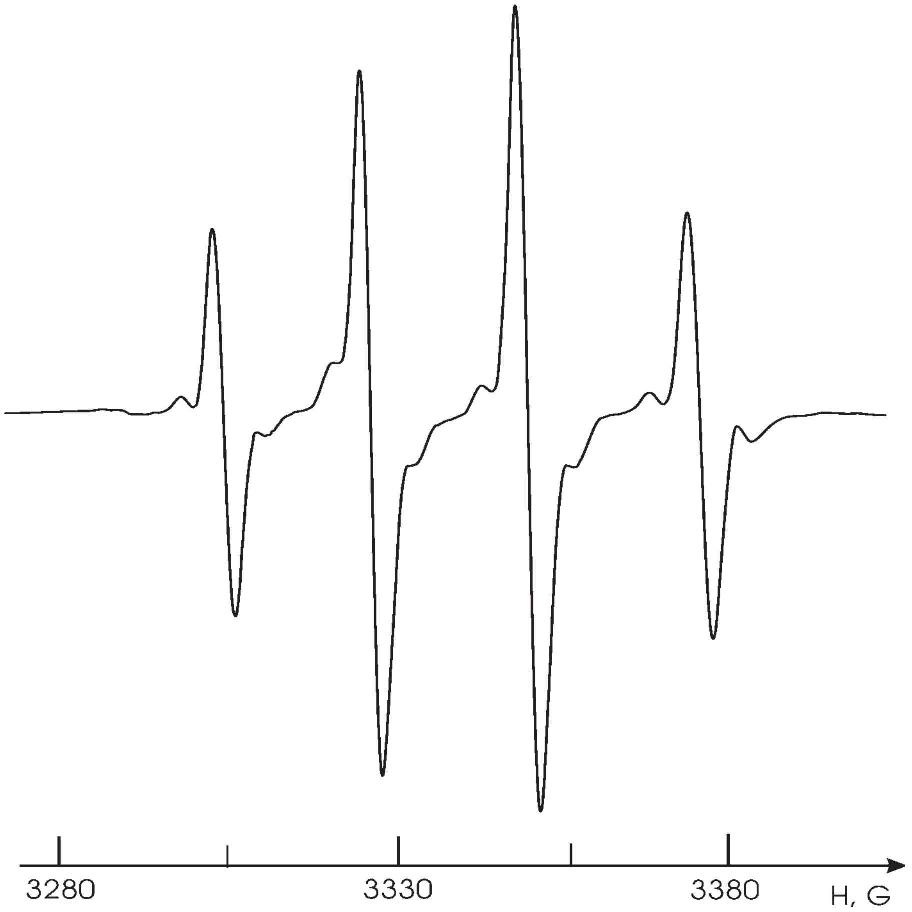

Fig. 4. EPR spectrum of CH_3 free radicals trapped at 4.2 K in CH_4 matrix which form under condition of small gas flow fed through the gas discharge onto the substrate. EPR resonance frequency $f_{\mathrm{res}} = 9355.22$ MHz.

it possible for the discharge to be operated. Examining Fig. 4, one can see only four-component spectrum which is characteristic of CH_3 radical in a CH_4 matrix and well studied by photolysis (Adrian et al. 1985). In the present experiment, CH_3 radicals are formed in the gas discharge through dissociation of part of the CH_4 molecules:

