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Matrix isolation in laboratory astrochemistry: state-of-the-art, implications and perspective

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Recent progress in observational astronomy and astrophysics has stimulated intensive laboratory studies aimed at elucidating the mechanisms of evolution of molecular matter in interstellar space and various space objects. One of the most intriguing and rapidly developing areas of these studies is the so-called "cold astrochemistry" devoted to the complex processes occurring in astrophysical ices. In this context, the matrix isolation technique (known for decades) is a very useful approach for both interpreting the results of astrophysical observations and verifying possible mechanisms of key astrochemical processes. This review outlines the most important results of recent studies using the matrix isolation technique. In fact, the results of these studies contribute to "cold" astrochemistry in two main aspects: (i) spectroscopy of astrochemically important molecules, ions and radicals stabilized in cryogenic matrices; (ii) experimental modeling of mechanisms of radiation-induced and "in dark" chemical reactions occurring in "cold" space environments (interstellar, cometary and planetary ices). In the first aspect, special attention is paid to new spectroscopic data obtained using various methods (electronic and vibrational absorption spectroscopy, electron paramagnetic resonance spectroscopy). In the second aspect, we consider the chemical effects resulting from both direct excitation of isolated molecules and the transfer of energy initially absorbed by the medium. Special attention has been paid to recent studies of spectroscopic characteristics and radiation-induced evolution of matrix-isolated weak intermolecular complexes, which can be considered "building blocks" for cold synthesis of complex molecules in the absence of diffusion mobility. In addition, we consider the use of matrix isolation for the studies of low-temperature chemical reactions "in dark" involving atoms and highly reactive intermediates, which can occur in cold space environments. In the final part, we briefly discuss the applicability of the results of matrix isolation experiments for interpretation of the mechanisms in molecular ices and highlight the prospects of this field. The review can also be useful for specialists in various aspects of chemistry and chemical physics (radiation chemistry, photochemistry, molecular spectroscopy, low-temperature chemistry).
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1. Introduction

According to a broad definition, astrochemistry (also referred to as molecular astrophysics) generally deals with the formation and evolution of molecules in astronomical environments and its effect on the dynamics and evolution of astronomical objects.[1] In a more specific context, it is devoted to chemical reactions occurring in different types of astrophysical media.[2] In fact, it is astrochemistry that lies behind the chemical diversity of the Universe and origin of life. A growing interest in this field during the past two decades has been associated with impressive progress in observational astronomy, which has made it possible to detect more than 200 molecular species in the interstellar medium (ISM), cometary and planetary material, including neutral closed-shell molecules, radicals, and positive and negative ions.[3] These findings partially inspired new ambitious space missions with one of the key objectives to search for "prebiotic" molecules and chemical signatures of life in extraterrestrial objects. On the other hand, they provide new challenges for simulations of chemical reactions in space, which constitute the main task of laboratory astrochemistry. The latter term broadly includes both theoretical (computational) and experimental model investigations. Theoretical simulations based on kinetic modelling are extensively developing within the concept of "astrochemical networks" (see, *e.g.*, Ref. 4 for a comprehensive overview of earlier works). One may also refer to a recent review[5] considering theoretical studies of suprathermal particles ('hot' atoms and molecules) as essential reagents of astrochemical processes in planetary atmospheres and dust clouds. Despite significant improvements in computational methods and approaches, theoretical astrochemistry crucially needs experimental verification of complex schemes, including a very large number of elementary reactions involving different types of intermediates. This part is the matter of experimental laboratory astrochemistry based on experimental simulation of chemical reactions in space and analysis of their products by different methods.

Considering the principles of laboratory simulation, one should bear in mind that the processes in different astrophysical media occur under different conditions. Generally, astrochemistry can be divided into "hot" and "cold" branches. "Hot" astrochemistry is related to the processes occurring in protoplanetary disks and plasmas, where the temperature may reach 100 to 1000 K or even above. On the other hand, "cold" astrochemistry is related to the processes occurring at temperatures below 100 K in a variety of astrophysical media (interstellar clouds, cometary and planetary ices, *etc.*) and is supposed to be extremely important for molecular and prebiotic evolution in space. Generally, cold astrochemical processes may occur both in the gas phase and in condensed media (dust grain surfaces, ice mantles consisting of 50 – 100 molecular layers and bulky ice particles).[6] Meanwhile, the surface and condensed phase "cold" astrochemistry is a particular focus of many experimental simulations, often defined as laboratory ice astrochemistry. It is worth noting that complex processes in astrophysically relevant ices are still not accessible by rigorous theoretical treatment, and experimental simulation is the main source of data for comparison with astronomical observations. In most cases, the processes in cosmic ices occurring at very low temperatures are initiated by high-energy photons or cosmic rays, so laboratory ice astrochemistry is closely related to photochemistry and radiation chemistry. Extensive studies in this field were carried out by many research groups, and one may refer to recent reviews to realize the potentiality of this approach and its relevance to astronomical observations (see, *e.g.*, Refs 7 – 10). Typically, the changes in ice composition induced by light or ionizing particles are monitored by FTIR (Fourier transform infrared) spectroscopy, and the desorbed molecular products are analyzed using mass spectrometry combined with other techniques. The development of advanced analytical techniques and the application of different radiation sources made it possible to obtain new insight into the possible routes of formation and degradation of key astrochemical molecules at low temperatures. Nevertheless, there are two significant limitations within the common experimental approach of laboratory ice astrochemistry, namely, poor quality of spectra in molecular ices and lack of direct information on the step-by-step mechanism of chemical transformations and the nature of intermediates. Both of these issues can be resolved with the application of matrix isolation as a complementary approach.

Matrix isolation is a well-established approach for studies of unstable molecules and intermediates stabilized in a rigid inert environment at low temperatures, known for more than sixty years.[11] Commonly, it implies the use of

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solid noble gases (from Ne to Xe) as media. Due to superior spectral resolution (compared to molecular solids), weak perturbation of spectroscopic characteristics of the studied species, and absence of intrinsic absorptions of the medium, matrix isolation may give unique and precise spectroscopic information on unstable molecules and intermediates for comparison with astronomical observations. Furthermore, and even more important for laboratory astrochemistry, matrix isolation experiments can be easily combined with UV photolysis and radiolysis, providing unique opportunities for studies of the mechanisms of photoinduced and radiation-induced transformations of molecules in cryogenic solids. It is also suitable for investigations of the intrinsic dynamics of molecular and ionic species, mobility of atoms in solids, and low-temperature chemical reactions, which may occur through both classic and tunneling mechanisms.

