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Experimental and theoretical studies of photoinduced reactions in the solid phase of the interstellar medium

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The current state of laboratory studies modelling the photoinduced chemical reactions in the solid phase of the interstellar medium is considered. It is shown that multistage processes including physical adsorption of atoms and molecules from the gas phase of the interstellar medium, their drift over the cosmic dust surface, heterogeneous catalysis, photolysis, radiolysis and desorption of the final products and also the photochemical evolution of the dust grains themselves should be adequately included into the astrochemical models of the interstellar medium. The lack of data on the fundamental thermodynamic and kinetic parameters of photoreactions, needed for quantitative description of the physicochemical transformations in the solid phase of the interstellar medium, is noted.
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1. Introduction

Currently, there are strong astronomical grounds for believing that synthesis and destruction of relatively complex molecular compounds on the cosmic dust surface, induced by interaction of the dust grain matter and/or icy mantle adsorbed on the dust grain with cosmic electromagnetic radiation, are important factors of chemical evolution of the Universe on the cosmological time scale. This may be either intense ultraviolet (UV) radiation in the vicinity of young stars, or the diffuse galactic UV field, or relatively weak UV radiation generated by the interaction of the interstellar and circumstellar matter with cosmic rays and/or X-rays. The solid phase of the interstellar medium (ISM), mainly consisting of carbon and silicate compounds, proved to be not only a unique astrochemical reactor for the photosynthesis of organic compounds, but also the place where these compounds survive under the harsh environmental conditions. Photochemical reactions are also important for the formation of molecular composition of nascent planetary systems, in particular, the proto-Solar System.

The baryonic Universe is known to be 98% hydrogen and helium, while carbon, oxygen and nitrogen are the next most abundant elements.[1] In some regions of the interstellar medium, conditions are favourable for chemical reactions involving these elements; therefore, today the detection of spectral lines of relatively complex inorganic and organic molecules no longer seems fantastic, as was the case several

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decades ago. However, there is still no full understanding of the mechanism of formation and temporal evolution of organic matter in the ISM, despite the experience in the fine organic synthesis on the Earth. Elucidation of the mechanisms of formation and the limiting possible complexity of the organic compounds formed in the ISM is among the fundamental problems faced by the modern observational and laboratory astrochemistry. Solution of this problem is important for both the general astronomical aspect of variation of the chemical composition of the Universe on the cosmological time scale and the astrobiological aspect associated with the protostellar and protoplanetary evolution of biologically important compounds, in particular, in the Solar System.[2]

Until early 1960s, it was believed that only simple molecules (mainly two- and three-atom ones) characterized by high dissociation (bond) energy can exist in the ISM gas phase,[3] for example, CO (11.16 eV), CO_2 (5.51 eV) and H_2O (5.15 eV) molecules. This assumption was based on the terrestrial experience of destructive action of hard UV radiation on organic compounds.

The electromagnetic radiation in the ISM is generated in a number of processes, including the emission of various stellar populations (producing both continuous and line spectra), thermal (infrared and submillimetre) radiation of cosmic dust, secondary UV radiation of the interstellar gas caused by interaction with cosmic rays and cosmic microwave background. As regards the physicochemical evolution of the interstellar matter, a rather narrow energy range (5 – 6 to 13.6 eV) of electromagnetic radiation proves to be most significant. This limitation is due to the fact that photons with energy below this range cannot induce electronic excitation of most molecules, while higher-energy photons are efficiently absorbed by interstellar hydrogen atoms; therefore, such photons are virtually absent in the general ISM. Hence, it can be considered that the galactic disc is pierced by short-wavelength UV radiation ($\lambda > 91.2$ nm), which mainly originates from hot stars. The presence in the ISM of UV radiation quanta, capable of thermodynamic cleavage of virtually any chemical bond, served as a major reason against the possibility of long-time existence of complex organic molecules in outer space.

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Nevertheless, currently more than 200 organic and inorganic molecules have been unambiguously detected in the ISM by spectral methods;[4] furthermore, there are both simple two-atom molecules, complex polyatomic molecules (composed of more than 12 atoms), radicals, ions and fullerenes.[5]

Two-atom: CH, CN, CH^+, OH, CO, H_2, SiO, CS, SO, SiS, NS, C_2, NO, HCl, NaCl, AlCl, KCl, AlF, PN, SiC, CP, NH, SiN, SO^+, CO^+, HF, N_2, CF^+, PO, O_2, AlO, CN^-, OH^+, SH^+, HCl^+, SH, TiO, ArH^+, NS^+, HeH^+.

Three-atom: H_2O, HCO^+, HCN, OCS, HNC, H_2S, N_2H^+, C_2H, SO_2, HCO, HNO, HCS^+, HOC^+, SiC_2, C_2S, C_3, CO_2, CH_2, C_2O, MgNC, NH_2, NaCN, N_2O, MgCN, H_3^+, SiCN, AlNC, SiNC, HCP, CCP, AlOH, H_2O^+, H_2Cl^+, KCN, FeCN, HO_2, TiO_2, CCN, SiCSi, S_2H, HCS, HSC, NCO.

Four-atom: NH_3, H_2CO, HNCO, H_2CS, C_2H_2, C_3N, HNCS, $HOCO^+$, C_3O, l-C_3H (l is linear), $HCNH^+$, H_3O^+, C_3S, c-C_3H (c is cyclo), HC_2N, H_2CN, SiC_3, CH_3, C_3N^-, PH_3, HCNO, HOCN, HSCN, HOOH, l-C_3H^+, HMgNC, HCCO, CNCN.

Five-atom: HC_3N, HCOOH, CH_2NH, NH_2CN, H_2CCO, C_4H, SiH_4, c-C_3H_2, CH_2CN, C_5, SiC_4, H_2CCC, CH_4, HCCNC, HNCCC, H_2COH^+, C_4H^-, CNCHO, HNCNH, CH_3 O, NH_3D^+, H_2NCO^+, $NCCNH^+$, CH_3Cl.

Six-atom: CH_3OH, CH_3CN, NH_2CHO, CH_3SH, C_2H_4, C_5H, CH_3NC, HC_2CHO, H_2C_6, C_5S, HC_3NH^+, C_5N, HC_4H, HC_4N, c-H_2C_3O, CH_2CNH, C_5N^-, HNCHCN, SiH_3CN.

Seven-atom: CH_3CHO, CH_3CCH, CH_3NH_2, CH_2CHCN, HC_5N, C_6H, c-C_2H_4O, CH_2CHOH, C_6H^-, CH_3NCO, HC_5O.

Eight-atom: $HCOOCH_3$, CH_3C_3N, C_7H, CH_3COOH, H_2C_6, CH_2OHCHO, HC_6H, CH_2CHCHO, CH_2CCHCN, NH_2CH_2CN, CH_3CHNH, CH_3SiH_3.

Nine-atom: CH_3OCH_3, CH_3CH_2OH, CH_3CH_2 CN, HC_7N, CH_3C_4H, C_8H, CH_3CONH_2, C_8H^-, CH_2CHCH_3, CH_3CH_2SH, HC_7O.

Ten-atom: $(CH_3)_2CO$, $HO(CH_2)_2OH$, CH_2CH_2 CHO, CH_3C_5N, CH_3CHCH_2O, CH_3OCH_2OH.

Eleven-atom: HC_9N, CH_3C_6H, CH_3CH_2OCHO, CH_3COOCH_3.

Twelve-atom: C_6H_6, n-C_3H_7CN, Pr^iCN.

Thirteen-atom: c-C_6H_5CN.

Fullerenes: C_{60}, C_{60}^+, C_{70}.

Initially, the presence of neutral saturated organic molecules in the ISM was a surprise to researchers. However, the subsequent astronomical observations demonstrated that these molecules mainly existed in the so-called molecular clouds, that is, regions composed of a very cold ($T \approx 10$ K) rarefied gas representing molecular hydrogen and helium atoms with $\geqslant 100$ cm^{-3} number density.[6,7] A considerable proportion of heavier chemical elements (C, O, N, Mg, Si, *etc.*) in the form of various chemical compounds is present in the so-called cosmic dust of the submicron size, the total weight of which is approximately two orders of magnitude lower than the weight of interstellar gas.[8] The solid cosmic dust grains markedly shield the inner areas of the dense molecular clouds from the intense UV radiation of stars, thus creating conditions for physicochemical processes, which not only generate organic compounds, but also ensure their long-term survival in the ISM. Among the molecules discovered to date in molecular clouds, mention should be made, first of all, of methanol, ethanol, dimethyl ether, methyl formate, acetic acid, glycol-

aldehyde, ethylene glycol, formamide and aminoacetonitrile molecules. The listed compounds play an important role for the prebiological chemistry, in particular, they are possible precursors of the simplest amino acid — glycine.

From the standpoint of terrestrial experience, neutral organic compounds could not be formed in the very cold and highly rarefied interstellar medium upon binary collisions in the gas phase when reactions have energy barriers and the excess internal energy has to be eliminated *via* ternary collisions. However, chemical reactions forbidden in the gas phase can efficiently proceed on the surface of interstellar dust grains, owing to the increase in the reactant concentrations, heterogeneous (in particular, photoinduced) catalysis, and because of the fact that the internal energy released upon collisions is resonantly absorbed by phonons of the substrate, thus stabilizing the final product.

While colliding with interstellar dust particles at temperatures about 10 K, which are characteristic of molecular clouds, atoms and molecules (except for molecular hydrogen and helium) are, most often, adsorbed on the particle surface.[9–12] It is believed that adsorbed atoms and molecules react with one another according to the Langmuir–Hinshelwood mechanism and, as long as the dust particle is not yet coated by a continuous icy mantle, react with molecules of the surrounding gas phase by the Eley–Rideal mechanism.[13] A textbook example of heterogeneous astrochemical reactions of this type is the formation of an H_2 molecule upon collision of two adsorbed hydrogen atoms.[14]

Apart from molecular hydrogen, the second most abundant (after H_2) carbon monoxide molecule is efficiently frozen out (physically adsorbed) on the dust grain surface. The surface reactions involving a CO molecule and impurity atoms (C, O, N) result in the formation of simple saturated molecular compounds, mainly water, methanol, ammonia, carbon dioxide and methane.[15] In particular, hydrogenation of CO is the only known efficient way of methanol formation in the ISM. Over a period of about a hundred thousand years, cosmic dust is covered by multilayer icy mantles consisting of a mixture of the above molecules, with the thickness of these mantles being up to hundreds of monomolecular layers.[16,17]

The possibility of spectral detection of compounds that compose the icy mantles of dust grains is limited, as they can be detected only by IR absorption spectroscopy in the presence of an appropriate background radiation source. For this reason, the number of molecules reliably identified in icy mantles is limited and methanol is the most complex among them.[18] However, molecular clouds evolve, and young stellar objects appearing in their most dense regions illuminate and heat the surrounding matter. This results in evaporation of icy mantles, *i.e.*, the products of heterogeneous astrochemical reactions migrate to the gas phase, in which they can be more readily detected.[19] The stellar envelopes rich in complex molecules, which have presumably evaporated from the dust grain surface, are called 'hot cores' or 'hot corinos', depending on their weight.

As the radiation intensity increases, not only thermal desorption, but also physical and chemical photodesorption processes are initiated in the vicinity of young stars. In the case of physical photodesorption, the detachment of the molecule from the mantle is accompanied by selective cleavage of the van der Waals bond between the whole molecule and the dust grain induced by absorption of IR and/or UV photons. In the case of chemical photodesorption, the absorbed photon (as a rule, from the UV or vacuum UV range) causes not only desorption of the molecule as a whole, but also dissociation and/or ionization of the molecule to give highly reactive chemical species (radicals and ions) both on the surface of the dust grain and in the surrounding gas-phase ISM. The key factors of evolution of cosmic dust as a result of interaction with photons and other high-energy particles are illustrated in Fig. 1.

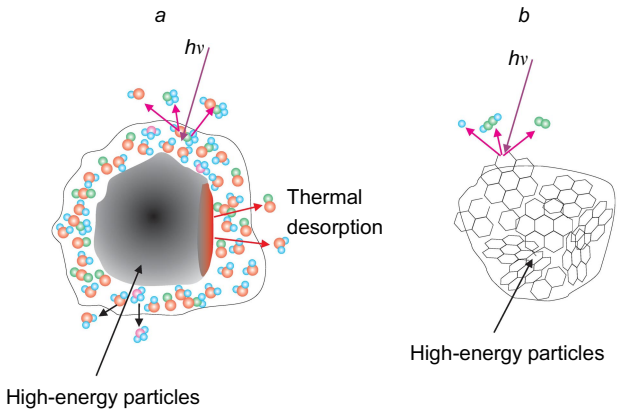


Figure 1. Main evolutionary factors of the cosmic dust mantles (*a*) and grains (*b*) induced by interaction with UV photons and other high-energy particles.[20]

The intense UV radiation affects mainly dust grains located in the vicinity of young stars; however, this does not mean that in dense clouds remote from the active star formation region, UV radiation is completely absent. Despite the fact that the most dense parts of molecular clouds are efficiently shielded from the external radiation by cosmic dust, local UV radiation may appear, as so-called cosmic rays consisting of atomic nuclei (mainly protons) moving at relativistic velocities penetrate even the most dense molecular clouds. The interaction of these particles and secondary electrons they generate with H_2 molecules brings the latter into the electronically excited state, the relaxation of which is accompanied by UV radiation in the Lyman and Werner molecular bands (Prasad–Tarafdar mechanism). These secondary photons generate a local UV field with an intensity of about 10^4 photons cm^{-2} s^{-1}, or 10^{-4} of the average interstellar radiation field[21] in unshielded ISM regions.[22,23] The dust grains are also exposed to UV radiation (and other sorts of radiation) in protoplanetary discs, that is, forming planetary systems.

The photoinduced processes occurring in the ISM solid phase should be discussed not only in the context of destruction and transformation of adsorbed molecules that form icy mantles, but also considering the chemical changes of the proper substrate, that is the dust grain, on which the mantle is formed. The structure of cosmic dust grains has not yet been unambiguously established; however, it is assumed that they consist of complex (and, further, varying over the lifetime of molecular clouds) mixtures of silicates, carbon allotropes and polycyclic aromatic hydrocarbon (PAH) clusters with a very high molecular mass.