$$CH_4 \rightarrow CH_3 + H. \quad (2)$$

The CH_3 radicals are subsequently trapped in solid CH_4. These records showed no EPR spectrum of hydrogen atoms. In the next experiment, two flows were simultaneously incident onto the substrate at the same substrate temperature of 4.2 K: one with the gas discharge products from channel A, with a flux matching that of the previous experiment, and the other of pure CH_4, an order of magnitude greater, from channel B. The EPR spectrum obtained after 30 min condensation is shown in Fig. 5a. This spectrum differs from that in Fig. 4 and matches the well-known spectrum of C_2H_5 ethyl radical (Cochran et al. 1970; Toriyama et al. 1979). It is reasonable to suppose that the spectrum in Fig. 5a is actually the sum of two spectra: for CH_3 and C_2H_5 radicals. By computer simulation (Toriyama et al. 1979), the spectrum could be matched assuming a ratio C_2H_5 to CH_3 of 7 to 3 (Fig. 5b). Figures 5c and d show simulated EPR spectra for C_2H_5 and CH_3 radicals respectively trapped in a polycrystalline solid CH_4. These spectra are added to obtain the two component composite spectrum (b). The spectra (c) and (d) for ethyl and methyl radicals were simulated from the following parameters: for C_2H_5, $A_{\parallel} = A_{zz} = 29.0$ G, $A_{\perp} = A_{xx} = A_{yy} = 18.4$ G for the α-H coupling and $A_{\parallel} = 29.2$ G and $A_{\perp} = 27.4$ G for the β-coupling, the g-factor being $g = 2.00232$; for CH_3, $A = 23.0$ G and $g = 2.00214$ (isotropic spectrum). A Gaussian lineshape with 3.5 G linewidth were assumed. (See also Toriyama et al. 1979.)

Note, that the appearance of a C_2H_5 spectrum in the second experiment was matched by the spectrum of hydrogen atoms. The purchased methane gas was of 99.99% purity.

With condensation at a substrate temperature lower than 4.2 K, the EPR spectrum shows the lines of the C_2H_5 radical even at the minimum CH_4 flow through channel A that can be set in the experimental conditions, and with no gas flow through channel B. These experiments yielded C_2H_5 lines even at 3.7 K. They became more intense with further decrease of the substrate temperature, T_{sub}. At $T_{\mathrm{sub}} = 1.5$ K, the spectra were similar to those in Fig. 5a. It turned out that even at $T_{\mathrm{sub}} = 4.2$ K and a flow through the channel A only, the C_2H_5 lines may be obtained by merely increasing the flow through channel A. In all cases in which the EPR spectrum of C_2H_5 radicals showed up it