Regarding applications to ice astrochemical simulations, it is often stated that the weak point of matrix isolation is a great difference in the medium composition.[8] Indeed, noble gases mostly used in matrix isolation studies do not occur in sufficient amounts in any astrophysical object, and cosmic ices are predominately composed of several basic molecular components (such as H_2O, CO, CO_2, N_2) doped with small amounts of other molecules. Nevertheless, considering the formation and transformations of complex molecular species, we may note that the common concept of an "isolated guest molecule in a solid ice" is relevant to both matrix isolation and a large part of ice astrochemistry. There is no strict boundary between "matrix" and "ice". For example, solid nitrogen may be considered both an inert matrix and molecular ice depending on the experimental conditions and target of the study. Moreover, the variations in the physical characteristics of the matrix within the matrix isolation approach may provide important insight into the general features of the medium effect in the radiation-induced transformations of guest molecules in rigid icy media.[12,13]

It should be noted that astrochemical motivation was actually one of the drivers of matrix isolation studies, starting from early works.[14] However, to the best of our knowledge, modern comprehensive reviews on the applications of matrix isolation for astrochemistry in various aspects are unavailable. The purpose of this review, predominately focusing on the works performed during the past two decades, is to analyze the achievements, implications and prospects of matrix isolation technique in view of major challenges of astrochemistry, including both spectroscopic and mechanistic issues.

2. Matrix isolation spectroscopy of astrochemically important species

As mentioned in the Introduction, matrix isolation is a powerful tool for detailed spectroscopic characterization of various reactive species extensively used for several decades (see, *e.g.*, Ref. 15). It should be emphasized that many important intermediates occurring in the space media were first identified and characterized in the matrix isolation experiments, which stimulated their subsequent detection by astrophysical tools.

The identification of matrix-isolated species relies on a number of different spectroscopic methods, depending on the chemical nature of the studied species and their electronic, vibrational, and magnetic properties. Definitely, the most common method for molecular systems (including molecular ions and radical ions) is IR (vibrational) absorption spectroscopy, which is currently used in the FTIR version. Generally, this method is applicable to nearly all molecular species (with the only exception of homonuclear diatomic molecules). In the context of laboratory astrochemistry, matrix isolation FTIR spectroscopy is a very useful complementary tool for model studies of the processes in astrophysical ices because the assignment of the spectroscopic features of the products appearing in ice transformations is often based on the data of matrix isolation experiments.[16–18] In addition to application to unstable intermediates, such as neutral radicals and ions, matrix isolation FTIR spectroscopy is also helpful for the characterization of astrophysically important unusual molecules (such as cyanopolyynes[19,20]), metastable structural isomers and high-energy conformers of common molecules.[21,22] UV/vis (electronic) absorption spectroscopy is typically a less informative method for neutral molecules and radicals. However, this method may be helpful for ionic species, which often show low-energy electronic transitions. Additionally, aromatic and conjugated species are suitable candidates for characterization by UV/vis spectroscopy in matrices. Some examples of the efficient application of the combination of UV/vis and FTIR matrix isolation spectroscopy for the characterization of astrophysically important aromatic molecules, carbon chains and ions can be found in earlier papers[23–27] (see also chapters 2.2 and 2.3 of this review). Another method based on probing electronic transitions is emission (luminescence) spectroscopy. Despite some complications and limitations, emission matrix isolation spectroscopy can also be useful for the characterization of astrophysically relevant species (in particular, in combination with electronic absorption spectroscopy).[28–30] Electron paramagnetic resonance (EPR) spectroscopy is a highly informative method for the investigation of isolated magnetic species (neutral radicals, radical ions, triplet and high-spin states). This method may provide precise identification of the radical structure and provide direct information on hyperfine interactions, which is important for the interpretation of rotational structures detected in natural astrophysical studies. Possible astrophysical implications of matrix isolation EPR spectroscopy were mentioned in a review by Weltner,[31] and in a wider context, early results were summarized by Symons.[32] Application of this method to the characterization of small astrophysically important radical ions in matrices has been demonstrated by Knight.[33,34] Meanwhile, it should be noted that astrochemically targeted matrix isolation EPR studies are still relatively limited, and the potential of this approach (particularly in combination with FTIR spectroscopy) is still not fully realized by the community.

In addition to characterization of highly reactive intermediates and metastable molecules, which could exist in interstellar media, matrix isolation spectroscopy may also be useful for detailed structural investigation of weak intermolecular complexes and products of their transformations. Elucidation of the features of these species is crucially important for understanding the radiation-driven astrochemical processes in rigid icy media occurring at extremely low temperatures. The effect of intermolecular interactions on the spectroscopic properties of molecules and radicals can be effectively probed by matrix isolation FTIR spectroscopy.[21,35] In certain cases, the complexation-induced perturbation of the electronic structure of radicals may be revealed by high-resolution matrix EPR spectroscopy.[36]

In this chapter of the present review, we will mainly focus on matrix isolation spectroscopic studies on reactive and metastable astrochemically important molecular species and their complexes performed during the last twenty years. The key early works will also be mentioned referring to the existing reviews, whenever possible. We may note that a comprehensive survey of matrix isolation studies, which could be indirectly related to astrochemical issues, is out of the scope of this review. The main goal is to give an overview of the research activity of world leading matrix isolation groups with respect to hot problems of astrochemistry and to identify major achievements.