The observational astronomical data, especially IR emission spectra and UV absorption spectra suggest that particularly the carbon-containing (so-called carbon aseous) dust is one of the major components of the ISM. However, the question of which particular carbon allotrope

is most typical of ISM is still under discussion. Carbon is a unique element since it can form several hundreds of topologies,[24] which can be interconverted under the action of external stimuli.[25–32]

Some carbon allotropes such as fullerenes[33,34] or nanodiamonds[35–37] were identified in the ISM with a high degree of confidence. The presence of other allotropes (graphite, amorphous carbon, *etc.*) is a debatable issue.[38] With a high degree of probability, carbon dust comprises aromatic compounds, which can exist as isolated PAH macromolecules located in the gas phase[39,40] or deposited on the dust surface.[41] In addition, dust grains may contain hydrogenated amorphous carbon (HAC)[28,42] and mixed aliphatic-aromatic compounds (MAACs).[43] A separate class of aromatic compounds are the PAH clusters — supramolecular complexes consisting of single PAH molecules connected by intermolecular forces. In the literature, they are often called very small grains. Currently, the most popular hypothesis implies that the fine cosmic dust consists, most often, of very large PAH molecules (isolated in the gas phase),[44] while larger cosmic dust grains are conglomerates of PAHs, HACs and MAACs.[28]

One more important component of cosmic dust are silicate particles.[45] In this review, we do not consider them in detail, as this type of dust is little prone to photoinduced reactions. More precisely, refractory silicate dust grains can also undergo changes in the interstellar and especially circumstellar medium; however, these changes (annealing, crystallization) are related to thermal heating rather than to the direct chemical action of the absorbed photons.[46–48] Nevertheless, it should be recalled that these are silicate dust grains that often serve as substrates for the formation of icy mantles and for the above-mentioned photochemical processes. Finally, composite particles consisting of a mixture of carbon and silicate materials can be present in the ISM.[49,50]

It should be admitted that, despite the large number of astronomical observations, the chemical composition of interstellar dust grains is still obscure. The only well-established experimental fact is that the ISM and circumstellar medium contain microparticles of silicon compounds (the presence of specific features at $\sim$10 and $\sim$20 μm in the spectra of cosmic objects) and hydrocarbons (the presence of emission bands in the near- and medium-IR ranges and specific absorption features at 2175 Å). In addition, it should be borne in mind that astrophysicists invariably consider iron and magnesium compounds (olivine, pyroxene) to be involved in the formation of cosmic dust. Also, sulfur compounds, in particular, troilite, were detected in meteorites, but they do not make a significant contribution to the optical properties of cosmic dust and, hence, they are not considered in the known astrochemical ISM models. It was assumed that iron particles are also present in the ISM. However, these assumptions are relevant only to very specific objects such as Cas A supernova remnant.

A high-level physicochemical modelling (including *ab initio* quantum chemical calculations), laboratory experiments and observational astronomy of chemical processes induced by electromagnetic irradiation of cosmic ice and the dust matter over a broad range of wavelengths are successfully developing; therefore, the gaps in our knowledge of the chemical evolution of the solid cosmic matter are being gradually filled.

This review presents a survey of modern studies aimed at determining physicochemical parameters of photoinduced chemical processes taking place on the surface of dust grains and on the icy mantles coating them. The key processes that can be verified experimentally are as follows (the subscript ads refers to molecules located in the solid phase):

photodesorption

$$CO_{(ads)} \longrightarrow CO$$

$$H_2O_{(ads)} \longrightarrow H_2O$$

$$NH_{3(ads)} \longrightarrow NH_3$$

photodissociation

$$CO_{2(ads)} \longrightarrow C_{(ads)} + CO_{(ads)} \longrightarrow C + CO$$

$$CH_3OH_{(ads)} \longrightarrow CH_{3(ads)} + OH_{(ads)} \longrightarrow CH_3 + OH$$

$$C_6H_{6(ads)} \longrightarrow H_{(ads)}, CH_{3(ads)}, C_2H_{2(ads)}, C_4H_{2(ads)} \longrightarrow$$
$$\longrightarrow CH_3, C_2H_2, C_4H_2, H$$

These photoprocesses can occur in various astrophysical objects, in particular:

— in the so-called photodissociation regions of the ISM where the UV radiation of massive stars penetrates into a neighbouring molecular cloud and starts to illuminate dust grains with icy mantles;

— in cold molecular clouds in which UV photons are generated by cosmic rays;

— in 'hot cores' in which the molecular cloud starts to be lightened by the protostar being formed;

— in cold (allowing the existence of icy mantles) regions of protoplanetary discs, with UV radiation sources being represented by an accretion region in the central part of the disc and UV photons generated by cosmic rays.

Without taking into account the photoinduced transformations, it is impossible to model the molecular evolution of interstellar matter and interpret the results of observations in various spectral ranges, from the vacuum UV range, in which, in particular, the early stages of molecular cloud formation take place, up to the submillimetre and radio ranges in which radiation of relatively complex molecules is observed at the stage of formation of stellar and planetary systems. Furthermore, the absence of detailed studies of astrochemical photoprocesses precludes studying the evolution of organic matter in the Universe, while without an understanding of the mechanism of astrochemical evolution as a whole, it is impossible to answer a key question of modern astrophysics concerning the scenario of formation of stars, especially massive stars ($>$10 Solar masses).

Several reviews addressing a similar subject have been reported previously.[51–55] More general information on the physics of interstellar medium, cosmic dust and astrochemistry can be found in the literature.[56–58]

The following designations and abbreviations are used:

A — pre-exponential factor of the Arrhenius rate constant,

a — semiempirical function used to estimate the vibrational state density,

DFT — density functional theory,

DIET — desorption induced electronic transitions,

E — internal energy of the system,

E_a — activation energy,

$F(E)$ — radiation energy flux density,

F_λ — radiation flux at the wavelength λ,

h — Planck constant,

HAC — hydrogenated amorphous carbon,

IR — infrared,

ISM — interstellar medium,
I_λ — emission band intensity at the wavelength λ,
$J(\lambda)$ — mean radiation field intensity,
k_B — Boltzmann constant,
k_{dis} — rate constant of monomolecular dissociation,
k_{dis}^{can} — dissociation rate constant in the canonical description,
k_{IR} — IR photon emission rate,
k_{ion} — ionization rate,
k_{pd} — rate constant of photodecomposition (photodissociation),
K_{dis}^{RRK} — dissociation rate constant in the RRK theory,
K_{dis}^{RRKM} — dissociation rate constant in the RRKM theory,
MAACs — mixed aliphatic-aromatic compounds,
N — total number of atoms in the molecule,
N_C — number of carbon atoms in the molecule,
N_H — number of hydrogen atoms in the molecule,
$P(T/E)$ — temperature or internal energy distribution of molecules,
PAHs — polycyclic aromatic hydrocarbons,
Q_{abs} — absorption efficiency factor,
R — universal gas constant,
RRK — Rice – Ramsperger – Kassel,
RRKM — Rice – Ramsperger – Kassel – Marcus,
s — number of internal degrees of freedom in the molecule,
ΔS — entropy change of the system on going to the activated state,
$S_{abs}(E)$ — photoabsorption cross-section,
T — kinetic temperature of the gas,
T_e — effective temperature of the system,
T_m — microcanonical temperature,
UV — ultraviolet,
VSG — very small grains,
Y_i — branching ratio,
$Y_{dis}(E)$ — probability of dissociation at the energy E,
Y_{total} — total dissociation probability integrated over energy,
ε — probability of dissociation as the dust grain is hit by a photon,
λ — electromagnetic radiation wavelength,
ν — frequency of molecular vibrations,
ν_i — frequency of molecular vibrations in the initial (ground) state,
ν_i^a — frequency of molecular vibrations in the activated (excited) state,
$\rho(E)$ — density of the vibrational states at the energy E,
$\sigma(\lambda)$ — monochromatic photodissociation cross-section,
σ_{CH}^{dis} — C – H bond dissociation cross-section.

2. Photoinduced processes in the icy mantles of cosmic dust

2.1. Physical and chemical photodesorption in the solid phase of the interstellar medium

The interaction of UV photons (and other high-energy particles, for example, cosmic rays) with molecules physically adsorbed on dust grains may result in the following events.

First, molecules located in the icy mantles, having absorbed a quantum of electromagnetic radiation, can be physically desorbed as is, without changing the chemical structure, to the surrounding gas. The second event resulting from interaction of the dust-grain icy mantles with high-energy photons is dissociation and ionization of saturated neutral molecules, which are the major component of icy mantles, to give the corresponding radicals and ions.[59] Indeed, stable molecules such as H_2O or CH_3OH can dissociate or ionize on exposure to UV photons to give chemically reactive radicals and ions (cations) on the cosmic dust surface:

$$H_2O + h\nu \longrightarrow OH + H \quad (1)$$

$$H_2O + h\nu \longrightarrow H_2O^+ + e \quad (2)$$

$$CH_3OH + h\nu \longrightarrow CH_2OH + H;\ CH_3 + OH \quad (3)$$

Finally, the third event induced by absorption of an UV photon by an adsorbed molecule is electronic excitation of the molecule accompanied by chemical reactions with the surrounding (non-excited) molecules located in the mantle and/or the gas phase.

A possible mechanism of formation of relatively complex organic compounds is photolysis, details of which in the solid phase of ISM are poorly known. While discussing the possible mechanisms of photoinduced reactions involving adsorbed molecules, one should take into account the following circumstances.

At very low temperature ($\sim$10 K), the adsorbed molecules occur in the cosmic icy mantles in the static position. In a multilayer coating, there is almost no temperature motion (drift) of molecules relative to one another due to spatial (steric) restrictions caused by van der Waals interactions with molecules of the local environment. Therefore, the radicals formed upon photolysis have low mobility and mainly recombine with the hydrogen atoms released upon photodissociation; hence, probably no significant accumulation of radicals in the icy mantles takes place. The situation is basically different in the early stages of star formation when the collapse of a dense gas-and-dust cloud forming a young protostar heats the dust and gas in the ISM. When the dust temperature is $>$20 K, atomic hydrogen released upon photodissociation of hydrocarbons is desorbed almost immediately into the surrounding gas; therefore, radicals can be accumulated in the matrix. Apparently, a similar process takes place in the case of photoionization products. On further temperature rise up to 35 – 50 K, the radicals located in the interior or on the surface of the icy mantles acquire mobility and start to react with one another to form polyatomic organic compounds,[60] for example

$$CH_3 + CH_2OH \longrightarrow CH_3CH_2OH \quad (4)$$

$$HCO + CH_2OH \longrightarrow CH_2OHCHO \quad (5)$$

$$HCO + CH_3O \longrightarrow HCOOCH_3 \quad (6)$$

The electronic ground state of physically adsorbed molecules virtually coincides with the ground state of an isolated molecule in the gas phase, whereas the electronically excited states of adsorbed molecules and molecular clusters (in the case of a multilayer coating) may significantly change, resulting in the formation of, for example, stable supramolecular compounds. In addition, intermolecular interactions usually increase the number and probability of optical transitions from the electronic ground state, because they are no longer spin-forbidden.

The interaction of an isolated molecule with the surface markedly increases the density of vibrational electronic states of the molecule, which form the so-called vibrational quasicontinuum. In turn, this leads to a significant accel-

eration of the intramolecular relaxation due to the appearance of numerous resonances with phonon vibrations of the dust grain. Thus, the quantum yield of the photodissociation for adsorbed molecules is often much lower than the quantum yield for the same molecules in the gas phase. A possible source of ultrafast electronic deactivation (comparable to the period of intramolecular vibrations) is the dipole–dipole interaction between the molecule and surface defects, if the luminescence spectrum of the isolated molecule overlaps with the electronic absorption spectrum of surface defects.[61] This mechanism of deactivation of photoexcited molecules is especially relevant for monolayer coatings, as it leads to local surface heating and selective physical desorption of molecules that have absorbed an UV quantum.

Unlike direct photodesorption, the thermal desorption is an activated process and, hence, there is a threshold of incident radiation intensity. This secondary process can be significant only for physical desorption of molecules (with activation energy of tenths of an electron volt), but not for dissociation (with bond energies of several electron volts). Hence, photolytic processes (photolysis) determine the yield of a chemical reaction at low incident radiation intensity.

Quantitative description of photolysis in interstellar ice requires the knowledge of several fundamental parameters. The first class of these parameters is represented by photodissociation cross-sections. With a known monochromatic photodissociation cross-section $\sigma(\lambda)$ (cm^2), the rate constant of photodecomposition (photo-induced decay) of the molecule (k_{pd}) is determined by the equation

$$k_{pd} = \int \sigma(\lambda) J(\lambda) d\lambda \quad (7)$$

where $J(\lambda)$ is the average radiation field intensity at the wavelength λ. The photodissociation cross-sections of many astrophysically relevant molecules in the gas phase are known and the actual information is available from the Leiden Collection of Photo Processes (https://home.strw.leidenuniv.nl/~ewine/photo/). Meanwhile, photodissociation cross-sections of molecules in the adsorbed state have been scarcely reported. Therefore, the current astrochemical models of photolysis and the descriptions of reactions in the adsorbed state use, most often, gas-phase cross-sections.[62]

The results of the few available laboratory studies indicate that at least the measured photodissociation cross-sections of molecules in the ice are significantly (in some cases, by an order of magnitude) smaller than the photodissociation cross-sections of the same molecules in the gas phase.[63, 64] It is possible that the true photodissociation cross-sections in ice are comparable with those in the gas phase, but the measured effective cross-sections turn out to be much smaller because of dissipation of the internal energy of the adsorbed molecules and the kinetic energy of the products of their photodissociation. Particularly, photodissociation products are adsorbed on the ice surface and are very likely to recombine. Unfortunately, reliable experimental data indicating a real decrease in the photodissociation cross-sections for molecules in ice in comparison with the gas phase are critically lacking.

One more class of parameters that have to be known for quantitative description of photolysis in ices are relative yields of particular photodissociation products (the so-called dissociative branching ratios). According to experiments, even relatively weak interaction between the molecule and the surface can considerably change the relative yields of products in comparison with the gas phase.[65] There is still no generally accepted explanation to this fact. The situation is complicated by recombination reactions of molecules and radicals formed upon photolysis of adsorbed molecules. In particular, photodissociation of CO_2 affords a carbon monoxide molecule in the electronically excited state, which can react with another CO molecule to give CO_2 and a carbon atom. It was suggested[66] that this process may result in the loss of some carbon atoms and erroneous determination of the parameters of photoinduced reactions in a mixed $CO:CO_2$ ice.

Finally, a quantitative description of the chemical evolution of ices is impossible without knowledge of the potential barriers to thermal diffusion in the ice for radicals resulting from photolysis, since these barriers determine the Langmuir kinetics of diffusion reactions.[15, 67] Apart from diffusion barriers, many reactions also have their own activation barriers. This mainly refers to reactions between radicals and atoms or molecules. Most reactions between radicals have no barriers.