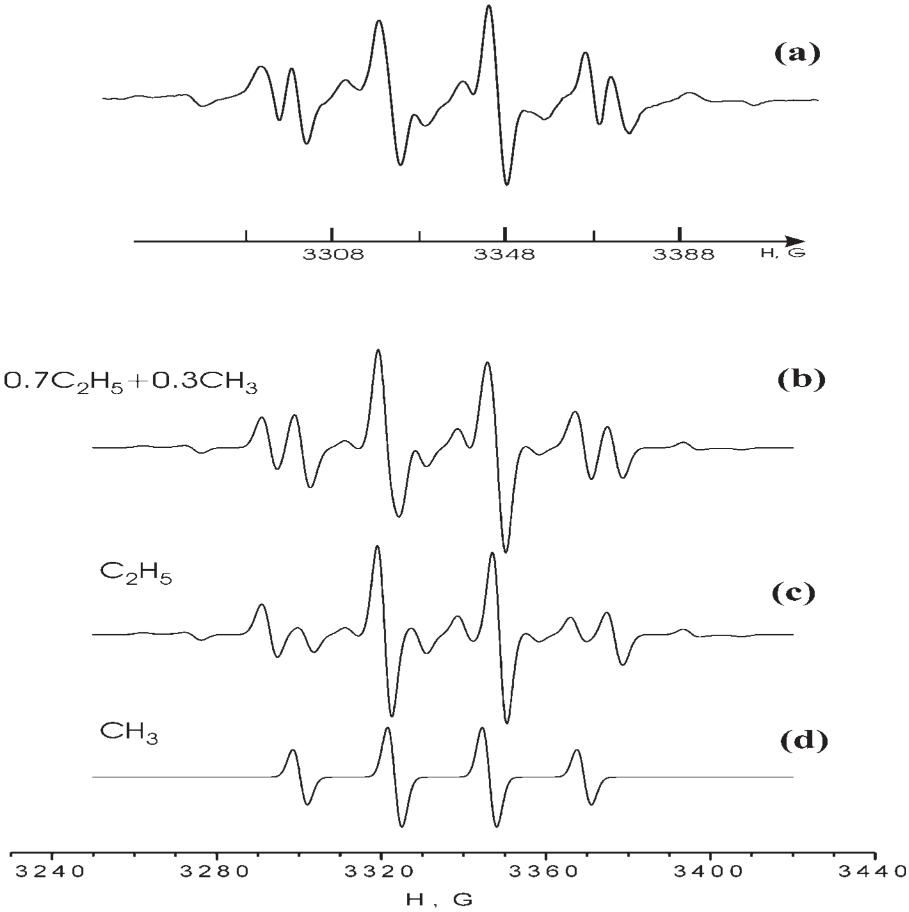

Fig. 5. **a)** The EPR spectrum of a mixture of C_2H_5 and CH_3 free radicals formed in a solid CH_4 sample that grows at 4.2 K with an addition of large CH_4 gas flow avoiding the discharge zone. C_2H_5 forms through reactions between gas discharge products being trapped in solid CH_4. The EPR resonance frequency $f_{\text{res}} = 9348.75$ MHz. **b)** The simulated EPR spectrum of the free radical mixture of C_2H_5 and CH_3 trapped in solid CH_4. The best fit of the simulated curve is obtained from a ratio for the C_2H_5 and CH_3 contents of 7:3. **c)** The simulated EPR spectrum of C_2H_5 radical trapped in solid CH_4, which is one of two components contributing to the composite spectrum **b)**. **d)** The simulated EPR spectrum of the CH_3 radical trapped in solid CH_4 which is the second component of spectrum **b)**. The EPR resonance frequency of the simulated spectrum equals 9348.7 MHz. The parameters of the simulation are given in the text.

was accompanied by the EPR spectrum of matrix isolated hydrogen atoms.

The obtained results can be interpreted as follows. It seems that most of the products formed in a methane gas discharge, which enter the cold substrate together with CH_4 molecules, is composed of hydrogen atoms, CH_3 radicals produced by dissociation of CH_4 molecules by electron impact, reaction (2), and C_2H_6 molecules formed in the discharge. The results of the mass-spectroscopy analysis of the products formed in a pure CH_4 gas discharge have been presented by Toyoda et al. (1989), Kojima et al. (1989), Sugai et al. (1990), Sugai & Toyoda (1992), Dagel et al. (1996). For a 5–25 W radio-frequency discharge with a plasma temperature of about 400 K and a low CH_4 pressure of ~0.005–0.02 Torr, the concentrations of the discharge products were found to be $[CH_3] = (2.5–4.7) \times 10^{11}$ cm^{-3}, $[C_2H_6] = 10^{11}–10^{12}$ cm^{-3}, $[CH_2] \sim 10^9$ cm^{-3}, while, the [H] value was estimated not to exceed 10^{13} cm^{-3}. It was also verified that at low pressures the electron impact dissociation of CH_4 molecules, reaction (2), was the major mechanism for producing CH_3 radicals. It turned out that at a CH_4 pressure in the discharge above 0.06 Torr, the $CH_4^+ + CH_4 \rightarrow CH_3 + C_2H_5^+$ ion-molecule reaction started to dominate the production of CH_3 and at higher pressure (>0.1 Torr) CH_3 radicals were produced almost exclusively by this process. At a CH_4 pressure of 0.3 Torr and 10 W RF power supplied to the discharge, the CH_3 density averaged over the discharge volume was estimated to be ~(6–7) × 10^{11} cm^{-3} (Sugai et al. 1990). The major loss channel of CH_3 radicals is due to the three-particle reaction of the radical recombination with participation of a CH_4 molecule:

$$CH_3 + CH_3 + (CH_4) \rightarrow C_2H_6 + (CH_4). \tag{3}$$

The same reaction, (3), is the major source of C_2H_6 molecules depleted through the electron collision dissociation:

$$C_2H_6 \rightarrow C_2H_5 + H. \tag{4}$$

The C_2H_5 density in the discharge seems to be very low because unlike the CH_3 radical, the C_2H_5 radical possesses a high sticking probability and the principal fate of C_2H_5 appears to be surface loss through reactions with other free radicals and H-atoms from the discharge (Dagel et al. 1996).