2.1. Small intermediates and metastable molecules

Ions, free radicals, carbenes and metastable closed-shell molecules — the species that have transient nature under terrestrial conditions — constitute approximately half of the chemical compounds detected in the ISM. Low temperatures and low densities are the determining factors for the "common" existence of metastable chemicals in space environments. For a molecule to be detected in space, ground-based knowledge of its spectra is required. From the laboratory perspective, obtaining spectra of a short-living intermediate requires using special experimental approaches to stabilize this transient species. The matrix isolation technique is one of those approaches. Very early matrix isolation studies performed in the 1950 – 60s brought first ever discoveries of some molecules, which later were found to exist in space. Nitroxyl (HNO) was first directly detected in matrix-isolation infrared spectroscopy experiments of Brown and Pimentel when they studied photolysis of nitromethane in solid argon.[37] Milligan first identified methyleneimine ($CH_2{=}NH$) prepared by the photolysis of methyl azide in solid argon.[38] Further investigations on photochemistry in that system led to the first discovery of hydrogen isocyanide (HNC), a very important species in astrochemistry.[39] Jacox and colleagues also performed the first direct detections of CCO radicals[40] and HOCN molecules.[41] Jacox first assigned the IR spectrum of ketenimine (CH_2CNH) in an Ar matrix.[42] Two decades later, ketenimine was discovered in the star-forming region Sagittarius B2(N),[43] and it is considered to form by reaction between C_2H_2 and NH[44] or tautomerization of CH_3CN[42] based on matrix-isolation studies. Methylene imino (H_2CN) free radicals were first detected in the laboratory by Cochran *et al.*, who applied matrix-isolation EPR spectroscopy to study the products of VUV photolysis of HCN molecules isolated in an argon matrix.[45]

Various preparation approaches can be used to prepare transient species in matrices, such as (1) vacuum or low-pressure flash pyrolysis of suitable precursors with subsequent isolation of pyrolysis products in matrices (see, *e.g.*, Refs 46, 47); (2) laser ablation — it was shown that small molecules may capture electrons under the codeposition of gaseous mixtures with laser-ablated metal atoms (see, *e.g.*, Refs 48, 49); (3) different types of gas discharge with direct discharge of a gaseous sample or codeposition of samples with a beam of excited atoms (see, *e.g.*, Refs 50 – 52); (4) UV photolysis or radiolysis of matrix-isolated precursors — either single molecules or binary systems; and secondary photolysis of matrix samples with UV or visible light to provide photodecomposition or photoisomerization of initially produced intermediate species (see, *e.g.*, Refs 53 – 57); (5) thermal-induced synthesis form initially produced intermediate species (see, *e.g.*, Refs 58, 59).

A large amount of spectroscopic data on various transient species obtained using the matrix isolation approach by the mid-2000s was thoroughly collected and systematized by M.Jacox[60, 61] and, with some later additions, is currently available as a part of the NIST Chemistry Webbook database.[62] There is also a relevant review from E.Baskir *et al.*,[63] which contains extensive bibliography on the IR and EPR spectroscopy of free radicals stabilized in cryogenic matrices.

Under the scope of the present review, we are willing to discuss the matrix isolation spectroscopy of astrochemically

Table 1. Bibliography of recent matrix-isolation studies on spectroscopy of metastable species, representing potential interest for astrochemistry.

Species/Matrix	Preparation approach	Spectroscopic method	Ref.
	Hydrogen – oxygen and hydrogen – nitrogen compounds		
OH^+/Ar; H_2O^+/Ar	high-frequency discharge	IR	50
H_2OOO^+/Ar	radiofrequency discharge	IR	65
trans-$HOOH^+$/Ne	microwave discharge	IR	51
$HOHOH^-$/Ne; $HOHO^-$/Ne; HO_2^+/Ne	microwave discharge	IR	52
NH_3^+/Ne	Penning ionization and/or photoionization by neon atoms in their first excited states	IR	66
NH_4^+/Ne	co-deposition with discharged neon atoms	IR	67
	Carbon, nitrogen, and phosphorus oxides		
$C_2O_3^-$/Ar	laser ablation	IR	68
N_2O_3/Ar	308 nm photolysis	IR	69
$(NO)_2^+$/Ne; $(NO)_2^-$/Ne; $(NO)_3^-$/Ne	microwave discharge	IR	70, 71
$OONO^-$/Ar	laser ablation	IR	72
NO_3/Ne and Ar	microwave discharge	IR	73, 74
PO_3^-/Ar; PO_2/Ar; PO_2^-/Ar; P_2O/Ar; OPOPO/Ar	laser ablation	IR	75
	Sulfur-bearing compounds		
S_2^-/Ne; S_3^-/Ne	hot-cathode discharge	electronic absorption	76
OSSO/Ar	microwave discharge	IR	77

Table 1 (continued).

Species/Matrix	Preparation approach	Spectroscopic method	Ref.
SO_2^+/Ne; SO_2^-/Ne; $(SO_2)_2^-$/Ne	Penning ionization and(or) photoionization by neon atoms	IR	78
OSOO and *cyc*-OS(=O)O/ N_2, Ne, and Ar	193 nm photolysis infrared light irradiation	IR, UV/vis	79, 80
CS_2^+/Ne and Ar; CS_2^-/Ne and Ar; $C_2S_4^+$/Ne and Ar	laser ablation	IR	49
$(CS_2)_2^-$ /Ne and Ar	high-frequency discharge	IR	81
CS_3/Ar	high-frequency discharge	IR	58
	Simple organic species		
CH_2^+/Ne	microwave discharge	IR	82
$C_2H_4^+$/Ne, Ar, Kr, and Xe	microwave discharge; electron bombardment of a gaseous mixture; UV photolysis or fast electron irradiation of matrix	IR, EPR	83 – 86
cyc-$C_3H_3^+$ and CH_2CCH^+/Ar	electron bombardment of a matrix	IR	87
CH_3O/*p*-H_2	UV-photolysis	IR	55, 88
CH_2OH/*p*-H_2	UV-photolysis	IR	55
$HOCO^+$/Ne and *p*-H_2	microwave discharge; electron bombardment	IR	89 – 91
HCO_2^-/Ne and *p*-H_2	microwave discharge; electron bombardment	IR	89 – 91
H_2CCN/Ar; H_2CNC/Ar	photolysis	IR	56
$(H\ddot{C}NH_2)$/Ar	high-vacuum flash pyrolysis	IR, UV/vis	92
	Polyheteroatomic species		
HSCN/Ar and N_2; HSNC/Ar and N_2	near-UV photolysis	IR	93
HCNS/Ar and Kr; H_2NCNX/Ar and Kr	254 nm photolysis	IR	94
H_2NNCX/Ar and Kr; *cyc*-$H_2NC(NX)$/Ar and Kr (X = O, S)	UV photolysis	IR, UV	95
HNNCHO/Ar and Kr; HNNCHS/Ar and Kr	UV photolysis	IR	96
NCXNC/Ar and Kr; NCNCX/Ar and Kr (X = S, Se)	254 nm photolysis	IR, UV	97
OCCNO/Ne, Ar, and N_2; CNO/Ne, Ar, and N_2	photolysis	IR	98
OSNSO/Ne, Ar, and N_2	flash vacuum pyrolysis	IR	99
OCNSO/Ar and N_2	flash vacuum pyrolysis	IR	100
SPN/Ar	193 nm photolysis	IR	101
OSSO/Ar and N_2	266 nm photolysis	IR, UV/vis	102
OSCN/Ar and N_2	vacuum pyrolysis	IR	46
H_2NSO/Ar and N_2	flash vacuum pyrolysis	IR	47
$HNSO_2$/Ar, Ne, and N_2	193 nm photolysis	IR, UV/vis	103
OSN/Ne and Ar	flash vacuum pyrolysis	IR	104
cyc-PON/Ne, Ar, and N_2; OPNCO/Ne, Ar, and N_2	193 nm photolysis; 365 nm photolysis	IR	105
HCCNCO/Ne, Ar, and N_2	high-vacuum flash pyrolysis	IR	106
trans-HNOH/*p*-H_2,	VUV irradiation	IR	107
NH_2NO/Ne; NH_2NO^+/Ne; $NNOH^+$/Ne	microwave discharge	IR	108
ONH(OH)/*p*-H_2	photolysis	IR	109
trans-HNNO/Xe	UV photolysis	IR	59
OCS^+/Ne; OCS^-/Ne	microwave discharge	IR	110
HSO_2/Ar, Kr, and Xe; *cis*-HOSO/Ar, Kr, and Xe	UV-photolysis	IR	57, 111
HSOH/Ar	low-pressure pyrolysis	IR	112
HOPO/N_2	high-vacuum flash pyrolysis	IR	64