Interestingly, the reaction rates in the solid phase depend on the relationship between the absolute activation barriers of the reactions and the diffusion barriers of the reactants.[68] In the solid phase, potential reactants can participate in several processes: the reaction itself, diffusion and, if the ice surface is involved, desorption. The process that would actually proceed depends on the relationship of the activation barriers. If the reaction activation barrier is lower than the reactant diffusion barriers, a chemical transformation event is likely to occur. Conversely, if the reaction barrier is higher than the diffusion barriers, the probability for the reaction to occur before the potential reactants diffuse away from each other rapidly decreases with increasing reaction barrier. The experimental determination of the diffusion barriers for reactions between radicals is based on measuring the yields of products of presumptive diffusion processes between the products of photolysis in a gradually heated ice sample. The reactions between radicals with low diffusion energies take place at low temperature, while radicals characterized by higher barriers obviously react at a higher temperature.

In some cases, this approach is actually suitable for estimating the diffusion barriers, but it has a number of limitations. First, heating of the ice is accompanied by desorption of atoms and molecules, which can significantly reduce the yield of reaction products. Second, if several reactions with different diffusion barriers take place simultaneously between the photolysis products during heating, the unambiguous interpretation of the results is often impossible. Finally, the diffusion energies in the ice depend on the ice spatial structure (compact, porous) and chemical composition ($H_2O:CH_3OH$, $H_2O:CO$); these energies determined in laboratory experiments may differ from those on the surface of interstellar dust grains. Thus, the number of diffusion barriers for atoms and molecules located on the surface and in the interior of interstellar ice analogues determined experimentally by now is quite limited. Therefore, astrochemical models make use of relatively rough estimates of diffusion energies, which are taken to be equal to fractions of the corresponding reactant desorption energies (as a rule, 0.3–0.8 of the desorption energy).[15, 62, 69]

It should also be noted that UV photons are not the only particles that interact with interstellar ices to induce disso-

ciation of saturated neutral molecules and formation of chemically reactive radicals. Interstellar ices are also exposed to cosmic rays and secondary electrons and cations generated by these rays. Finally, X-ray radiation and ^{26}Al isotope decay may act as significant factors affecting the ices in protoplanetary discs that surround young stars. Examples of modelling of radiation-induced transformations of astrochemically important molecules at cryogenic temperatures using matrix isolation technique have been reported.[70–73]

The efficiency of physical and chemical desorption induced by cosmic rays hitting the mantle has been scarcely studied. The few experiments on ion bombardment of water ice using an ion accelerator showed a quadratic dependence of the desorption efficiency on the energy of cosmic rays. For heavy ions, the desorption efficiency is about 10^4 molecules per ion.[74,75] The estimates reported by Dartois *et al.*[74] indicate that under conditions typical of dense molecular clouds, the total rates of photodesorption and cosmic ray-induced desorption coincide in the order of magnitude.

The results of studies of the effects of X-rays, electrons and accelerated ions on analogues of interstellar ices attest to a qualitative similarity between the results of photolysis and radiolysis of ice under the influence of various agents.[76–78] This suggests that the chemical evolution of interstellar ices is likely to depend on the total amount of absorbed energy to a higher extent than on the way this energy was delivered. However, there are theoretical studies predicting that the interaction of heavy cosmic rays (*e.g.*, iron nuclei) can, in rare cases, result in explosive desorption of the material of the icy mantles of dust grains.[79]

2.2. Laboratory modelling of photodesorption of astrochemically important molecules

Experimental studies of photodesorption require special installations combining the possibility of forming mono- and multilayer coatings of the desired composition, UV irradiation and analysis of desorption products. Experiments of this type are carried out in vacuum chambers with a residual pressure of 10^{-11}–10^{-10} mbar at temperatures of 10–100 K. The possible UV radiation sources include both continuous spectrum sources (hydrogen or deuterium lamps or synchrotron radiation) and quasimonochromic sources (solid-state and excimer lasers, tunable dye lasers, hydrogen lamps with monochromators). Deposition is performed onto a substrate simulating a dust grain, the composition of which depends on the problem to be solved and the method for interpretation of experimental results.

If the interaction of the substrate with the deposition products can be neglected, photodesorption is analyzed by IR and UV spectroscopy. In this case, the substrate can be fabricated from potassium bromide, caesium iodide or a chemically inert metal (for example, gold or silver). IR spectroscopy is convenient because the structure of the adsorbed layer does not change during the experiment; therefore, its composition can be monitored. A drawback of this method is that it is applicable only to molecules that show intense transitions in the IR range. UV spectroscopy is often used in experiments with PAHs and related compounds, which actively absorb in the UV range.

If the interaction between the substrate and deposited products is important, the substrate should be manufactured from materials that are more realistic for the ISM such as graphite, silicate minerals or quartz. In this case, the photodesorption products are usually detected by various sorts of mass spectrometry.

Experimenters determining the thermodynamic and kinetic parameters of photoinduced processes important in the astrochemical aspect are faced with two fundamental difficulties. The first one is to bring the conditions of a model laboratory experiment as close as possible to real conditions of the astronomical object. As noted above, for molecular clouds, these are temperatures of about 10 K and a pressure not exceeding 10^{-12} mbar. The second difficulty is to relate experimentally determined parameters to the parameters needed for subsequent astrochemical modelling. In the case of physical photodesorption, this parameter is the efficiency (quantum yield), that is, the number of desorbed molecules per absorbed photon. It is important to distinguish the yield based on a photon absorbed by a dust grain and the yield based on a photon absorbed by a particular molecule. Below we have in mind the former value.

Characteristics of physical photodesorption are determined, first of all, for molecules that are assumed to form the basis of interstellar ices, namely, carbon monoxide and water molecules. For instance, Öberg *et al.*[80] studied the photodesorption of pure CO ice with a thickness of up to 350 monolayers from a gold substrate under the action of continuous radiation of a hydrogen lamp in the 120–170 nm. Experiments showed that photodesorption takes place only from several outer layers of the ice and occurs as non-thermal evaporation caused by transition of the CO molecule into the electronically excited state upon absorption of a vacuum UV photon. Excitation of the molecule induced by photon absorption is transmitted to neighbouring molecules and can lead to desorption of not necessarily one molecule and not necessarily exactly the molecule that have absorbed the photon. This mechanism is called the desorption induced electronic transitions (DIET); its efficiency is determined by the depth of photon penetration into the ice (Fig. 2).[81]

The yield of CO was found to be approximately 3×10^{-3} molecules per photon.[80] However, the efficiency of photodesorption depends apparently on many factors, including the energy of absorbed photons and the structure and composition of ice; therefore, the indicated yield was reconsidered many times. In particular, it was shown[59] that the yield of CO photodesorption depends on temperature on which CO has been deposited onto the substrate (because the temperature is likely to determine the ice structure): as the temperature is increased from 15 to 27 K, the yield decreases several-fold. Hence, the yield for a real molecular cloud may depend on its thermal prehistory.[82] The yield of CO decreases to $< 10^{-4}$ in the case of evaporation of a mixed $CO:N_2$ ice.[59]

Different results were reported by Muñoz Caro *et al.*,[83] who concluded that photodesorption affects only five outer monolayers of ice. However, the determined yield of CO proved to be an order of magnitude greater: $(3–6) \times 10^{-2}$ molecules per photon in the temperature range from 7 to 15 K and photon energies of 7.3–10.5 eV. Even a higher yield (almost 0.1) was obtained by Chen *et al.*[84] Meanwhile, later measurements[85] also gave a yield of approximately 10^{-3}. These pronounced differences can be attributed, on the one hand, to a strong dependence of the photodesorption efficiency on the particular type of excitation spectrum,[86] and, on the other hand, to the difficulty of calibrat-

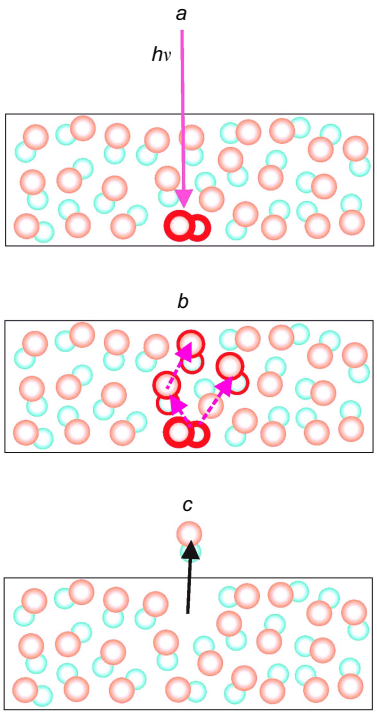


Figure 2. Schematic illustration of the DIET mechanism.[81] (*a*) A photon penetrates into the interior of the ice mantle and is absorbed by a molecule, which rises to an electronically excited state; (*b*) the excitation energy is transferred to neighbouring molecules, including those located on the surface; (*c*) a molecule on the surface gets enough kinetic energy to be detached from the dust grain.

ing the absolute intensity of hydrogen lamps used in the experiments.[84]

The above results were obtained for a pure CO ice; therefore, they are unlikely to be directly applicable to real conditions in molecular clouds, as the presence of other molecules in the adsorbent layer markedly complicates the situation. It was noted above that CO molecules are desorbed less efficiently when mixed with molecular nitrogen. The presence of even a thin N_2 layer above the CO layer stops CO photodesorption almost completely (the efficiency of N_2 desorption simultaneously increases).[87] Meanwhile, for a CO mixture with methanol, the yield is approximately the same as for pure CO ice.[88]

The estimates of the water photoevaporation yield are also somewhat scattered, although to a lesser extent than the values for CO. In experiments,[89] water ice was deposited on to a gold surface and illuminated with a discharge lamp with emission maximum near the L_α hydrogen line. The measured quantum yield was $(3-8)\times10^{-3}$ depending on temperature (in the range from 35 to 100 K). The authors also noted that the yield depended on the radiation dose and was negligibly low at moderate doses. Therefore, they concluded that the photodesorption of water is not a direct (single-photon) process, but requires preliminary irradiation. The particular mechanism can include, for example, ejection of a water molecule from the ice surface by a hot hydrogen atom generated upon preceding photodissociation of another water molecule,[90] or to desorption of the H_2O molecule arising upon recombination of H and OH radicals, products of photodissociation of this or another water molecule.[91]

Öberg *et al.*[92] also deposited water molecules on a gold substrate and then exposed the water molecules to radiation of a hydrogen lamp in the 7–10.5 eV range. The yield they found was $\sim1.3\times10^{-3}$ at $T = 10$ K. As the temperature was raised, the yield increased, which was confirmed by Bertin *et al.*;[88] however, no dependence of the yield on the irradiation dose was revealed. A detailed experimental and theoretical study of these processes[90] resulted in an estimated yield approximately an order of magnitude lower than that determined by DeSimone *et al.*;[91] however, this result is questionable. Generally, the modern estimates of the photodesorption yield for water are approximately $10^{-4}-10^{-3}$.

The desorption of a methanol molecule also receives attention of experimentalists. This is due to the fact that radiation of methanol located in the gas phase can be observed in cold molecular clouds where it should be frozen out on cosmic dust grains. At low temperature (few Kelvin degrees), evaporation of methanol from icy mantles should be associated with some non-thermal process, in particular, photodesorption of molecules upon absorption of photons generated by cosmic rays. However, whereas the yield of methanol photodesorption estimated by Öberg *et al.*[93] was $\sim2.1\times10^{-3}$, *i.e.*, approximately the same value as for water, the estimates made in subsequent studies were much lower. Cruz-Diaz *et al.*[94] exposed an adsorbed methanol layer at a residual pressure of $(3-4)\times10^{-11}$ mbar to radiation of a gas discharge hydrogen lamp; however, no signal of evaporating methanol was detected and only the upper limit of the photodesorption yield was determined to be 3×10^{-5}. This is two orders of magnitude lower than that found in earlier experiments (see Ref. 92). A value of about 10^{-5} was also obtained in experiments reported by Bertin *et al.*[87] It is of interest that the yield decreases when an icy mixture of CO and methanol is used. As shown in this and other experiments,[95] co-desorption of methanol together with photodesorbed CO, which was proposed as one more mechanism for evaporation of adsorbed methanol, is highly inefficient. However, it is noteworthy that in the case of methanol (as in the case of water or CO_2), study of photodesorption is complicated by the fact that absorption of a photon results not only (and rather not) in evaporation of molecules, but also in their photolysis followed by evaporation of the products of photolytic reactions. In particular, the low yield of photodesorbed methanol can be a consequence of its photodissociation during desorption.

We would like to mention several other studies. Experiments on evaporation of adsorbed benzene and water from a sapphire substrate using the second harmonics of a dye laser at the benzene absorption wavelength (250 nm) have been reported.[96] The authors proposed three desorption mechanisms manifested in their experiments: direct excitation of an adsorbed benzene molecule, excitation transfer to the neighbouring water molecule and heating of the substrate. The translational temperatures of photodesorbed benzene and water molecules were in all cases markedly higher than the ice temperature. It was noted that in astrochemistry this may generate molecules with above-thermal velocity[64] and, hence, induce deviation of chemical reaction rates from equilibrium values. Fayolle *et al.*[97] reported experimental determination of the photodesorption yields of N_2 and O_2 molecules, which proved to be $10^{-3}-10^{-2}$ depending on the composition of ice and the

shape of the excitation spectrum. Similar yields were found for ammonia[98] and methane molecules.[99] For formaldehyde, the photodesorption yields were $(4-10)\times10^{-4}$ under different astrochemical conditions.[100]

Generally, it can be stated that, according to laboratory experiments, the yield of physical photodesorption is about 10^{-3} for simple two- and three-atom molecules and 10^{-5} for more complex molecules. The exact values considerably depend on ice composition and thermal prehistory (which determines the spatial structure of ice), intensity distribution in the excitation spectrum and so on.

It should be emphasized that there are very few laboratory experiments conducted to establish the mechanisms of photolysis of adsorbed molecules. For example, a study of the CH_3I molecule undertaken in the 1990s demonstrated that the only result of UV irradiation is the cleavage of the relatively weak carbon–halogen bond.[101–104] The key feature of these results is that they established a difference of several orders of magnitude (from 10^{-3} to 10^{4}) between the photodissociation cross-sections of adsorbed molecules and molecules in the gas phase.[105–107] Although there are several assumptions on this issue, there is no exhaustive explanation of these differences.