In the present study, the CH_4 pressure in discharge was set to a value of the order of several Torrs, i.e. several times as great as in the cited papers by Toyoda et al. (1989), Kojima et al. (1989), Sugai et al. (1990), Sugai & Toyoda (1992), and Dagel et al. (1996). It is hard to predict how such an increase in the CH_4 pressure would alter the C_2H_6 density in the gas discharge, since the rising

CH_4 base pressure is expected to increase the probability of the three-particle reaction, (3), with a greater yield of C_2H_6. On the other hand, this increases the probabilities of the C_2H_6 dissociation in reaction (4) due to the higher electron concentration, and also of the three-particle recombination CH_3 + H + (CH_4) → CH_4 + (CH_4) which competes with reaction (3). The most significant difference, though, between our methane discharge and those of Toyoda et al. (1989), Kojima et al. (1989), Sugai et al. (1990), Sugai & Toyoda (1992), Dagel et al. (1996) is that the walls of the discharge tube in the present study were cooled with liquid nitrogen vapor of about 120 K, while in the cited papers the walls were at temperatures of 300–400 K. At 120 K, the saturated C_2H_6 vapor pressure is about a factor of 1.25×10^4 lower than the pressure at 300 K. This implies that the sticking probability on the 120 K walls of a gas discharge tube is far above that on the 300–400 K walls. An estimate shows that the C_2H_6 density would decrease with the increase of the sticking coefficient. Such a low wall temperature of the discharge tube would, therefore, reduce the relative concentration of C_2H_6 molecules in our methane discharge with the CH_4 density estimated to be about (3–6) $\times 10^{16}$ cm^{-3}.

Apart from the trapping of C_2H_6 molecules coming from the gas discharge onto the sample, ethane molecules may form during the condensation, onto the sample surface, of the CH_4 flow which has passed through the discharge and contains methyl radicals which may take part in reaction (3). A contribution to this surface reaction is expected from those CH_3 radicals which meet before loosing their mobility and becoming matrix-isolated. C_2H_6 molecules thus formed are expected to be trapped more easily in the matrix than CH_3 radicals. It is hard to assess, at present, the quantity of matrix-isolated ethane molecules produced by the above process. Finally, the C_2H_6 molecules trapped in the matrix can form through the photolysis of the parent CH_4 molecules due to UV radiation from the gas discharge (this process has been described by Gerakines et al. 1996). The contribution of this process is, however, likely to be small under the present experimental conditions because of the weak discharge used and the low radiation intensity.

It follows from the above discussion that in our experiments, the sample of solid CH_4 being condensed onto the substrate at 1.5–4.2 K preferably traps CH_3 radicals, H-atoms, C_2H_6 molecules, and a small amount of other molecules, like C_mH_n. The link between the processes described and the experimental results can be verified by considering the EPR spectrum in Fig. 4. It shows that, under certain conditions, matrix isolation of CH_3 radicals may occur while neither C_2H_5 radicals nor hydrogen atoms are trapped. The matrix isolation of hydrogen atoms is discussed below. It must also be stressed that Fig. 4 suggests that no appreciable amount of C_2H_5 radicals comes from the discharge onto the growing sample; otherwise this radical should be visible in Fig. 4, because heavy C_2H_5 radicals are expected to be trapped with no less efficiency than light CH_3 radicals.

In our experiments, C_2H_5 radicals matrix-isolated in the CH_4 solid (Fig. 5a) can be assumed to form as follows. The surface layer of the growing sample must include mobile hydrogen atoms that have come from the discharge as a product of dissociation reaction (2). These highly mobile hydrogen atoms travel for long distances in the surface layer and, encountering immobilized C_2H_6 molecules, they abstract an H-atom through the well-known abstraction reaction (Toriyama et al. 1979; Adrian et al. 1994):

$$C_2H_6 + H \rightarrow C_2H_5 + H_2. \tag{5}$$

When both the concentration of H atoms and their mobility in the surface layer are high enough, abstraction reaction (5) may appreciably contribute to the yield of matrix-isolated C_2H_5 radicals. Matrix-isolated C_2H_5 radicals formed in this way, as well as trapped CH_3 radicals become visible in the EPR spectrum shown in Fig. 5a. The above gas-grain reactions should be of considerable importance in the interstellar medium.