relevant compounds. Chemical composition in space varies in different types of cosmic objects. Meanwhile, hydrogen is generally the most abundant element in cosmic media, followed by helium, nitrogen, oxygen, carbon, and sulfur.[2] Although phosphorus is a minor element, it should play an important role in prebiotic astrochemistry.[64] Taking elemental composition as a necessary (but not sufficient) criterion of potential astrochemical relevance, below, we give an overview of matrix-isolation studies (performed during the past two decades), which were related to the spectroscopy of small-size (no more than 6 atoms) transient species composed of H, C, N, O, S, and P atoms. Some summary is given in Table 1, while additional information is provided in further text.

2.1.1. Hydrogen – oxygen and hydrogen – nitrogen compounds

Water is quite abundant in space, both in the ISM and solar system bodies.[113] Various hydroxo-, hydroperoxo- and related species are produced upon irradiation of water ices. H_2O^+ and OH^+ ions solvated in solid argon (produced using high-frequency discharge) were studied by means of infrared spectroscopy in Ref. 50 Absorptions of H_2O^+ in Ar are redshifted with respect to the gas-phase fundamentals, while the opposite is true for OH^+. Both OH^+ and H_2O^+ cations can form complexes with argon atoms $OH^+ - Ar_5$ and $H_2O^+ - Ar_4$, respectively. Zhou *et al.*[65] obtained the H_2OOO^+ radical cation by condensation of H_2O/Ar and O_2/Ar mixtures *via* radiofrequency discharge. This species was identified by infrared spectroscopy using isotopic substitutions, while quantum chemical calculations

supported the spectral assignment and gave insight into the structure and nature of bonding. It was concluded that the H_2OOO^+ structure is not simply ion-molecule complex $O_2^+\cdots H_2O$ but includes a three-center one-electron bond. The H_2OOO^+ cation was found to be sensitive to UV photolysis but stable under visible light. High reactivity of H_2OOO^+ was evidenced by annealing-induced (20 K) decay of its absorptions, although decomposition products were not uniquely identified. Infrared absorptions of *trans*-$HOOH^+$, $HOHOH^-$, $HOHO^-$, HO^{2+} ions and their isotopologues were ascribed (with tentative assignments for the two latter species) by Thompson and Jacox.[51, 52]

Ammonia is one of the most abundant astrochemical species, and its derivatives are thought to play an important role in amino acids formation.[113, 114] NH_3^+ and NH_4^+ ions and their isotopologues were also trapped in the neon matrix and investigated by means of infrared spectroscopy.[66, 67]

2.1.2. Nitrogen and phosphorus oxides

Infrared spectroscopy of NO_3 radicals trapped in solid neon was studied by Jacox and Thompson in 700 – 3000 and 7000 – 10000 cm^{-1} ranges.[73,74] The peroxynitrite anion $OONO^-$ (both cis and trans isomers) was identified in the Ar matrix by means of IR spectroscopy.[72]

Infrared spectra of *trans*-$ONNO^+$, *trans*-$ONNO^-$, *cis*-$ONNO^-$, $(NO)_3^-$ were measured in solid neon.[70, 71] Y.-P.Lee obtained IR spectra of *asym*-N_2O_3, *sym*-N_2O_3, and *trans* – *cis*-N_2O_3 isomers in an Ar matrix and studied their photoinduced interconversions.[69] UV photolysis of *sym*-N_2O_4 in the Ne matrix resulted in *trans*-$ONONO_2$, a weakly interacting $(NO_2)_2$ radical pair, and traces of *cis*-$N_2O_2\cdot O_2$, which were detected by IR spectroscopy.[115]

P_4 and different phosphorus oxides (PO_2, PO_2^-, P_2O, OPOPO) were obtained and characterized by infrared spectroscopy in an Ar matrix.[75] IR spectra of *syn*- and *anti*-conformations of metaphosphorous acid (HOPO) were measured in a N_2 matrix.[64]

2.1.3. Sulfur-bearing compounds

Sulfur-bearing molecules are of specific interest in the context of diverse astrochemical evolution.[116, 117] Shnitko *et al.* reported the electronic absorption spectra of S_2^- and S_3^- ions isolated in neon.[76] The ions were produced in a hot-cathode discharge source and then mass-selected for neon matrix deposition.