Starting from 2007, systematic laboratory studies of laser-induced dissociation of simple organic molecules, physically adsorbed on the fused quartz surface cooled by liquid nitrogen in high vacuum, have been carried out at the Division of Laser Chemistry of the Department of Chemistry, M.V.Lomonosov Moscow State University. Molecules of benzene and its derivatives (toluene and chlorobenzene) were the first objects of laboratory models. The basic diagram of the experimental setup is presented in Fig. 3. The major source of UV radiation was the KrF excimer laser at the excitation wavelength of 248 nm. The power of pulsed laser radiation was sufficient to perform multiphoton transitions, which made it possible to model both the UV excitation of adsorbed molecules and vacuum UV excitation with simultaneous absorption of two photons with a total energy of ~10 eV. The photofragments that leave the surface were detected by a quadrupole mass spectrometer located in front of the irradiated site of the surface. The kinetic energies of the fragments were determined from the time of their flight from the target to the mass spectrometer.

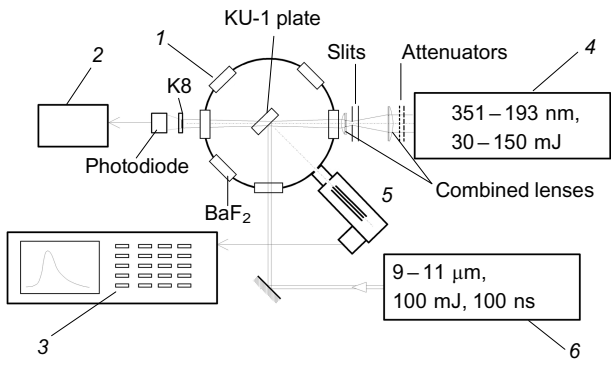


Figure 3. Basic diagram of the experimental setup for mass spectrometric analysis of the products of the laser-induced dissociation of simple organic molecules physically adsorbed on a cooled fused quartz surface in high vacuum.[108–110] Depending on the time of exposure of the quartz surface to the vapour of analyzed molecules, modelling of protoprocesses in either monolayer or multilayer coating is possible. (*1*) Ultrahigh vacuum chamber, (*2*) digital PC oscilloscope, (*3*) digital C8-9 storage oscilloscope, (*4*) excimer laser, (*5*) Riber QMM-17 quadrupole mass spectrometer, (*6*) pulsed CO_2 laser.

The mass spectrometric detection of the products of laser-induced dissociation of adsorbed aromatic molecules showed a cubic dependence of the yield of photofragments on the laser energy density and low (hundredths of electron volt) kinetic energies of all particles observable by mass spectrometry. Unlike the gas-phase molecules, in this case, no ions of initial molecules or their fragments were observed, although the energy of two laser photons (~10 eV) was somewhat greater than the ionization potentials of all considered molecules.

The photolysis of adsorbed benzene, toluene and chlorobenzene molecules was accompanied by elimination of a hydrogen atom, a methyl group and chlorine atoms from the benzene ring, respectively. Cleavage of the benzene ring resulted in the formation of hydrocarbon fragments C_2H_2, C_4H_2 and C_2H_4. The same photolysis products (apart from the chlorine-containing counterparts) were formed upon three-photon dissociation of adsorbed chlorobenzene molecules. The cleavage of stronger bonds (with bond energy exceeding the laser photon energy of 5 eV) takes place upon the action of four laser photons. For example, formation of the C_2H_3 fragment from C_6H_5Cl required an energy of 7.6 eV, which proved to be supplied upon simultaneous action of four photons. The thermodynamically allowed processes such as dissociation of benzene, toluene or chlorobenzene to give C_6H_4 and H_2, CH_4 or HCl, respectively, were not observed for adsorbed molecules. A possible cause is the necessity of preliminary isomerization of the initial molecule,[111] while the possibility of changing the spatial geometry for an adsorbed species is limited. It was shown[108] that the HCl molecule observed in the experiment with chlorobenzene results from the reaction of primary H fragments with initial chlorobenzene molecules.

The results of the above-considered studies are concerned with monolayers of adsorbed molecules; however, as shown by more recent experiments, the general three-photon mechanism of photodissociation is also retained in the case of multilayer coatings. The new observable process is photodesorption of molecular clusters.[109] The desorbed cluster, which remains in the radiation field during the laser pulse (20 ns long), loses molecular fragments; this is similar to photodissociation of gas-phase (isolated) molecules. In the case of a monolayer coating, photodesorption of the initial molecules was only due to the short-term heating of the substrate surface upon absorption of laser radiation by surface defects.

Comparison of experimental results on adsorbed molecules and gas-phase molecules obtained under collision-free conditions (in particular, in a molecular beam) or in a low-pressure gas led to several conclusions on the photochemistry of molecules on the surface. In the chlorobenzene molecular beam irradiated with a KrF laser, elimination of chlorine atoms took place *via* two channels, which were interpreted[112] considering the mechanisms of predissiociation and formation of 'hot' molecules. In experiments with adsorbed C_6H_5Cl molecules, absorption of one photon (5 eV) did not induce fragmentation. Benzene and toluene present in a molecular beam did not dissociate at low intensities of a KrF laser (in the single-photon absorption mode);[113] however, absorption of two photons from the

radiation of this laser induced elimination of hydrogen atoms.[114] In experiments with adsorbed benzene[110] and toluene,[108] absorption of one or two photons from KrF laser radiation did not induce detachment of photofragments from the surface. Thus, the adsorbed molecules are more stable to UV radiation than molecules in the gas phase. The astrochemical applications of the results were reported by Murga *et al.*[115]

One more factor that considerably affects the photodissociation quantum yield of adsorbed molecules is the degree of surface roughness. In experiments with toluene, one and the same yield of H fragments can be attained at 50 times lower incident energy density as the laser irradiation time is increased,[108] with the cubic dependence on the energy density remaining invariable. The mass spectrometric signal increased by a factor of 10^5 with the incident energy being the same.

In conclusion, note that during temporal evolution, the surface of cosmic dust grains is exposed to the action of high-energy particles and hard electromagnetic radiation, which should inevitably give rise to surface defects and nonuniform (at the microscopic level) surface structure. A similar result is apparently attained on exposure to a powerful laser radiation, which gives rise to defects and a microcrack network on the substrate surface as a result of multiphoton processes.

3. Photoinduced processes in cosmic dust grains

3.1. Spectral signatures of carbon dust

The IR emission bands in the range from 3 to 20 μm, in particular, near the wavelengths at 3.3, 6.2, 7.7, 8.6 and 11.2 μm are considered to be signatures of the presence of aromatic compounds in the ISM. These wide bands are universally observed both in our Galaxy (regions of ionized hydrogen, planetary and reflection nebulae, protoplanetary discs, molecular clouds) and in other galaxies.[116–124] The general shape of the IR spectrum of the ISM in the range from 3 to 20 μm can be considered universal, but band profiles, positions, widths and intensities can vary from one object to another[44, 125, 126] and even within a single object.[122, 127, 128]

It is assumed that the observed emission bands are generated by molecular vibrations, while the spectral properties of bands (width, position, profile) are determined by the nature of vibrations (Fig. 4).

For example, the band at 3.3 μm corresponds to stretching modes of aromatic C–H bonds, the 6.2 μm band corresponds to C–C stretching modes, the 7.7 μm band is a combination of several C– C stretching modes, the band at 8.6 μm is due to in-plane C–H bending vibrations, and finally the band at 11.2 μm reflects out-of-plane (torsional) C–H bending modes.[129] Apart from the main broad IR bands, the astronomical spectra of hydrocarbons also exhibit narrower bands at wavelengths of 3.4, 3.5, 5.25, 5.75, 6.0, 6.9, 7.5, 10.5, 11.0, 13.5, 14.2, 17.4 and 18.9 μm. By assignment of vibrations responsible for these bands, it is possible to establish the molecular structure and allotropy of compounds. For example, the bands at 17.4 and 18.9 μm are assigned to fullerenes,[33] the 5.25 and 10.5 μm bands are related to dehydrogenated PAHs or carbon chains,[130] while the band at 3.4 μm corresponds to stretching modes of aliphatic C–H bonds. There are no such bonds in PAH molecules, which consist only of benzene rings and hydrogen atoms and in which one peripheral carbon atom can be bound to only one hydrogen atom. Several assignments were proposed for the registered astronomical IR emission characteristics of aliphatic compounds, in particular

— PAH molecule is bound to additional hydrogen atoms (the peripheral carbon atom adds two or more hydrogen atoms);[131]

— PAH molecule contains methyl or methylene groups;[132]

— this emission is due not to PAH molecules but to molecules of hydrogenated amorphous carbon (HAC) and mixed aliphatic-aromatic compounds (MAACs).[28, 43]

The spectral parameters of the observed bands are affected by properties of PAH molecules such as their size, degree of ionization and replacement of carbon atoms by other atoms (for instance, nitrogen). The measured intensity ratio (T) of the bands at 3.3 and 11.2 μm provides data on the size of PAH molecules.[128, 133, 134] Indeed, the predominant contribution to the emission at 3.3 μm is made by molecules with the number of carbon atoms $N_C < 30–40$,

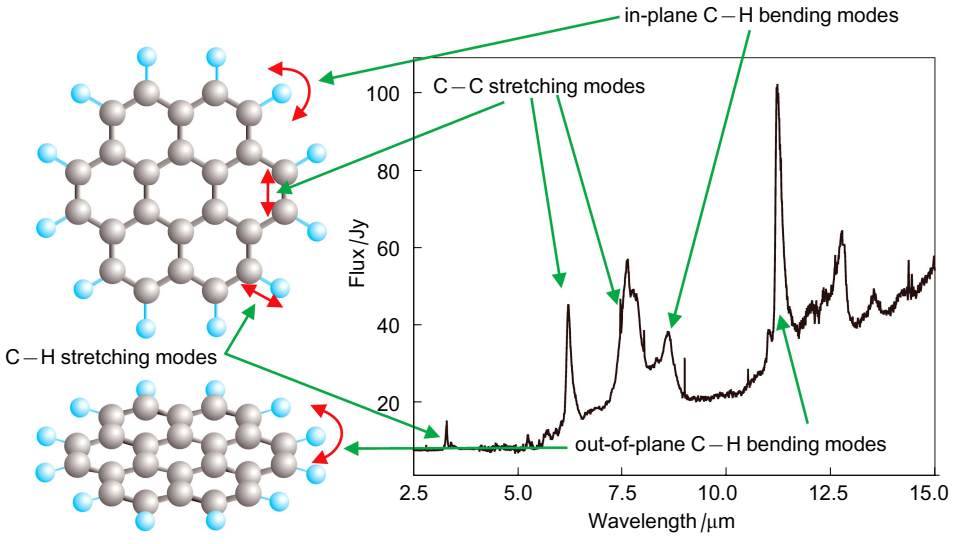


Figure 4. 3D visualization of the spectral assignment of vibrational modes for an isolated coronene (superbenzene) molecule.[44]

while the band at 11.2 μm is largely due to big molecules with $N_C > 60$. The intensity ratio of the 6.2 and 11.2 μm bands can be used to evaluate the ionization state,[135, 136] indicating the ratio of abundances of ionized and neutral PAHs. When carbon atoms in a PAH molecule are replaced by nitrogen, the 6.2 μm band shifts.[137] From the position of this band, it is possible to make inferences about the presence and character of substitution (at the centre or at the periphery of the molecule). The intensity ratio of the bands at 3.3 and 3.4 μm depends on the ratio of aliphatic to aromatic C–H bonds.

3.2. Experimental and quantum chemistry studies of the photolysis of carbon dust

A key evolutionary process involving carbon-containing dust particles (in particular, PAH molecules) is their partial or complete destruction under the influence of various factors. One of these factors is intense UV radiation. The radiation effect can be followed by examining the IR spectra of objects with a powerful radiation source. For example, the $I_{11.2}/I_{3.3}$ ratio in the reflection nebula NGC 7023 varies depending on the distance to the star: as the star is approached, the average size of PAHs decreases, which attests to their destruction.[133] In another reflection nebula NGC 2023, characteristics of PAHs also change on approaching the star, in particular, small PAH molecules disappear.[138] Numerous examples of destruction of PAHs by a strong UV radiation field generated by young stars are observed in star-formation regions, regions of ionized hydrogen and infrared clouds.[139–142] In the Orion Bar photodissociation region, the intensity of the band at 3.4 μm decreases with respect to the band at 3.3 μm, which means destruction of weaker aliphatic bonds.[143] From changes in the IR spectra and contribution of the continuum, it is also possible to derive information about the content of PAH clusters.[144, 145] It is believed that PAH clusters can exist only in the regions of reduced UV radiation field, as they split into separate molecules in the vicinity of the ionizing radiation source. The presented examples of photolytic processes involving aromatic compounds in the ISM require theoretical and experimental comprehension.

The benzene rings and PAH molecules consisting of them are considered to be resistant against radiation; however, their stability is limited and depends on the number of rings in the molecule, molecular structure and other factors. The photostability of PAH molecules was repeatedly studied in laboratory experiments, the vast majority of which addressed relatively small molecules with a total number of carbon atoms of < 30. According to modern views, the size of PAH molecules in the ISM should be, on average, larger;[146] therefore, the photostability of interstellar PAHs is estimated using models which generalize and extrapolate the results of experiments conducted for small PAHs.

Among important experiments, the results of which are most often used in astrochemistry, mention should be made of the study of Jochims *et al.*[147] The authors measured the internal energy at which dissociation along a particular channel takes place for eleven neutral PAHs with different molecular size (from benzene with $N_C = 6$ to coronene with $N_C = 24$). Three major dissociation channels were identified: hydrogen atom loss, hydrogen molecule loss or acetylene molecule loss; the loss of a hydrogen atom was the most likely. The determined values for internal energy needed for dissociation varied from ~4.5 to ~12 eV depending on the dissociation channel and size of the molecule. It was found that linear PAHs are less stable than more compact PAHs. As shown by experiment reported by Ekern *et al.*,[148] no unique correlation is detected between the PAH destruction and characteristics such as the size of the molecule (up to coronene), molecular structure, hydrogen to carbon ratio, *etc*. The authors noted only that a defective ring consisting of four or five rather than six carbon atoms present in the molecule increases its stability, although there are some exceptions. It was also found that some PAHs become photostable after the loss of a hydrogen atom or an acetylene molecule. Perhaps, this depends on the structure of the resulting fragment and the type of isomerization that occurred upon photodissociation. It was shown[149] that elimination of a photofragment may afford different structures; therefore, the subsequent dissociation is not necessarily similar to the initial one (the pathway and rate change).