Thus, we conclude that the rate of formation of matrix-isolated ethyl radicals can be defined as

$$\frac{\mathrm{d}[C_2H_5]}{\mathrm{d}t} = k_\mathrm{r}'[\mathrm{H_r}][C_2H_6]. \tag{6}$$

Here, $[C_2H_6]$ is the ethane molecule concentration in the sample, which seems to be independent of the substrate temperature. An EPR spectrum of CH_4 matrix-isolated C_2H_5 radicals formed in reaction (5) similar to that in Fig. 5 was reported earlier by Toriyama et al. (1979) and Bhattacharia et al. (1981). They observed the radical formation with a molecular ethane impurity in CH_4 of 0.5–0.8%. A sample of CH_4 solid was γ-irradiated at 4.2 K. The subsequent temperature rise detrapped hydrogen atoms which migrated through the crystal to encounter ethane molecules and abstract a hydrogen atom, thus forming ethyl radicals. Turning to Eq. (6), $[\mathrm{H_r}]$ is the density of hydrogen atoms in the surface layer of our sample which are mobile enough to participate in reaction (5). The conditions that have an effect on the density of such atoms will be discussed below. Bhattacharya et al. (1981) found that the H-atoms trapped in CH_4 and CD_4 matrices become largely immobilized below 12 K. The rate constant, k_r', is unavailable in the literature. This constant seems to depend on the diffusion coefficient, D_H, of hydrogen atoms at the solid CH_4 surface, as well as on its temperature. It follows from the obtained results, however, that the C_2H_5 yield may vary considerably in the narrow temperature range from 4.2 to 3.7 K, where k_r' may be taken to be constant. Thus, the relationship between the C_2H_5 yield and experimental conditions we observed relates to a change in the $[\mathrm{H_r}]$ quantity, i.e. this yield is supposedly governed by the density of hydrogen atoms which remain mobile long enough to encounter and react with trapped C_2H_6 molecules. Bhattacharya et al. (1981) found that below 12 K the trapped H-atoms in solid CH_4 do not decay significantly over many minutes. They observed that the trapped H atoms in CH_4 could react with captured C_2H_6 to form C_2H_5 when the temperature was increased above 12 K. Consider the phenomena affecting the density, $[\mathrm{H_r}]$, of mobile atoms. Let us write the product, $k'_\mathrm{r}[\mathrm{H_r}]$ as $k_\mathrm{r}[\mathrm{H}]$, i.e. $k'_\mathrm{r}[\mathrm{H_r}] = k_\mathrm{r}[\mathrm{H}]$, where [H] is the surface density of hydrogen atoms, and the ratio, $k_\mathrm{r}/k'_\mathrm{r} = [\mathrm{H_r}]/[\mathrm{H}]$, is for that portion of the atoms which participates in reaction (5). In the steady state, the surface density of hydrogen atoms may be found from the following equality:

$$\begin{aligned} I_\mathrm{H} \;=\; & k_\mathrm{d}[\mathrm{H}] + k_0[\mathrm{H}]^2 + k_\mathrm{t}[\mathrm{H}] + k_\mathrm{r1}[\mathrm{H}][\mathrm{CH_3}] \\ & + k_\mathrm{r}[\mathrm{H}][\mathrm{C_2H_6}] = \mathrm{const.} \end{aligned} \tag{7}$$

Here, I_H is the flux of free hydrogen atoms from the gas discharge onto the unit sample surface per unit time. On the right hand side of Eq. (7), the first term represents the loss of H atoms through desorption, the second term reflects the recombination of hydrogen atoms with each other, the third represents the matrix isolation of H atoms, the forth stands for the recombination of hydrogen atoms and methyl radicals: $\mathrm{CH_3 + H = CH_4}$, and the fifth stands for the loss of H atoms in abstraction reaction (5) with ethane molecules. Thermalized hydrogen atoms in the ground state are known to be nonreactive with $\mathrm{CH_4}$ molecules, i.e. with the matrix molecules in the present study.