Recently, *cis*- and *trans*-OSSO were obtained in an argon matrix.[77] OSSO and other sulfur-bearing (S_2O, S_3, cyclic and trigonal S_2O_2) molecules were discussed as possible components of the Venus atmosphere.[77] The vibrational spectra of molecular ions SO_2^+, SO_2^- and $(SO_2)_2^-$ were measured in a neon matrix after deposition of an ionized SO_2/Ne mixture.[78] The SO_3 isomers [*cis*-OSOO and cyclic OS(=O)O] were studied in matrices by means of IR spectroscopy.[79, 80] HSO_2 and its isomer *cis*-HOSO were prepared in noble-gas matrices by reaction of photoproduced (from UV-photolysis of H_2S or H_2O) hydrogen atoms with SO_2 and characterized by infrared spectroscopy.[57, 111] Light-induced interconversion of the isomers was also investigated. Laser photolysis (266 nm) of HOSO radical in the Ar matrix results in the OH···OS complex.[118] Beckers *et al.* reported both matrix isolation and gas-phase IR spectroscopic detection of HSOH prepared by low-pressure pyrolysis of di-*tert*-butyl sulfoxide (Bu^t_2SO).[112]

In laser ablation experiments, CS_2^+, CS_2^-, $C_2S_4^+$, and $C_2O_3^-$ anions were prepared and characterized by infrared absorption spectroscopy (two latter ions — for the first time).[49, 68] Interestingly, the $(CS_2)_2^-$ anion was not formed in the laser ablation experiments (codeposition of CS_2/Ng mixtures with laser-ablated atoms), presumably due to the significant activation energy of the $CS_2^- + CS_2$ reaction. It was later prepared by the deposition of CS_2/Ng (Ng = Ne, Ar) mixtures *via* high-frequency discharge.[81] Carbon trisulfide was prepared in argon matrices by thermally induced reaction of CS and S atoms (both reactants had been produced using high-frequency discharge) and characterized by infrared spectra.[58] It was found that visible light decomposed CS_3 into the weakly bound SCS···S complex.

2.1.4. Simple organic species

Small hydrocarbons are interstellar widespread molecules observed on comets and in molecular clouds.[113, 114] Preliminary infrared detection of neon-isolated CH_2^+ ions (968.4/961.1 cm^{-1} doublet) was reported in Ref. 82. The first infrared detection of the $C_2H_4^+$ cation and its d isotopologue has been provided in Ref. 83. Later, Chen *et al.* prepared $C_2H_4^+$ in an argon matrix, provided further vibrational assignments and investigated its photochemistry.[84] UV photolysis (225 – 345 nm) of argon matrices containing $C_2H_4^+$ led to both neutralization and decomposition (forming C_2H_2 and C_2H_3). Y.J.Wu and co-workers used 120-nm photolysis of C_2H_4/Ne ice to obtain the IR spectrum of C_2H_3 radicals.[85] FTIR and EPR spectra of C_2H_3 radicals isolated in Ar, Kr, and Xe matrices were revisited by Tanskanen *et al.*[86] IR spectra of *cyc*-$C_3H_3^+$ and CH_2CCH^+ cations (possibly involved in the synthesis of cumulenic and cyclic C_3H_2 in the interstellar medium) were measured in Ar matrices in Ref. 87.

Small oxygen- and nitrogen-bearing compounds are considered building blocks for the prebiotic evolution of organic matter in extraterrestrial media.[4, 113, 114] Elusive methoxy radical CH_3O and its deuterated analogues were prepared by UV photolysis (355 nm) of nitromethane in a *p*-H_2 matrix and thoroughly characterized by infrared spectroscopy.[55, 88] It was also shown that methoxy radicals react rapidly with H_2 to form hydroxymethyl radicals, and rate coefficients were determined for the decay of different isotopologues of methoxy radical. *trans*-$HCOOH^+$, $HOCO^+$, HCO_2^- ions were produced by codeposition of a H_2/CO_2/Ne mixture with excited Ne atoms and characterized by infrared spectra in a Ne matrix.[89, 90] Notably, the $H_2\cdots CO_2^-$ complex was also detected by means of IR spectroscopy.[90] Electron bombardment of the *p*-H_2 matrix containing CO_2 results in *trans*-$HOCO^+$, HCO^-, and $H^+(CO_2)_2$ ions.[91] The ν_1 IR absorption line of *trans*-$HOCO^+$ in *p*-H_2 and Ar is redshifted in comparison to the gas phase spectrum by 972 and 702 cm^{-1}, respectively, due to partial proton sharing between CO_2 and the matrix.

Cyano and isocyano methyl radicals (H_2CCN and H_2CNC) were obtained in argon matrices as the products of CH_3CN photolysis upon exposure to laser ablation plume irradiation.[56] This work provided further knowledge of the infrared spectra of these species. Another possible isomer, cyc-H_2CCN, was not stabilized because of its high energy and low barriers to H_2CCN and H_2CNC. In addition, UV-induced photoconversion of H_2CCN to H_2CNC was also found. The simplest amino carbene $H\ddot{C}NH_2$ was prepared by high-vacuum flash pyrolysis of cyclopropyl-

amine and characterized in an Ar matrix by IR and UV/Vis spectroscopy.[92]

2.1.5. Polyheteroatomic species

Small polyheteroatomic species, *i.e.*, compounds containing more than one heteroatom, have a rich diversity of isomers, while some of the isomers are often elusive. Matrix isolation experiments may be very valuable for the stabilization and spectroscopic characterization of transient isomers. Wierzejewska and Mielke performed near-UV photolysis of matrix-isolated isothiocyanic acid HNCS and for the first time obtained its metastable isomers — thiocyanic acid HSCN and isothiofulminic acid HSNC — which were characterized by means of infrared spectroscopy.[93] Another [H, C, N, S] isomer, thiofulminic acid HCNS, was characterized later. Pasinszki *et al*. prepared HCNS in cryogenic matrices by 254-nm photolysis of 1,2,5]thiadiazole.[94] We may note that so far, only HNCS and HSCN were detected in the ISM. A similar preparation approach (photolysis of matrix-isolated heterocyclic compounds) has been used in other recent works by Prof. Tarczay's group, who reported the characterization of various [NH_2, C, N, O] and [NH_2, C, N, S] isomers.[95,96] Another example of polyheteroatomic species of potential astrochemical interest, which have been prepared and investigated using matrix-isolation spectroscopy, are NCXNC and NCNCX (X = S, Se) compounds.[97]

Various heteroatomic transient species have been investigated in the group of Prof. Zeng during the last decade. Many of these compounds represent potential astrochemical interest, namely, OCCNO,[98] OSNSO[99] and OCNSO[100] heterocumulenes; various SPN,[101] OSSO,[102] OSCN,[46] H_2NSO,[47] and $HNSO_2$ isomers;[103] CNO,[98] OSN,[104] and *cyc*-PON[105] triatomics; and HCCNCO[106] and OPNCO.[105]