For solution of astrochemical problems, it is of interest to consider photolysis of large PAH molecules; however, the number of such experiments is scarce. Among these studies, mention should be made of the studies carried out at the Leiden observatory (the Netherlands).[150–153] The authors investigated photolysis of the $C_{42}H_{18}^+$, $C_{60}H_{22}^+$, $C_{66}H_{26}^+$ and $C_{78}H_{26}^+$ cations and concluded that, unlike neutral PAHs with $N_C \leqslant 24$, fragmentation of the cations mainly follows the hydrogen loss channel, whereas the channels including destruction of the carbon skeleton *via* the loss of acetylene or C_2 molecules start to be effective only when the PAH molecule has been considerably (or fully) dehydrogenated. This is indicated by intense mass-spectroscopic signals corresponding to bare carbon structures formed from the molecules: C_{42}^+, C_{66}^+, C_{60}^+, *etc*. It is of interest that fullerene C_{60}^+ is formed as one of $C_{66}H_{26}^+$ fragmentation products, that is, the elimination of dicarbon from the periphery of the molecule gives rise to defective rings, distortion of the molecular plane and successive formation of a spherical structure. From the experimental results, the authors concluded that the larger the PAH molecule, the more often the ionization rather than dissociation is induced by absorption of an UV photon.

The stability of PAHs to destruction under UV irradiation decreases in the presence of additional hydrogen atoms. As the hydrogen saturation of PAH molecules increases, their destruction becomes easier and the dissociation pathways related to the loss of carbon-containing C_xH_y groups become more relevant (and diverse).[154–156] As a PAH molecule is hydrogenated, the addition of the next hydrogen atom starts to compete with dissociation. As a result of efficient dissociation, not all of the PAHs reach complete saturation where each peripheral carbon atom bears two hydrogen atoms. This should be taken into account when considering PAHs as catalysts in the formation of molecular hydrogen,[157] because in molecular clouds PAHs can exist in the hydrogenated state, and H_2 loss competes with elimination of C_xH_y groups.

Photolysis of hydrogenated PAHs resembles photolysis of HAC particles, which was also studied in laboratory experiments. The results are equally relevant for studying the ISM, because the material of large interstellar dust particles apparently includes hydrogenated amorphous carbon. Dissociation of HAC particles induced by UV irradiation can result in the elimination of hydrogen atoms and molecules and small hydrocarbons C_xH_y.[25, 158–161] Moreover, PAH molecules with $N_C \approx 30–40$ and fullerene mol-

ecules were found among the HAC dissociation products. Thus, HAC may serve as the source of aromatic molecules in the ISM. Study of the spectra of HAC dissociation products demonstrated that UV radiation couses a decrease in the IR band at the wavelength of 3.4 μm and an increase in the band at 3.3 μm, that is, hydrogenated amorphous carbon gradually loses aliphatic bonds, which are weaker than aromatic bonds, and acquires a more regular and stable aromatic structure.

It is assumed that PAH clusters are present among the dust components in the ISM and are fragmented in the photodissociation regions of the ISM. The energies of the intermolecular interactions connecting PAH molecules into clusters are several times lower than the chemical bond energies in an isolated PAH molecule. Laboratory studies confirm the instability of PAH clusters to radiation. Their degradation into separate PAH molecules is faster than the destruction of these molecules and, hence, it is the prevailing process.[162, 163]

In recent years, due to the development of quantum chemistry methods and computing facilities, the experimental approach has been supplemented by numerical calculations of the electronic structures, which simulate the properties of real molecular systems and interpret the results of laboratory experiments. Despite the obvious drawbacks associated with inevitable systematic bias and uncontrolled systematic error, quantum chemical calculation techniques possess a number of advantages over the experimental methods. For example, they make it possible to systematically follow the evolution of polyatomic structures, while the results of *ab initio* thermodynamic calculations actually correspond to very low temperatures, which are highly difficult to attain in a real thermochemical experiment.

Ab initio quantum chemical calculations are also widely used in the studies of the spectral properties of PAHs and other hydrocarbons. For example, the NASA Ames PAH IR database [164] containing spectral characteristics of PAHs in the IR range includes the results of laboratory experiments for only 75 PAHs, while data for more than 3000 PAH molecules were obtained theoretically using the density functional theory (DFT) method. The PAH dissociation was also calculated by DFT in combination with molecular dynamics.[165, 166] The results of model calculations largely coincide with the experimental results: the same dissociation pathways were identified and it was shown that the ratio between the hydrogen atoms and acetylene molecules formed as dissociation products increases with increasing size of PAH molecules and depends on the internal energy of the system. The calculations have been performed only for PAHs with N_C up to 24; however, in the future, the results for larger molecules would apparently be obtained.

Using modelling, the most stable forms of PAH clusters and their dissociation energies and preferable formation and destruction mechanisms were determined.[167, 168] The results of quantum chemical modelling of the transformation of the disordered amorphous carbon structure into the graphite structure have been reported.[26, 169] The models follow the dynamic details of isolated atoms, which cannot be resolved by modern experimental methods.

3.3. Kinetic modelling of photochemical evolution of carbon dust

Intense UV radiation has the most pronounced destructive action on the smallest dust grains, namely, isolated PAH molecules and PAH clusters. The reactions of PAHs with photons are described and the rate constants of their photodissociation are calculated mainly by statistical methods. In astrochemistry, the simplest kinetic models are used most often, some of which are briefly discussed below.

First, we will consider the model of unimolecular decay based on the simplified Rice – Ramsperger – Kassel (RRK) theory according to which a molecule is a set of s identical oscillators with the vibrational frequency v. Each oscillator is characterized by a critical energy or activation energy (E_a). If the internal energy of the system is $E > E_a$, dissociation takes place. In the general form, the rate constant of unimolecular decay (k_{dis}^{RRK}) is determined by the equation

$$k_{dis}^{RRK} = v\left(1 - \frac{E_a}{E}\right)^{s-1} \tag{8}$$

which was used [146] to approximate the experimental results. The s value is the number of internal (vibrational) degrees of freedom of the molecule

$$s = 3N - 6 \tag{9}$$

or for linear molecules

$$s = 3N - 5 \tag{10}$$

where N is the total number of atoms in the molecule. The parameter v has values of 10^{16}, 10^{16} and 10^{15} s^{-1} for H, H_2 and C_2H_2 loss reactions, respectively. The activation energy is estimated empirically; the values are 2.8 – 2.9 eV for the H, H_2 and C_2H_2 fragments. The authors noted that E_a can be considered as a value related, but not equal, to the dissociation energy.

The approach based on a combination of a theoretical description and experimental results is widely used in astrochemistry to calculate the chemical evolution of PAHs.[170, 171] The rate constant for dissociation of molecules with $N_C > 50$ found in this way was markedly overestimated; therefore, the following empirical equation was proposed for larger molecules:[169]

$$k_{dis}(N_C > 50) = k_{dis}^{RRK}(N_C = 50)10^{-0.3373\,(N_C - 5)} \tag{11}$$

However, this highly simplified approach has serious limitations and is not always applicable to real molecular systems.[44]

A more substantiated approach is based on the Rice – Ramsperger – Kassel – Marcus (RRKM) theory, according to which a molecule is considered as a set of oscillators with different harmonic vibrational frequencies. In this case, the dissociation rate constant (k_{dis}^{RRKM}) can be expressed as

$$k_{dis}^{RRKM} = \left(1 - \frac{E_a}{E}\right)^{s-1} \frac{\prod_{i=1}^{s} v_i}{\prod_{i=1}^{s-1} v_i^a} \tag{12}$$

where v_i and v_i^a are vibrational frequencies of the molecule in the initial (ground) and activated (excited) states, respectively. Evidently, this approach requires the knowledge of all vibrational frequencies for all molecular geometries. This is difficult to accomplish in practice, especially for very large PAH molecules. Therefore, Le Page *et al.*[172] made an additional simplification by using only two frequencies

corresponding to C–H and C–C vibrations for all PAH molecules.

A very large PAH molecule can also be described using Gibbs microcanonical and canonical distributions. In the former case, the system is considered to be isolated and its energy is taken to be constant, while in the latter case, the system is in heat equilibrium with the environment, the average thermal energy of the system is constant, but can experience fluctuations. When a PAH molecule is hit by a photon, it can be considered as a microcanonical ensemble; however, in many cases, it is easier to describe a molecule by a canonical distribution with a fixed temperature. In astrochemistry, both approaches are used for determining the dissociation rate constants for PAH molecules. One of the models was reported by Tielens,[173] who described the PAH molecule *via* a microcanonical distribution. In this case, the expression for dissociation rate constants has the form of Arrhenius equation

$$k_{\rm dis}^{\rm Ar} = A{\rm e}^{-E_{\rm a}/k_{\rm B}T_{\rm e}} \tag{13}$$

where A is a constant representing the vibrational frequency of the bond being cleaved, $k_{\rm B}$ is the Boltzmann constant, $T_{\rm e}$ is some effective temperature of the system that is related to the microcanonical temperature ($T_{\rm m}$) and to the internal energy of the system (E) by the empirical equation

$$T_{\rm e} \approx T_{\rm m}\left(1 - 0.2\frac{E_{\rm a}}{E}\right) \tag{14}$$

In turn, the microcanonical temperature can be approximately related to E (eV) by the experssion [132]

$$T_{\rm m} \approx 2000\left(\frac{E}{N_{\rm C}}\right)^{0.4} \tag{15}$$

According to the data reported by Le Page *et al.*,[172] the parameter A can be approximated by the formula

$$A = \frac{k_{\rm B}T_{\rm e}}{h}\exp\left(1 + \frac{\Delta S}{R}\right) \tag{16}$$

where h is the Planck constant, ΔS is the entropy change of the system on going to the activated state, R is the universal gas constant. The $E_{\rm a}$ and ΔS values are determined from the experimental data. They differ for molecules with different sizes and structures and degrees of ionization and hydrogenation. In some studies, average values are used for all PAH molecules: $E_{\rm a} \approx 3.0$ eV and $\Delta S = 5$ cal K^{-1} mol^{-1} for the C–H bond [174] and 4.6 eV and 10 cal K^{-1} mol^{-1}, respectively, for the C–C bond.[175] In other studies, different values are taken depending on the particular molecule and its state.[176]

Finally, one more model widely used in astrochemistry is based on the canonical description of PAH molecules; in this case, the rate constant is found by the inverse Laplace transformation of the Arrhenius law [177–179]

$$k_{\rm dis}^{\rm can} = A\frac{\rho(E - E_{\rm a})}{\rho(E)} \tag{17}$$

where $\rho(E - E_{\rm a})$ and $\rho(E)$ are densities of the vibrational states at energies $(E - E_{\rm a})$ and E, respectively. The state densities are calculated using the Whitten–Rabinovich approximation

$$\rho(E) = \frac{(E + aE_{\rm a})^{s-1}}{(s-1)!\prod_i^s h\nu_i} \tag{18}$$

where a is the semiempirical function taking values from 0 to 1 depending on the set of vibrational frequencies and energy.[180] The A and $E_{\rm a}$ values are found experimentally. As in the previous model, they depend on the molecule and its state; however, the following typical values can be indicated: $A = 1.5\times10^{15}$ s^{-1}, $E_{\rm a} = 4.65$ eV for the C–H bond; $A = 3.5\times10^{17}$ s^{-1}, $E_{\rm a} = 7.5$ eV for the C–C bond. It should be borne in mind that the activation energy for PAH in the hydrogenated states can be several times lower, while the value for dehydrogenated PAH can be higher,[153] *i.e.*, the PAH molecules saturated with hydrogen or containing aliphatic bonds can dissociate more easily than bare carbon lattices. For the correct application of this method, experimental data on the parameters for all states of PAHs are required; since the known data are incomplete, it is often necessary to use approximations.

The dissociation rate constants estimated by various methods demonstrate the same trends: their values increase with increasing internal energy and decrease with increasing size of the PAH molecule. However, in some cases, these constants differ significantly. For example, for an internal energy of >15 eV, the differences can reach several orders of magnitude. Pronounced differences are also present at low internal energies. Each method has its benefits and drawbacks, and it is difficult to decide which of them is more realistic. While using each method, one should bear in mind its limitations (in energy or size of the PAH molecule).

Irrespective of which particular method was used to determine the rate constant, calculations of PAH dissociation rate should take into account the fact that dissociation is only one of the possible processes that can occur upon absorption of a photon by the molecule. This process competes with other processes: emission of IR photons and ionization. The probability of each process (branching ratio Y_i) is determined by the ratio of the process rate to the sum of rates of all processes

$$Y_i = \frac{k_i}{k_{\rm dis} + k_{\rm IR} + k_{\rm ion}} \tag{19}$$

where the rates of emission of the IR photon ($k_{\rm IR}$) and ionization ($k_{\rm ion}$) are derived from the absorption behaviour and ionization potential of the molecule, respectively.[170]

The relations presented above are suitable for describing the absorption event of a single photon. In this situation, the molecule has only one internal energy or temperature. In reality, the thermal history of PAHs (and other small dust grains) in the ISM has an intermittent character. Upon absorption of a photon, the molecule rapidly warms up and then, having reached the temperature maximum, cools down to a temperature of several Kelvin degrees. If during cooling, the molecule is hit by one more photon, its temperature, without decreasing down to the minimum, starts again to increase. Thus, the internal energy of PAHs can be several-fold higher than the energy of single photons that hit the molecule. This is the essence of multiphoton heating. Due to the probabilistic nature of photon collisions with a particular molecule, it is impossible to unambiguously determine the temperature of PAHs. The molecule is characterized by temperature $P(T)$ or internal energy $P(E)$ distributions. In view of this fact, it is necessary to calculate

the probability of dissociation $Y_{\rm dis}(E)$ over the whole temperature or internal energy ranges. The total probability $Y_{\rm total}$ corresponding to heating by the interstellar radiation field over a broad energy range is determined as

$$Y_{\rm total} = \int Y_{\rm dis}(E)\,{\rm d}E \qquad (20)$$

The rate of dissociation of a PAH molecule in the interstellar radiation field characterized by the energy flux density $F(E)$ is found by the relation

$$Y_{\rm total} = \int_0^\infty C_{\rm abs}(E)\,F(E){\rm d}E \qquad (21)$$

where $C_{\rm abs}$ is the absorption cross-section.

The PAH molecule can lose hydrogen and carbon atoms; hence, depending on the particular bond (C – H or C – C) for which the rate constant is calculated, it is possible to obtain both the dehydrogenation rate of the molecule and the rate of destruction of the carbon skeleton. Note that for dehydrogenation, it is also necessary to take into account the probability of compensating the hydrogen atom loss *via* the reverse process: hydrogen atom addition. Under certain conditions, namely, at high density of atomic hydrogen, this process can be very efficient.