Expressions (6) and (7) make it possible to account for the dependence of the yield of ethyl radicals (see the last term of expression (7)) on the variation of our experimental conditions, in particular, on the substrate temperature and matrix flux. It stems from the above discussion that the change in the $\mathrm{C_2H_5}$ radical yield matches the change in the quantity of "active" hydrogen atoms $\mathrm{H_r}$ (i.e. those participating in reaction (5)), which contribute to the last term of Eq. (7). At a constant rate of the hydrogen flow onto the sample surface, $I_\mathrm{H} = \mathrm{const.}$, $[\mathrm{H_r}]/[\mathrm{H}]$ varies with the sample temperature, depending on the change in the coefficients k_d, k_0, k_t, and k_r1. Decreasing any of these coefficients would increase the yield of $\mathrm{C_2H_5}$ and vice versa. As the substrate temperature is lowered, k_d becomes smaller: $k_\mathrm{d} = k^0_\mathrm{d}\exp(-E_\mathrm{d}/kT)$. Here, E_d is the activation energy for the desorption of hydrogen atoms from the surface of the sample growing from the gas phase, and k is the Boltzmann constant. The recombination rate constant, k_0, would also decrease following a decrease in the mobility of hydrogen atoms. At the same time, lowering the temperature would presumably give rise to matrix isolation coefficient, k_t, of the hydrogen atoms, which would lower $[\mathrm{H_r}]$. The contribution of the two last terms of expression (7) to the variation of $[\mathrm{H_r}]$ seems to be smaller than that of the first terms presumably because of a weaker dependence of k_r1 and k_r on the temperature and on the finite concentration of $[\mathrm{CH_3}]$ and $[\mathrm{C_2H_6}]$. For these reasons, the temperature decrease (down from 4.2 K in our runs) should be followed by a change in the $[\mathrm{H_r}]$ density and, hence, in the $\mathrm{C_2H_5}$ yield. A major part may also be played by the first term, since the coefficient k_d varies exponentially with the temperature. This would increase the yield of $\mathrm{C_2H_5}$ radicals in reaction (5). At a higher temperature a large k_d keeps the steady state concentration, [H] on the solid surface quite low. With a decrease of temperature, k_d decreases exponentially, increasing [H] on the sample surface. This is probably why the $\mathrm{C_2H_5}$ yield is increased with a substrate temperature decrease and why no EPR signal is obtained of $\mathrm{C_2H_5}$ and H atoms in the spectra in Fig. 4, taken at 4.2 K with a small $\mathrm{CH_4}$ flux onto the substrate. The appearance of trapped $\mathrm{C_2H_5}$ radicals at 4.2 K following the increase in the matrix $\mathrm{CH_4}$ flux onto the substrate is probably due to a decrease of the H atom desorption from the surface because of the higher matrix gas pressure near the surface. Thus, the reactions discussed are governed by the conditions in the surface layer of the sample being condensed from the gas phase, i.e. by an existence or absence of a sufficient concentration of mobile hydrogen atoms, $[\mathrm{H_r}]$, (expression (6)) which have enough time to participate in reaction (5). A further detailed study of these processes including, perhaps, a quantitative assessment of the experimental relations is being planned by increasing the substrate temperature above 4.2 K and utilizing other techniques for the sample preparation.

It is worth noting that Hiraoka et al. (1999, 2000) failed to detect the $\mathrm{C_2H_5}$ radicals when H-atoms were sprayed over solid $\mathrm{C_2H_2}$, $\mathrm{C_2H_4}$ and $\mathrm{C_2H_6}$ films at 10–13 K, i.e. no low-temperature reactions of H-atom addition to $\mathrm{C_2H_4}$ molecule and H-atom abstraction from $\mathrm{C_2H_6}$ molecule were observed. In these runs they tried to detect $\mathrm{C_2H_5}$ radicals by thermal desorption mass-spectrometry and Fourier transform- infrared (FT–IR) spectrometry. It seems likely that, with the former technique, $\mathrm{C_2H_5}$ radicals may be lost in chemical reactions induced by the heating used for sample desorption, while the latter technique is insufficiently sensitive to these radicals. The EPR technique utilized here to study free radicals in gas-grain reactions may be considered as most promising.

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