Infrared spectra of OCS^+, OCS^-, NH_2NO, NH_2NO^+, and $NNOH^+$ species produced in the gas phase and trapped in the neon matrix were measured by Jacox.[108,110] *trans*-HNNO obtained in xenon matrix by thermal-induced reaction was identified by IR spectroscopy in Ref. 59. Photolysis of *p*-H_2 matrix samples was used to obtain and characterize *trans*-HNOH[107] and ONH(OH)[109] radicals by IR spectroscopy. Although HNOH and ONH(OH) have not been identified in extraterrestrial media to date, they can play important roles in the N/O chemical networks in space at low temperatures.[109] IR spectra of *syn*- and *anti*-conformations of metaphosphorous acid (HOPO) were measured in a N_2 matrix.[64]

2.2. Carbon chains

A variety of highly unsaturated carbon chains were observed in different interstellar objects. Such species are typically extremely unstable under ambient conditions, so matrix isolation experiments were very helpful for their identification. In addition to hydrocarbon cumulenic chains (HC_nH, HC_n, C_n, *etc.*), carbon forms different types of linear compounds, including heteroatoms (N, O and S).[2,119] The list of unusual carbon chain species definitely or tentatively detected in interstellar and circumstellar media includes neutral molecules, radicals and several ions.[2] The longest known extraterrestrial linear carbon chain ($HC_{10}CN$) contains 11 carbon atoms.[2,26] Most of these compounds were observed in extraterrestrial space by microwave spectroscopy. Meanwhile, they are considered possible carriers of DIBs in the 400–900 nm range.[2,120] Assignment of DIBs requires knowledge of the electronic spectra of these unstable species. Meanwhile, measuring the gas phase electronic spectra of new molecules with unknown transition energies is rather difficult. For this reason, spectral characteristics obtained by the matrix isolation technique serve as a good starting point for further gas phase experiments.[121] For instance, the gas phase electronic spectrum of H_2CCC was assigned on the basis of the radical spectrum in the Ne matrix. The combination of matrix isolation experiments and gas phase cavity ring-down spectroscopy made it possible to identify the H_2CCC radical as carrier of DIBs at 488.1 and 545.0 nm.[122] The assignment of DIB at 506.9 nm to the HC_4H^+ cation was made on the basis of the gas-phase spectrum, and two additional bands of this species in the characteristic spectral region of DIBs were predicted taking into account matrix isolation experiments.[123–125] Characteristics of electronic spectra of different carbon chains of astrochemical interest (C_n, C_nH, HC_nH, C_nN, HC_nN, C_nO, HC_nO and corresponding ions) in solid Ne matrices and gas phase were collected in a review by Nagarajan.[26] IR spectroscopy is useful in the case of carbon-chain species with low dipole moments when microwave detection is not effective. For example, C_5 was identified in an obscured carbon star IR spectrum by its rovibrational transition near 2170 cm^{-1}.[126] A matrix isolation study devoted to IR spectroscopy of C_5 in argon matrix[127] served as background for this identification. One more technique that could be mentioned in this context is EPR spectroscopy. Although EPR spectroscopy is often considered a rather exotic method for studying matrix-isolated carbon chains, it may be useful for investigation of their electronic properties and comparison with optical spectra and computational results. In particular, this method was used for experimental investigations of C_4, C_6, C_8 and C_{10} linear molecules in their ground triplet states in Ne and Ar matrices.[128,129]

2.2.1. C_n, C_n^-, C_n^+

Comprehensive information about the electronic spectra of C_n, C_n^-, and C_n^+ species can be found in the review by Nagarajan and Maier[26] and references therein. Electronic spectra of bare carbon chains C_n with $n = 3–11$ and odd $n = 11–21$ were measured under matrix isolation conditions.[26,130–133] In addition, electronic spectra of cyclic isomers with $n = 6$, 8, 10, 12, 14 were obtained in a Ne matrix.[26] Codeposition of mass-selected carbon anions with Ne followed by electron detachment by a UV source was applied in the studies of electronically excited C_n chains. Absorption corresponding to the $^3\Sigma_u^+ \leftarrow X\,^1\Sigma_g^+$ or $^3\Sigma_u^- \leftarrow X\,^1\Sigma_g^-$ transition (for odd or even n, respectively) shifts to higher wavelengths with increasing chain length.[26] C_n^- anions are thermodynamically stable species with several excited electronic states below the electron detachment threshold because of the high electron affinities of neutral C_n ($n = 2–11$, except for C_3^-, which has a low electron affinity of 1.99 eV).[26] Electronic spectra of open-shell C_n anions up to $n = 11$ were first measured in noble gas matrices.[26] In contrast, the data related to C_n^+ cations are rather sparse, and electronic transitions of only a few species (C_6^+, C_7^+, C_8^+, and C_9^+) were studied in noble gas matrices.[26] IR spectra of C_n ($n = 3–12$) were measured in solid noble gases and parahydrogen matrices as described in works[134–138] and references therein. C_6^+ cations[139] and C_{10}^- anions[138] were studied by IR spectroscopy in solid neon.

2.2.2. C_nH, C_n^-, C_nH^+; HC_nH, HC_nH^-, HC_nH^+

The electronic absorption spectroscopy of different hydrogen terminated carbon chains, polyacetylenes and corresponding ions in the gas phase and matrices was discussed in a review by Nagarajan and Maier.[26] It should be noted that electronic spectra of a few C_nH^+ (C_5H^+, C_6H^+ and C_8H^+) systems were measured in neon matrices,[26,140] and only the C_6H^+ cation was identified in the gas phase by electron spectroscopy on the basis of matrix isolation experiment data.[141] Bands in electronic absorption spectra of polyacetylenes HC_nH shift in longer wavelengths with increasing chain size.[26] IR spectra of neutral C_nH ($n = 2-5$) and HC_nH ($n = 2, 4, 8$) in noble gas matrices were presented in recent works.[137,138,142] Even C_nH^- anions ($n = 8-14$) were also observed in solid neon by IR spectroscopy.[138,143]