The above models were used to estimate the times needed for complete dehydrogenation and destruction of PAHs under different external conditions. The key results of calculations of PAH evolution are as follows:

— PAHs with $N_{\rm C} < 30-40$ dissociate under the ISM conditions;[169]

— in the enhanced UV radiation field corresponding to photodissociation regions, PAHs with $N_{\rm C} \approx 60-70$ are dehydrogenated and can isomerize to be converted to fullerenes, which are found in these objects;[173]

— PAHs with $N_{\rm C} > 80$ are stable to UV radiation.[175]

An important subject of studies of the evolution of PAHs and other aromatic compounds is their comparison with large dust grains, which are less susceptible to the action of destructive factors. The emission of large dust grains, unlike PAH emission, occurs in a longer-wavelength spectral region from 20 to 1000 μm. Usually, emission at the wavelength of 70 or 160 μm is used as the signature for large particles, whereas emission at 8 μm should be assigned to PAHs. The photometric bands at wavelengths of 8, 70 and 160 μm were used in the Spitzer and Herschel Space Observatories. Variations of the ratio of radiation fluxes at these wavelengths, F_8/F_{70}, F_8/F_{160}, attest to increasing (or decreasing) content of fine aromatic particles relative to the large dust grains upon the change in the external conditions or object characteristics. These ratios can vary depending on the age of objects, chemical composition of the medium, radiation field intensity and gas velocity.[181–186]

Whereas photolysis of PAHs in the ISM is being actively studied, photolysis of larger dust particles is scarcely addressed. A number of studies consider the stability of PAH clusters[29,167] and demonstrate that the rate of destruction of clusters sharply decreases with increasing number and size of single PAHs. It was found that only clusters consisting of very large PAH molecules can survive in the photodissociation regions; therefore, it is believed that these are large PAHs that are the major components of dust. Clusters of coronene molecules decompose rapidly even at low UV radiation intensities, circumcoronene ($C_{54}H_{18}$) clusters decompose only at high field intensity, whereas clusters of $C_{96}H_{24}$ molecules have longer lifetimes compared with the characteristic lifetimes of ISM photodissociation regions.

The influence of UV radiation on large dust particles is considered in the context of the model accepted for PAHs. If large dust particles are taken to be graphite, UV radiation does not have any effect. However, if large dust particles consist of hydrogenated amorphous carbon, changes should be taken into account, because this material undergoes photolysis of aliphatic bonds and the subsequent loss of hydrogen atoms.[28] The lattice rearrangements change the material properties — density, band gap, refractive index, absorption cross-section, *etc*. These changes can be monitored using IR spectra; this possibility has already been implemented in laboratory.[157] A relationship was established[28,157] between the relative content of hydrogen in the substance and the intensity of the emission band at 3.4 μm and other bands at 7.0 and 7.3 μm, which also characterize aliphatic bonds. The dissociation cross-section ($\sigma_{\rm CH}^{\rm dis}$) of the C – H bond depending on the photon energy was measured by laboratory methods, and a model for aromatization of amorphous carbon was developed. The rate of hydrogen atom loss in the interstellar radiation field with the photon flux density F is estimated as

$$\frac{{\rm d}N_{\rm H}}{{\rm d}t} = \varepsilon\sigma_{\rm CH}^{\rm dis} Q_{\rm abs} F \qquad (22)$$

where t is time, ε is the probability of dissociation as the dust grain is hit by a photon, $Q_{\rm abs}$ is the absorption efficiency.

In the MMP83 radiation field typical of the ISM,[21] dust grains are aromatized, depending on their size, within the time of $\sim 1-100$ million years; this means that, in terms of this model, dust generally exists in the ISM in the dehydrogenated state. If the dust grain is small (with a radius of up to 20 nm), changes occur throughout the bulk, whereas for larger dust grains, changes occur only on the surface. Under certain conditions (in dense and cold areas), the reverse process — aliphatization of the material — can take place, and the properties of dust will change again.[187] It is worth noting that dehydrogenated amorphous carbon is not equivalent to graphite; however, it also has an ordered structure relative to the structure formed initially as the dust appeared.

According to experiments, carbon-containing fragments can be desorbed from the HAC dust surface[159] and the aromatic molecules adsorbed on the surface can be destroyed on exposure to UV radiation.[114] However, currently there are no models in astrochemistry that could take into account photoerosion — the loss of carbon atoms from the surface of large dust particles. This issue requires detailed consideration in the future.

Gas-phase photolysis of very large aromatic compounds is intensively studied in modern astrochemistry; a variety of models and experiments substantiating these models were proposed. However, there are virtually no adequate models for PAH clusters, which are only several-fold larger than the initial single PAH molecules, not to mention larger dust grains.

Thus, modern astrochemical models, which include chemical reactions both in the gas phase and on the surface and also in the interior of the icy mantles of dust grains, largely rely on a rough description of photoinduced proc-

esses, which are thought to substantially affect the interstellar chemistry. Evaluation of the accuracy of astrochemical models showed that at present, the accuracy of determination of the contents of molecules in the interstellar medium is rarely better than an order of magnitude.[188, 189] However, rapid progress in the astronomical observations and an increasing number of laboratory experiments aimed at solving key issues of astrochemistry give hope that the situation will improve in the near future. One of the actively developed complex astrochemical models is MONACO,[190 – 192] which appeared at the Laboratory of Astrochemistry and Extraterrestrial Physics of the Ural Federal University. This model is widely used by both Russian and foreign research groups.[193 – 206] Refinement of the conceptual component of the model is based, first of all, on a regular inclusion (after critical analysis) of the results of recent experimental and theoretical studies of astrochemically important processes.

4. Conclusion

The material covered in the review reveals the dual role of photochemical processes in the formation of complex organic molecules under the specific conditions of the ISM. On the one hand, an intense UV field of active stars efficiently destroys polyatomic molecules, thus preventing the development of complex organic chemistry in the regions that are insufficiently protected from primary UV radiation sources. On the other hand, in the ISM regions that are efficiently shielded from the UV radiation of stars by cosmic dust, a weak secondary UV field, together with cosmic rays and, in some cases, X-rays, is an important factor stimulating the synthesis of relatively complex organic molecules. Currently, it is believed that the key chemical reactions are the formation of molecular radicals in interstellar ices *via* photolysis and radiolysis [70 – 73] and the subsequent reactions between them. The complex multistage mechanism of these reactions started to be studied only recently, and a multitude of laboratory and astronomical studies are still to be performed to gain a satisfactory understanding of the astrochemistry of interstellar ice.

All illustrations presented in the review were prepared by the authors on the basis of original data references to which are given in the figure captions.

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References

1. T.L.Wilson, R.Rood. *Annu. Rev. Astron. Astrophys.*, **32**, 191 (1994)
2. P.Caselli, C.Ceccarelli. *Astron. Astrophys. Rev.*, **20**, 56 (2012)
3. Y.R.Luo. *Comprehensive Handbook of Chemical Bond Energies*. (Boca-Raton, FL: CRC Press, 2007)
4. B.A.McGuire. *Astrophys. J. Suppl.*, **239**, 17 (2018)
5. E.Herbst, E.F.van Dishoeck. *Annu. Rev. Astron. Astrophys.*, **47**, 427 (2009)
6. E.F.van Dishoeck, G.A.Blake. *Annu. Rev. Astron. Astrophys.*, **36**, 317 (1998)
7. E.A.Bergin, M.Tafalla. *Annu. Rev. Astron. Astrophys.*, **45**, 339 (2007)
8. B.T.Draine. *Annu. Rev. Astron. Astrophys.*, **41**, 241 (2003)
9. E.Herbst, W.Klemperer. *Astrophys. J.*, **185**, 505 (1973)
10. P.Caselli, C.M.Walmsley, M.Tafalla, L.Dore, P.C.Myers. *Astrophys. J. Lett.*, **523**, L165 (1999)
11. P.Caselli, F.F.S.van der Tak, C.Ceccarelli, A.Bacmann. *Astron. Astrophys.*, **403**, L37 (2003)
12. C.Ceccarelli, P.Caselli, E.Herbst, A.G.G.M.Tielens, E.Caux. In *Protostars and Planets V*. (Eds B.Reipurth, D.Jewitt, K.Keil). (Tucson, AZ: University of Arizona Press, 2006). P. 47
13. J.Le Bourlot, F.Le Petit, C.Pinto, E.Roueff, F.Roy. *Astron Astrophys.*, **541**, A76 (2012)
14. D.Hollenbach, E.E.Salpeter. *Astrophys. J.*, **163**, 155 (1971)
15. T.I.Hasegawa, E.Herbst, Ch.M.Leung. *Astrophys. J. Suppl.*, **82**, 167 (1992)
16. H.M.Cuppen, E.Herbst. *Astrophys. J.*, **668**, 294 (2007)
17. R.T.Garrod, T.Pauly. *Astrophys. J.*, **735**, 15 (2011)
18. A.C.A.Boogert, P.A.Gerakines, D.C.B.Whittet. *Annu. Rev. Astron. Astrophys.*, **53**, 541 (2015)
19. S.Bottinelli, C.Ceccarelli, B.Lefloch, J.P.Williams, A.Castets, E.Caux, S.Cazaux, S.Maret, B.Parise, A.G.G.M.Tielens. *Astrophys. J.*, **615**, 354 (2004)
20. D.A.Williams, C.Cecchi-Pestellini. *The Chemistry of Cosmic Dust*. (London: The Royal Society of Chemistry, 2016). P. 1
21. J.S.Mathis, P.G.Mezger, N.Panagia. *Astron. Astrophys.*, **128**, 212 (1983)
22. S.S.Prasad, S.P.Tarafdar. *Astrophys. J.*, **267**, 603 (1983)
23. C.J.Shen, J.M.Greenberg, W.A.Schutte, E.F.van Dishoeck. *Astron. Astrophys.*, **415**, 203 (2004)
24. R.Hoffmann, A.A.Kabanov, A.A.Golov, D.M.Proserpio. *Angew. Chem.*, **55**, 10962 (2016)
25. A.Scott, W.W.Duley, G.P.Pinho. *Astrophys. J. Lett.*, **489**, L193 (1997)
26. N.Marks, C.Kocer. *Mol. Simul.*, **32**, 1271 (2006)
27. J.Gaudin, O.Peyrusse, J.Chalupský, M.Toufarová, L.Vyšín, V.Hájková, R.Sobierajski, T.Burian, Sh.Dastjani-Farahani, A.Graf, M.Amati, L.Gregoratti, S.P.Hau-Riege, G.Hoffmann, L.Juha, J.Krzywinski, R.A.London, S.Moeller, H.Sinn, S.Schorb, M.Störmer, Th.Tschentscher, V.Vorlíček, H.Vu, J.Bozek, C.Bostedt. *Phys. Rev. B*, **86**, 024103 (2012)
28. A.P.Jones, L.Fanciullo, M.Köhler, L.Verstraete, V.Guillet, M.Bocchio, N.Ysard. *Astron. Astrophys.*, **558**, A62 (2013)
29. J.Montillaud, C.Joblin. *Astron. Astrophys.*, **567**, A45 (2014)
30. F.R.Eder, J.Kotakoski, U.Kaiser, J.C.Meyer. *Sci. Rep.*, **4**, 4060 (2014)
31. J.O.Berné, J.Montilaud, C.Joblin. *Astron. Astrophys.*, **577**, A133 (2015)
32. L.Loisel, M.Châtelet, G.Giudicelli, M.Lebihain, Y.Yang, C.-S.Cojocaru, A.Constantinescu, B.K.Tay, B.Lebental. *Carbon*, **105**, 227 (2016)
33. J.Cami, J.Bernard-Salas, E.Peeters, S.E.Malek. *Science*, **329**, 1180 (2010)

34. K.Sellgren, M.W.Werner, J.G.Ingalls, J.D.T.Smith, T.M.Carleton, Ch.Joblin. *Astrophys. J. Lett.*, **722**, L54 (2010)
35. O.Guillois, G.Ledoux, C.Reynaud. *Astrophys. J. Lett.*, **521**, L133 (1999)
36. O.Pirali, M.Vervloet, J.E.Dahl, R.M.K.Carlson, A.G.G.M.Tielens, J.Oomens. *Astrophys. J.*, **661**, 919 (2007)
37. M.Goto, Th.Henning, A.Kouchi, H.Takami, Y.Hayano, T.Usuda, N.Takato, H.Terada, S.Oya, C.Jäger, A.C.Andersen. *Astrophys. J.*, **693**, 610 (2009)
38. R.Papoular, J.Conard, O.Guillois, I.Nenner, C.Reynaud, J.-N.Rouzaud. *Astron. Astrophys.*, **315**, 222 (1996)
39. J.L.Puget, A.Leger. *Annual Rev. Astron. Astrophys.*, **27**, 161 (1989)
40. L.J.Allamandola, D.M.Hudgins, S.A.Sandford. *Astrophys. J. Lett.*, **511**, L115 (1999)
41. W.W.Duley, D.A.Williams. *Monthly Not. Roy. Astron. Soc.*, **260**, 37 (1993)
42. W.W.Duley, A.Hu. *Astrophys. J.*, **761**, 115 (2012)
43. S.Kwok, Y.Zhang. *Nature (London)*, **479**, 80 (2011)
44. A.G.G.M.Tielens. *Annu. Rev. Astron. Astrophys.*, **46**, 289 (2008)
45. J.S.Mathis, W.Rumpl, K.H.Nordsieck. *Astrophys. J.*, **217**, 425 (1977)
46. D.Cesarsky, A.P.Jones, J.Lequeux, L.Verstraete. *Astron. Astrophys.*, **358**, 708 (2000)
47. Ya.Pavlyuchenkov, C.P.Dullemond. *Astron. Astrophys.*, **471**, 833 (2007)
48. Ch.M.Wright, T.Do Duy, W.Lawson. *Monthly Not. Roy. Astron. Soc.*, **457**, 1593 (2016)
49. V.Zubko, E.Dwek, R.G.Arendt. *Astrophys. J. Suppl.*, **152**, 211 (2004)
50. N.V.Voshchinnikov, V.B.Il'in, Th.Henning. *Astron. Astrophys.*, **429**, 371 (2005)
51. G.M.Muñoz Caro, E.Dartois. *Chem. Soc. Rev.*, **42**, 2173 (2013)
52. S.Ioppolo, K.I.Öberg, H.Linnartz. In *Laboratory Astrochemistry*. (Eds S.Schlemmer, T.Gliesen, H.Mutschke, C.Jäger). (Weinheim: Wiley-VCH, 2015). P. 289
53. K.I.Öberg. *Chem. Rev.*, **116**, 9631 (2016)
54. H.M.Cuppen, C.Walsh, T.Lamberts, D.Semenov, R.T.Garrod, E.M.Penteado, S.Ioppolo. *Space Sci. Rev.*, **212**, 1 (2017)
55. G.M.Muñoz Caro, R.Martín Doménech. In *Laboratory Astrophysics*. (Eds G.Muñoz Caro, R.Escribano). *Astrophysics and Space Science Library*. Vol. 451. (Cham: Springer, 2018). P. 133
56. N.G.Bochkarev. *Osnovy Fiziki Mezhzvezdnoy Sredy: Uchebnoe Posobie*. (Fundamentals of Physics of the Interstellar Medium: A Textbook). (Moscow: Knizhnyi Dom 'LIBROKOM', 2010)
57. N.V.Voshchinnikov. *Mezhzvezdnaya Pyl'. Issledovanie Kosmicheskogo Prostranstva. (Itogi Nauki i Techniki)*. [Interstellar Dust. Space Exploration. (Advances in Science and Engineering)]. (Moscow: VINITI AN SSSR, 1986). Vol. 25
58. V.I.Shematovich. *Russ. Chem. Rev.*, **88**, 1013 (2019)
59. K.I.Öberg, E.F.van Dishoeck, H.Linnartz. *Astron. Astrophys.*, **496**, 281 (2009)
60. R.T.Garrod, E.Herbst. *Astron. Astrophys.*, **457**, 927 (2006)
61. D.L.Andrews. *Tutorials in Complex Photonic Media*. Vol. PM194. (Eds M.A.Noginov, G.Dewar, M.W.McCall, N.I.Zheludev). (Bellingham, WA: SPIE, 2009). P. 461
62. D.P.Ruffle, E.Herbst. *Monthly Not. Roy. Astron. Soc.*, **322**, 770 (2001)
63. H.Cottin, M.H.Moore, Y.Bénilan. *Astrophys. J.*, **590**, 874 (2003)
64. E.F.van Dishoeck, B.Jonkheid, M.C.van Hemert. *Faraday Discuss.*, **133**, 231 (2006)
65. P.Maksyutenko, L.G.Muzangwa, B.M.Jones, R.I.Kaiser. *Phys. Chem. Chem. Phys.*, **17**, 7514 (2015)
66. N.-E.Sie, G.M.Muñoz Caro, Z.-H.Huang, R.Martín-Doménech, A.Fuente, Y.-J.Chen. *Astrophys. J.*, **874**, 35 (2019)
67. T.I.Hasegawa, E.Herbst. *Monthly Not. Roy. Astron. Soc.*, **263**, 589 (1993)
68. Q.Chang, H.M.Cuppen, E.Herbst. *Astron. Astrophys.*, **469**, 973 (2007).
69. D.Semenov, F.Hersant, V.Wakelam, A.Dutrey, E.Chapillon, S.Guilloteau, Th.Henning, R.Launhardt, V.Piétu, K.Schreyer. *Astron. Astrophys.*, **522**, 42 (2010).
70. V.I.Feldman, S.V.Ryazantsev, E.V.Saenko, S.V.Kameneva, E.S.Shiryaeva. *Radiat. Phys. Chem.*, **124**, 7 (2016)
71. E.V.Saenko, V.I.Feldman. *Phys. Chem. Chem. Phys.*, **18**, 32503 (2016)
72. S.V.Kameneva, D.A.Tyurin, V.I.Feldman. *Phys. Chem. Chem. Phys.*, **19**, 24348 (2017)
73. A.D.Volosatova, S.V.Kameneva, V.I.Feldman. *Phys. Chem. Chem. Phys.*, **21**, 13014 (2018)
74. E.Dartois, B.Augé, P.Boduch, R.Brunetto, M.Chabot, A.Domaracka, J.J.Ding, O.Kamalou, X.Y.Lv, H.Rothard, E.F.da Silveira, J.C.Thomas. *Astron. Astrophys.*, **576**, A125 (2015)
75. E.Dartois, M.Chabot, T.Id.Barkach, H.Rothard, B.Augé, A.N.Agnihotri, A.Domaracka, P.Boduch. *Astron. Astrophys.*, **618**, A173 (2018)
76. M.J.Loeffler, G.A.Baratta, M.E.Palumbo, G.Strazzulla, R.A.Baragiola. *Astron. Astrophys.*, **435**, 587 (2005)
77. S.Pilling, E.Seperuelo Duarte, A.Domaracka, H.Rothard, P.Boduch, E.F.da Silveira. *Astron. Astrophys.*, **523**, A77 (2010)
78. F.Islam, G.A.Baratta, M.E.Palumbo. *Astron. Astrophys.*, **561**, A73 (2014)
79. A.V.Ivlev, T.B.Röcker, A.Vasyunin, P.Caselli. *Astrophys. J.*, **805**, 59 (2015)
80. K.I.Öberg, G.W.Fuchs, Z.Awad, H.J.Fraser, S.Schlemmer, E.F.van Dishoeck, H.Linnartz. *Astrophys. J. Lett.*, **662**, L23 (2007)
81. M.Bertin, E.C.Fayolle, C.Romanzin, K.I.Öberg, X.Michaut, A.Moudens, L.Philippe, P.Jeseck, H.Linnartz, J.-H.Fillion. *Phys. Chem. Chem. Phys.*, **14**, 9929 (2012)
82. G.M.Muñoz Caro, Y.-J.Chen, S.Aparicio, A.Jiménez-Escobar, A.Rosu-Finsen, J.Lasne, M.R.S.McCoustra. *Astron. Astrophys.*, **589**, A19 (2016)
83. G.M.Muñoz Caro, A.Jiménez-Escobar, J.Á.Martín-Gago, C.Rogero, C.Atienza, S.Puertas, J.M.Sobrado, J.Torres-Redondo. *Astron. Astrophys.*, **522**, A108 (2010).
84. Y.-J.Chen, K.-J.Chuang, G.M.Muñoz Caro, M.Nuevo, C.-C.Chu, T.-S.Yih, W.-H.Ip, C.-Y.R.Wu. *Astrophys. J.*, **781**, 15 (2014)

85. D.M.Paardekooper, G.Fedoseev, A.Riedo, H.Linnartz. *Astron. Astrophys.*, **596**, A72 (2016)
86. E.C.Fayolle, M.Bertin, C.Romanzin, X.Michaut, K.I.Öberg, H.Linnartz, J.-H.Fillion. *Astrophys. J. Lett.*, **739**, L36 (2011)
87. M.Bertin, E.C.Fayolle, C.Romanzin, H.A.M.Poderoso, X.Michaut, L.Philippe, P.Jeseck, K.I.Öberg, H.Linnartz, J.-H.Fillion. *Astrophys. J.*, **779**, 120 (2013)
88. M.Bertin, C.Romanzin, M.Doronin, L.Philippe, P.Jeseck, N.Ligterink, H.Linnartz, X.Michaut, J.-H.Fillion. *Astrophys. J. Lett.*, **817**, L12 (2016)
89. M.S.Westley, R.A.Baragiola, R.E.Johnson, G.A.Baratta, *Nature (London)*, **373**, 405 (1995)
90. T.Hama, M.Yokoyama, A.Yabushita, M.Kawasaki, S.Andersson, C.M.Western, M.N.R.Ashfold, R.N.Dixon, N.Watanabe. *J. Chem. Phys.*, **132**, 164508 (2010)
91. A.J.DeSimone, V.D.Crowell, C.D.Sherrill, Th.M.Orlando. *J. Chem. Phys.*, **139**, 164702 (2013)
92. K.I.Öberg, H.Linnartz, R.Visser, E.F.van Dishoeck. *Astron. Astrophys.*, **693**, 1209 (2009)
93. K.I.Öberg, R.T.Garrod, E.F.van Dishoeck, H.Linnartz. *Astron. Astrophys.*, **504**, 891 (2009)
94. G.A.Cruz-Diaz, R.Martín-Doménech, G.M.Muñoz Caro, Y.-J.Chen. *Astron. Astrophys.* **592**, A68 (2016)
95. N.F.W.Ligterink, C.Walsh, R.G.Bhuin, S.Vissapragada, J.Terwisscha van Scheltinga, H.Linnartz. *Astron. Astrophys.*, **612**, A88 (2018)
96. J.D.Thrower, D.J.Burke, M.P.Collings, A.Dawes, P.D.Holtom, F.Jamme, P.Kendall, W.A.Brown, I.P.Clark, H.J.Fraser, M.R.S.McCoustra, N.J.Mason, A.W.Parker. *Astrophys. J.*, **673**, 1233 (2008)
97. E.C.Fayolle, M.Bertin, C.Romanzin, H.A.M.Poderoso, L.Philippe, X.Michaut, P.Jeseck, H.Linnartz, K.I.Öberg, J.-H.Fillion. *Astron. Astrophys.*, **556**, A122 (2013)
98. R.Martín-Doménech, G.A.Cruz-Díaz, G.M.Muñoz Caro. *Monthly Not. Roy. Astron. Soc.*, **473**, 2575 (2018)
99. R.Dupuy, M.Bertin, G.Féraud, X.Michaut, P.Jeseck, M.Doronin, L.Philippe, C.Romanzin, J.-H.Fillion. *Astron. Astrophys.*, **603**, A61 (2017)
100. G.Féraud, M.Bertin, C.Romanzin, R.Dupuy, F.Le Petit, E.Roueff, L.Philippe, X.Michaut P.Jeseck, J.-H.Fillion. *ACS Earth Space Chem.*, **3**, 1135 (2019)
101. J.Kutzner, G.Lindeke, K.H.Welge, D.Feldmann. *J. Chem. Phys.*, **90**, 548 (1989)
102. M.I.McCarthy, R.B.Gerber, K.A.Trentelman, P.Strupp, D.H.Fairbrother, P.C.Stair, E.Weitz. *J. Chem. Phys.*, **97**, 5168 (1992)
103. D.H.Fairbrother, K.A.Briggman, P.C.Stair, E.Weitz. *J. Chem. Phys.*, **102**, 7267 (1995)
104. J.C.Polanyi, N. S.-K.Sze, J.-X.Wang. *J. Phys. Chem. A*, **101**, 6679 (1997)
105. K.Domen, T.J.Chuang. *J. Chem. Phys.*, **90**, 3318 (1989)
106. K.Leggett, J.C.Polanyi, P.A.Young. *J. Chem. Phys.*, **93**, 3645 (1990)
107. S.Y.Nishimura, D.N.Aldrich, M.T.Hoerth, C.J.Ralston, N.J.Tro. *J. Phys. Chem. B*, **103**, 9717 (1999)
108. V.N.Varakin. *Chem. Phys. Lett.*, **714**, 114 (2019)
109. V.N.Varakin. *Laser Phys.*, **26**, 016001 (2016)
110. V.N.Varakin. *J. Photochem. Photobiol. A: Chem.*, **356**, 298 (2018)
111. V.V.Kislov, T.L.Nguyen, A.M.Mebel, S.H.Lin, S.C.Smith. *J. Chem. Phys.*, **120**, 7008 (2004)
112. T.Ichimura, Y.Mori, H.Shinohara, N.Nishi. *Chem. Phys.*, **189**, 117 (1994)
113. C.K.Ni, C.M.Tseng, M.F.Lin, Y.A.Dyakov. *J. Phys. Chem. B*, **111**, 12631 (2007)
114. T.Kovacs, M.A.Blitz, P.W.Seakins, M.J.Pilling. *J. Chem. Phys.*, **131**, 204304 (2009)
115. M.S.Murga, V.N.Varakin, A.V.Stolyarov, D.S.Wiebe. *Astron. Rep.*, **63**, 633 (2019)
116. K.I.Uchida, K.Sellgren, M.W.Werner, M.L.Houdashelt. *Astrophys. J.*, **530**, 817 (2000)
117. L.Verstraete, C.Pech, C.Moutou, K.Sellgren, C.M.Wright, M.Giard, A.Léger, R.Timmermann, S.Drapatz. *Astron. Astrophys.*, **372**, 981 (2001)
118. E.Peeters, N.L.Martín-Hernández, F.Damour, P.Cox, P.R.Roelfsema, J.-P.Baluteau, A.G.G.M.Tielens, E.Churchwell, M.F.Kessler, J.S.Mathis, C.Morisset, D.Schaerer. *Astron. Astrophys.*, **381**, 571 (2002)
119. M.Goto, W.Gaessler, Y.Hayano, M.Iye, Y.Kamata, T.Kanzawa, N.Kobayashi, Y.Minowa, D.J.Saint-Jacques, H.Takami, N.Takato, H.Terada. *Astrophys. J.*, **589**, 419 (2003)
120. J.D.T.Smith, B.T.Draine, D.A.Dale, J.Moustakas, R.C.Kennicutt Jr., G.Helou, L.Armus, H.Roussel, K.Sheth, G.J.Bendo, B.A.Buckalew, D.Calzetti, C.W.Engelbracht, K.D.Gordon, D.J.Hollenbach, A.Li, S.Malhotra, E.J.Murphy, F.Walter. *Astrophys. J.*, **656**, 770 (2007)
121. J.V.Perea-Calderón, D.A.García-Hernández, P.García-Lario, R.Szczerba, M.Bobrowsky. *Astron. Astrophys.*, **495**, L5 (2009)
122. E.Peeters, A.G.G.M.Tielens, L.J.Allamandola, M.G.Wolfire. *Astrophys. J.*, **747**, 44 (2012)
123. C.Boersma, R.H.Rubin, L.J.Allamandola. *Astrophys. J.*, **753**, 168, (2012)
124. N.L.J.Cox, P.Pilleri, O.Berné, J.Cernicharo, C.Joblin. *Monthly Not. Roy. Astron. Soc.*, **456**, L89 (2016)
125. C.Joblin, A.Abergel, J.Bregman, L.D.Hendecourt, A.M.Heras, M.Jourdain de Muizon, C.Pech, A.G.G.M.Tielens. In *ISO Beyond the Peaks: The 2nd ISO Workshop on Analytical Spectroscopy*. (Eds A.Salama, M.F.Kessler, K.Leech, B.Schulz). (Madrid: ESASP-456, 2000). P. 49
126. E.Peeters, S.Hony, C.Van Kerckhoven, A.G.G.M.Tielens, L.J.Allamandola, D.M.Hudgins, C.W.Bauschlicher. *Astron. Astrophys.*, **390**, L5 (2002)
127. J.Bregman, K.Larson, D.Rank, P.Temi. *Astrophys. J.*, **423**, 326 (1994)
128. G.C.Sloan, J.D.Bregman, T.R.Geballe, L.J.Allamandola, E.Woodward. *Astrophys. J.*, **474**, 735 (1997)
129. L.J. Allamandola, A.G.G.M.Tielens, J.R.Barker. *Astrophys. J. Suppl.*, **71**, 733 (1989)
130. C.J.Mackie, E.Peeters, C.W.Bauschlicher Jr., J.Cami. *Astrophys. J.*, **799**, 131 (2015)
131. S.A.Sandford, M.P.Bernstein, Ch.K.Materese. *Astrophys. J. Suppl.*, **205**, 8 (2013)
132. X.J.Yang, R.Glaser, A.Li, J.X.Zhong. *Astrophys. J.*, **776**, 110 (2013)
133. W.A.Schutte, A.G.G.M.Tielens, L.J.Allamandola. *Astrophys. J.*, **415**, 397 (1993)
134. B.A.Croiset, A.Candian, O.Berné, A.G.G.M.Tielens. *Astron. Astrophys.*, **590**, A26 (2016)
135. F.Galliano, S.C.Madden, A.G.G.M.Tielens, E.Peeters, A.P.Jones. *Astrophys. J.*, **679**, 310 (2008)
136. C.Boersma, J.Bregman, L.J. Allamandola. *Astrophys. J.*, **858**, 67 (2018)
137. D.M.Hudgins, Ch.W.Bauschlicher Jr., L.J.Allamandola. *Astrophys. J.*, **632**, 316 (2005)