2.2.3. C_nN, C_nN^+, C_nN^-; HC_nN, HC_nN^+, HC_nN^-; NC_nN, NC_nN^+

Nitrogen-containing compounds are widely spread in cosmic media. These species attract specific interest in astrochemistry as possible precursors for prebiotic synthesis. Species with two terminated nitrogen atoms have not yet been detected in extraterrestrial space; nevertheless, this type of molecule is worth mentioning in view of its possible role in astrochemical processes. Detailed information on the electronic spectroscopy of nitrogen-containing carbon chains and references to original matrix isolation works can be found in an earlier review.[26] In addition, electronic absorption and luminescence spectra of nitriles (HC_nN, C_nN, and C_nN^-) in noble gas matrices were presented in recent works.[19,144–147] Matrix isolation was applied for characterization of vibrational (IR and Raman) spectra of unstable HC_nN, NC_nN, C_nN, and C_nN^- species and their isomers.[145,146,148–151] IR spectra of the C_2N^-, C_3N^-, C_5N^-, C_7N^-, and C_9N^- anions were observed in a Ne matrix.[143,147,151–153] It is worth mentioning that the EPR spectra of NCCCN, HCCN, and HCCCCN triplet carbenes were measured in solid argon.[154]

2.2.4. Oxygen- and sulfur-containing carbon chains

Experimental information about oxygen- and sulfur-containing carbon chains is rather limited. C_nO are linear molecules that have $^1\Sigma^+$ and $^3\Sigma^-$ ground electronic states for odd and even n, respectively, as confirmed by matrix isolation EPR experiments.[155,156] OC_nO are also known to have $^1\Sigma^+$ and $^3\Sigma^-$ ground states for odd and even members, respectively, and the electronic spectra for C_3O_2, C_5O_2, and C_7O_2 were measured in Ar matrices.[26] Small C_2O^- and C_4O^- anions were investigated by electron spectroscopy in noble gas matrices.[26] Recently, electronic spectra of neutral C_7O and C_7O^+ ($^2\Sigma^+$) and HC_7O^+ ($^1\Sigma^+$) cations were measured in a Ne matrix.[157,158] IR spectra of several species, such as C_2O, C_3O, C_3O_2, C_4O, C_4O_2, C_5O_2, C_6O, and C_7O_2, in matrices were obtained in recent decades, whereas the IR absorptions of longer chains ($C_{13}O$ and $C_{15}O_2$) in an Ar matrix were tentatively assigned only recently.[27]

Electronic spectra in noble gas matrices were measured for C_nS ($n = 2-6$) and SCCS neutrals and C_2S^-, C_4S^-, C_6S^- anions.[26] The C_nS and SC_nS species with $n = 1-5$ were studied by matrix isolation IR spectroscopy in the 1990s,[159] while the IR spectrum of C_7S in an Ar matrix was reported recently.[160]

2.3. Polycyclic aromatic hydrocarbons (PAHs)

The so-called diffuse interstellar bands (DIBs) are observed in astronomic spectra of reddened stars in the near infrared, visible and UV regions. The astronomical observations on DIBs include a number of intriguing features referred to as unidentified interstellar infrared (UIR) bands at 3.3, 6.2, 7.7, 8.6, and 11.2 μm (3030, 1610, 1300, 1160, 890 cm^{-1}).[161–164] The origin of these bands has remained a great challenge for astrochemists for decades. According to a widely spread hypothesis, PAHs and their derivatives are possible carriers of the UIR bands.[120,163,165] Despite the fact that no particular species has been identified in DIB spectra to date, the PAHs derivatives are believed to contain 9–18% of interstellar carbon.[120,165] In fact, neutral PAH molecules are not good candidates for DIB sources. The most intense absorptions of PAHs in vibrational spectra belong to out-of-plane CH-bending modes in an 11.2 μm (3030 cm^{-1}) region, whereas the UIR bands at 6.2, 7.7, 8.6, and 11.2 μm demonstrate similar intensities.[166] It is also known that PAHs absorb in the UV and violet edges of the visible region. In contrast, the richest DIBs range lies between red and near IR.[163] For these reasons, PAH cations ($PAHs^+$) are extensively studied species as more probable candidates for DIBs carriers.[163] Another group of PAHs derivatives attracting considerable interest from the astrochemical viewpoint is the protonated PAH molecules (H^+-PAHs). Taking into account hydrogen abundance in the Universe, protonation reactions are evidently very important in interstellar chemistry.[161]

Matrix samples containing PAH^+ cations may be prepared by codeposition of PAHs after gas discharge with noble gas. Another way is exposure of a noble gas solid doped with PAH to ionizing radiation. Electron scavengers (such as freons) are often used to stabilize cations. H^+-PAHs are formed by proton transfer from another ion, demonstrating lower proton affinity than the PAH molecule.

Quantum solid parahydrogen (p-H_2) is a novel rather specific matrix, which reveals some important opportunities for matrix isolation experiments. In particular, protonated species may be obtained by electron bombardment of a mixture of p-H_2 with molecules of interest during deposition of the sample without additional reagents.[161] Additionally, matrix isolation experiments using a p-H_2 matrix make it possible to obtain sufficient amounts of monohydrogenated PAHs (H-PAHs), whereas attempts to add H atom to a PAH molecule in gas-phase experiments generally result in the formation of more hydrogenated products.[161]

2.3.1. PAHs cations ($PAHs^+$)

Electronic absorption spectra of a number of PAH^+ cations from $C_{10}H_8^+$ to $C_{32}H_{14}^+$ were measured in Ne and Ar matrices.[25,163] The data are summarized in Table 2. It should be emphasized that the DIBs region includes the bands of $PAHs^+$ measured in laboratory studies, which generally lie in visible and near UV regions. Nevertheless, no particular assignment of these bands is currently available. Attempts to establish correlations between electronic absorption spectra and the number of C atoms in $PAHs^+$ and create a predictive model were also unsuccessful.[163]

IR spectroscopy should be a more informative method due to the rather clear dependence of spectral parameters on the PAH^+ size. Laboratory IR spectroscopy of PAHs and

Table 2. Electronic absorption characteristics of the matrix-isolated PAH^+ cations.