138. E.Peeters, Ch.W.Bauschlicher Jr., L.J.Allamandola, A.G.G.M.Tielens, A.Ricca, M.G.Wolfire. *Astrophys. J.*, **836**, 198 (2017)
139. V.Lebouteiller, J.Bernard-Salas, D.G.Whelan, B.Brandl, F.Galliano, V.Charmandaris, S.Madden, D.Kunth. *Astrophys. J.*, **728**, 45 (2011)
140. L.D.Anderson, T.M.Bania, D.S.Balser, V.Cunningham, T.V.Wenger, B.M.Johnstone, W.P.Armentrout. *Astrophys. J. Suppl.*, **212**, 1 (2014)
141. I.W.Stephens, J.M.Evans, R.Xue, Y.-H.Chu, R.A.Gruendl, D.M.Segura-Cox. *Astrophys. J.*, **784**, 147 (2014)
142. A.P.Topchieva, D.S.Wiebe, M.S.Kirsanova, V.V.Krushinskii. *Astron. Rep.*, **61**, 1015 (2017)
143. X.J.Yang, A.Li, R.Glaser, J.X.Zhong, G.C.Sloan, J.D.Bregman, T.R.Geballe, L.J.Allamandola, E.Woodward. *Astrophys. J.*, **825**, 22 (2016)
144. P.Pilleri, J.Montillaud, O.Berné, C.Joblin. *Astron. Astrophys.*, **542**, A69 (2012)
145. P.Pilleri, C.Joblin, F.Boulanger, T.Onaka. *Astron. Astrophys.*, **577**, A16 (2015)
146. H.Andrews, C.Boersma, M.W.Werner, J.Livingston, L.J.Allamandola, A.G.G.M.Tielens. *Astrophys. J.*, **807**, 99 (2015)
147. H.W.Jochims, E.Ruhl, H.Baumgartel, S.Tobita, S.Leach. *Astrophys. J.*, **420**, 307 (1994)
148. S.P.Ekern, A.G.Marshall, J.Szczepanski, M.Vala. *J. Phys. Chem. A*, **102**, 3498 (1998)
149. H.A.B.Johansson, H.Zettergren, A.I.S.Holm, N.Haag, S.B.Nielsen, J.A.Wyer, M.-B.S.Kirketerp, K.Støchkel, P.Hvelplund, H.T.Schmidt, H.Cederquist. *J. Chem. Phys.*, **135**, 084304 (2011)
150. J.Zhen, D.M.Paardekooper, A.Candian, H.Linnartz, A.G.G.M.Tielens. *Chem. Phys. Lett.*, **592**, 211 (2014)
151. J.Zhen, P.Castellanos, D.M.Paardekooper, H.Linnartz, A.G.G.M.Tielens. *Astrophys. J. Lett.*, **797**, L30 (2014)
152. J.Zhen, P.Castellanos, D.M.Paardekooper, N.Ligterink, H.Linnartz, L.Nahon, Ch.Joblin, A.G.G.M.Tielens. *Astrophys. J. Lett.*, **804**, L7 (2015)
153. J.Zhen, P.Castellanos, H.Linnartz, A.G.G. M.Tielens. *Mol. Astrophys.*, **5**, 1 (2016)
154. M.Wolf, H.V.Kiefer, J.Langeland, L.H.Andersen, H.Zettergren, H.T.Schmidt, H.Cederquist, M.H.Stockett. *Astrophys. J.*, **832**, 24 (2016)
155. H.M.Quitián-Lara, F.Fantuzzi, M.A.C.Nascimento, W.Wolff, H.M.Boechat-Roberty. *Astrophys. J.*, **854**, 61 (2018)
156. M.Rapacioli, S.Cazaux, N.Foley, A.Simon, R.Hoekstrad, Th.Schlathölterd. *Phys. Chem. Chem. Phys.*, **20**, 22427 (2018)
157. E.Habart, F.Boulanger, L.Verstraete, C.M.Walmsley, G.Pineau des Forêts. *Astron. Astrophys.*, **414**, 531 (2004)
158. V.Mennella, G.M.Muñoz Caro, R.Ruiterkamp, W.A.Schutte, J.M.Greenberg, J.R.Brucato, L.Colangeli. *Astron. Astrophys.*, **367**, 355 (2001)
159. I.Alata, G.A.Cruz-Diaz, G.M.Muñoz Caro, E.Dartois. *Astron. Astrophys.*, **569**, A119 (2014)
160. I.Alata, A.Jallat, L.Gavilan, M.Chabot, G.A.Cruz-Diaz, G.M.Muñoz Caro, K.Béroff, E.Dartois. *Astron. Astrophys.*, **584**, A123 (2015)
161. W.W.Duley, A.Zaidi, M.J.Wesolowski, S.Kuzmin. *Monthly Not. Roy. Astron. Soc.*, **447**, 1242 (2015)
162. M.Schmidt, A.Masson, C.Bréchignac. *Int. J. Mass Spectrom.*, **252**, 173 (2006)
163. A.Simon, Ch.Joblin. *J. Phys. Chem. A*, **113,** 4878 (2009)
164. Ch.W.Bauschlicher Jr., A.Ricca, C.Boersma, L.J.Allamandola. *Astrophys. J. Suppl.*, **234**, 32 (2018)
165. Ch.W.Bauschlicher, A.Ricca. In *Isaiah Shavitt: a Memorial Festschrift from Theoretical Chemistry Accounts*. (Berlin, Heidelberg: Springer, 2014). P. 245
166. A.Simon, M.Rapacioli, G.Rouaut, G.Trinquier, F.X.Gadéa. *Phil. Transact. Roy. Soc. A*, **375**, Art. ID 20160195 (2017)
167. M.Rapacioli, F.Calvo, F.Spiegelman, C.Joblin, D.J.Wales. *J. Phys. Chem. A*, **109**, 2487 (2005)
168. M.Rapacioli, F.Calvo, C.Joblin, P.Parneix, D.Toublanc, F.Spiegelman. *Astron. Astroph*ys., **460**, 519 (2006)
169. N.A.Marks. In *Computer-Based Modeling of Novel Carbon Systems and Their Properties*. Vol. 3. (Dordrecht, London: Springer, 2010). P. 129
170. T.Allain, S.Leach, E.Sedlmayr. *Astron. Astrophys.*, **305**, 602 (1996)
171. M.S.Murga, S.A.Khoperskov, D.S.Wiebe. *Astron. Rep.*, **60**, 233 (2016)
172. V.Le Page, Th.P.Snow, V.M.Bierbaum. *Astrophys. J. Suppl.*, **132**, 233 (2001)
173. A.G.G.M.Tielens. *The Physics and Chemistry of the Interstellar Medium*. (Cambridge: Cambridge University Press, 2005)
174. O.Berné, A.G.G.M.Tielens. *Proc. Natl. Acad. Sci., USA*, **109**, 401 (2012)
175. E.R.Micelotta, A.P.Jones, A.G.G.M.Tielens. *Astron. Astrophys.*, **510**, A37 (2010)
176. H.Andrews, A.Candian, A.G.G.M.Tielens. *Astron. Astrophys.*, **595**, A23 (2016)
177. A.Leger, L.D'Hendecourt, P.Boissel, F.X.Desert. *Astron. Astrophys.*, **213**, 351 (1989)
178. R.Visser, V.C.Geers, C.P.Dullemond, J.-C.Augereau, K.M.Pontoppidan, E.F.van Dishoeck. *Astron. Astrophys.*, **466**, 229 (2007)
179. J.Montillaud, C.Joblin, D.Toublanc. *Astron. Astrophys.*, **552**, A15 (2013)
180. G.Z.Whitten, B.S.Rabinovitch. *J. Chem. Phys.*, **38**, 2466 (1963)
181. B.T.Draine, D.A.Dale, G.Bendo, K.D.Gordon, J.D.T.Smith, L.Armus, C.W.Engelbracht, G.Helou, R.C.Kennicutt Jr., A.Li, H.Roussel, F.Walter, D.Calzetti, J.Moustakas, E.J.Murphy, G.H.Rieke, C.Bot, D.J.Hollenbach, K.Sheth, H.I.Teplitz. *Astrophys. J.*, **663**, 866 (2007)
182. L.K.Hunt, T.X.Thuan, Y.I.Izotov, M.Sauvage. *Astrophys. J.*, **712**, 164 (2010)
183. A.Tappe, J.Rho, C.Boersma, E.R.Micelotta. *Astrophys. J.*, **754**, 132 (2012)
184. M.S.Khramtsova, D.S.Wiebe, P.A.Boley, Ya.N.Pavlyuchenkov. *Monthly Not. Roy. Astron. Soc.*, **431**, 2006 (2013)
185. D.S.Wiebe, M.S.Khramtsova, O.V.Egorov, T.A.Lozinskaya. *Astron. Lett.*, **40**, 278 (2014)
186. B.T.Draine, A.Li. *Astrophys. J.*, **657**, 810 (2007)
187. A.P.Jones, N.Ysard, M.Koehler, L.Fanciullo, M.Bocchio, E.Micelotta, L.Verstraete, V.Guillet. *Faraday Discuss.*, **168**, 313 (2014)
188. A.I.Vasyunin, A.M.Sobolev, D.S.Wiebe, D.A.Semenov. *Astron. Lett.*, **30**, 566 (2004)
189. A.I.Vasyunin, D.Semenov, Th.Henning, V.Wakelam, E.Herbst, A.M.Sobolev. *Astrophys. J.*, **672**, 629 (2008)
190. A.I.Vasyunin, E.Herbst. *Astrophys. J.*, **762**, 86 (2013)
191. A.I.Vasyunin, E.Herbst. *Astrophys. J.*, **769**, 34 (2013)

192. A.I.Vasyunin, P.Caselli, F.Dulieu, I.Jiménez-Serra. *Astrophys. J.*, **842**, 33 (2017)
193. V.V.Akimkin, Y.N.Pavlyuchenkov, A.I.Vasyunin, D.S.Wiebe, M.S.Kirsanova, T.Henning. *Astrophys. Space Sci.*, **335**, 33 (2011)
194. V.Akimkin, S.Zhukovska, D.Wiebe, D.Semenov, Ya.Pavlyuchenkov, A.Vasyunin, T.Birnstiel, Th.Henning. *Astrophys. J.*, **766**, 8 (2013)
195. T.Vasyunina, A.I.Vasyunin, E.Herbst, H.Linz, M.Voronkov, T.Britton, I.Zinchenko, F.Schuller. *Astrophys. J.*, **780**, 85 (2014)
196. A.Occhiogrosso, A.Vasyunin, E.Herbst, S.Viti, M.D.Ward, S.D.Price, W.A.Brown. *Astron. Astrophys.*, **564**, A123 (2014)
197. D.M.Graninger, E.Herbst, K.I.Öberg, A.I.Vasyunin. *Astrophys. J.*, **787**, 74 (2014)
198. V.M.Rivilla, F.Fontani, M.T.Beltrán, A.Vasyunin, P.Caselli, J.Martín-Pintado, R.Cesaroni. *Astrophys. J.*, **826**, 161 (2016)
199. I.Jiménez-Serra, A.I.Vasyunin, P.Caselli, N.Marcelino, N.Billot, S.Viti, L.Testi, Ch.Vastel, B.Lefloch, R.Bachiller. *Astrophys. J. Lett.*, **830**, L6 (2016)
200. V.A.Sokolova, A.B.Ostrovskii, A.I.Vasyunin. *Astron. Rep.*, **61**, 678 (2017)
201. C.Mininni, F.Fontani, V.M.Rivilla, M.T.Beltrán, P.Caselli, A.Vasyunin. *Monthly Not. Roy. Astron. Soc.*, **476**, L39 (2018)
202. B.Müller, B.M.Giuliano, L.Bizzocchi, A.I.Vasyunin, P.Caselli. *Astron. Astrophys.*, **620**, A46 (2018)
203. G.-Y.Zhang, J.-L.Xu, A.I.Vasyunin, D.A.Semenov, J.-J.Wang, S.Dib, T.Liu, Sh.-Y.Liu, Ch.-P.Zhang, X.-L.Liu, K.Wang, D.Li, Zh.-Z.Wu, J.-H.Yuan, D.-L.Li, Y.Gao. *Astron. Astrophys.*, **620**, A163 (2018)
204. A.Chacón-Tanarro, P.Caselli, L.Bizzocchi, J.E.Pineda, O.Sipilä, A.Vasyunin, S.Spezzano, A.Punanova, B.M.Giuliano, V.Lattanzi. *Astron. Astrophys.*, **622**, A141 (2019)
205. V.M.Rivilla, M.T.Beltrán, A.Vasyunin, P.Caselli, S.Viti, F.Fontani, R.Cesaroni. *Monthly Not. Roy. Astron. Soc.*, **483**, 806 (2019)
206. Ch.N.Shingledecker, A.I.Vasyunin, E.Herbst, P.Caselli. *Astrophys. J.*, **876**, 140 (2019)