PAH^+ cation	Matrix	$\lambda\,(0_0^0)$, nm	Electronic transition	Ref.
naphthalene$^+$	Ar	675.2	$^2B_{3g}(D_2) \leftarrow X^2A_u(D_0)$	167
naphthalene$^+$	Ne	674.1	$^2B_{3g}(D_2) \leftarrow X^2A_u(D_0)$	167
anthracene$^+$	Ar	722.4	$^2A_u(D_2) \leftarrow {}^2B_{2g}(D_0)$	168
		428	$^2B_{1u}(D_4) \leftarrow {}^2B_{2g}(D_0)$	
		352.1	$^2B_{1u}(D_5) \leftarrow {}^2B_{2g}(D_0)$	
phenanthrene$^+$	Ne	898.3	$^2A_2(D_2) \leftarrow X^2B_1(D_0)$	169
1-methyl-phenanthrene$^+$	Ne	931.0	$D_2 \leftarrow X^2A(D_0)$	169
pyrene$^+$	Ar	443.5	$D_5 \leftarrow D_0$	163, 170
pyrene$^+$	Ne	439.5	$D_5 \leftarrow D_0$	163, 170
1-methylpyrene$^+$	Ne	444.2	$D_5 \leftarrow D_0$	170, 171
tetracene$^+$	Ar	868.0	$^2B_{3g} \leftarrow {}^2A_u$	172
benzo(ghi)-perylene$^+$	Ne	758.4	?	163
		502.2		
corannulene$^+$	Ne	601.2	?	163
		590.0		
coronene$^+$	Ne	946.5	$D_2 \leftarrow D_0$	163, 173
		680.0	$D_3 \leftarrow D_0$	
		459.0	$D_4 \leftarrow D_0$	
ovalene$^+$	Ne	978.0	$A_u \leftarrow B_{2g}$	174
		463.2		

PAH^+, including matrix isolation spectroscopy, was discussed in a review by Oomens.[175] It is worth noting that Hudgins and Allamandola previously summarized the databases of IR spectra of PAH^+ cations from $C_{10}H_8^+$ to $C_{48}H_{20}^+$ in noble gas matrices and tried to extrapolate these results to larger molecules.[176] According to this work, $PAHs^+$ containing 50–80 carbon atoms could be carriers of DIBs, while relatively small PAH^+ species (such as naphthalene$^+$) contribute very little to the envelope of the interstellar feature at 1610 cm^{-1}. On the other hand, the species containing 20 carbon atoms are also important since they would emit near 1560 cm^{-1}.

2.3.2. Protonated PAHs (H^+-PAHs)

It is important that UIR bands 6.2, 7.7, 8.6, and 11.2 μm demonstrate similar intensities, when absorptions of PAH molecules at 11.2 μm are generally significantly higher in intensity than other bands. For this reason, IR spectra of protonated benzene ($C_6H_7^+$), naphthalene (1- and 2-$C_{10}H_9^+$), pyrene (1-$C_{16}H_{11}^+$), coronene (1-$C_{24}H_{13}^+$),[28] and ovalene (7-$C_{32}H_{15}^+$)[161] were investigated in *p*-H_2, and a correlation between the H^+-PAH size and characteristics of the vibrational spectra was established (see Ref. 161 and references therein). The intense absorptions due to CC stretching vibrations of different H^+-PAHs lie close to the band at 6.2 μm revealed in astronomical observations. Ring-deformation and CH_2-scissoring modes are associated with rather intense features in the 7.0–7.5 μm region. These features demonstrate redshifts with increasing PAH molecule size. The in-plane CH-bending modes of H-PAH^+ also shift to higher wavelengths for larger species. In contrast, the out-of-plane CH bending modes demonstrate a blue-shift. Authors conclude that relative intensities of H^+-PAHs features in IR spectra are in better agreement with the UIR bands, than those related to neutral PAHs, and protonated ovalene seems to be one of the UIR carriers among other larger H^+-PAHs.[161] The characteristics of the most intense IR bands of ovalene and protonated ovalene are presented in Table 3.

Table 3. IR absorptions of matrix-isolated ovalene and H^+-ovalene.

Mode	Matrix	Wavenumber, cm^{-1}
$C_{32}H_{14}$; Ref. 166		
CH stretch	*p*-H_2	3065
	Ne	3069
oop CH bend	*p*-H_2	885.3 (the most intense)
	Ne	885
7-$C_{32}H_{15}^+$; Ref. 177		
Combination	*p*-H_2	1649.7
Combination	*p*-H_2	1643.3
CC stretch	*p*-H_2	1613
CC stretch	*p*-H_2	1611
ring deform + ip CH bend + CH_2 wag	*p*-H_2	1335.5 (the most intense)

2.3.3. Hydrogenated PAHs (H-PAHs)

The formation of extraterrestrial H_2 involves reactions on the grain surface or probably interactions with PAH molecules. Therefore, hydrogenated PAHs are suggested as intermediates of H_2 synthesis in interstellar medium.[161, 179] Hydrogenated benzene (C_6H_7), naphthalene ($C_{10}H_9$), pyrene ($C_{16}H_{11}$), coronene ($C_{24}H_{13}$), and ovalene ($C_{32}H_{15}$)[166] were obtained in *p*-H_2 matrices and characterized by IR spectroscopy.[161] Recent matrix-isolation experiments provided by Tarczay's group revealed low-barrier formation of phenalenyl radicals from 1*H*-phenalene under UV photolysis.[179] Possible hydrogen atom abstraction from 1*H*-phenalene by a thermally induced reaction was also reported.[179]

2.4. Fullerenes

Fullerenes are among the most recently discovered chemical species in extraterrestrial space and contain 0.1–1.5% of interstellar carbon.[120, 180–184] The importance of fullerenes and their derivatives for astrochemistry was predicted more than 30 years ago.[180] Two diffuse interstellar bands were assigned to the C_{60}^+ cation for the first time in 1994 on the basis of laboratory spectra of this species in a Ne matrix.[181] Later, the identification of C_{60}^+ cations in diffuse interstellar clouds was confirmed by laboratory gas phase data.[182] Infrared emission spectra of neutral C_{60} and C_{70} fullerenes were first detected in young planetary nebula in the region of carbon-rich stars and then were also found in other ISM objects. The laboratory spectra of fullerenes in solid *p*-H_2 were used for identification.[183, 184]

C_{60} is a highly symmetrical icosahedral molecule with a rather simple IR spectrum, which has been obtained in the gas phase and molecular solids in many works.[185] However, there are only a few reports on the IR spectrum of C_{60} in Ne, Ar and *p*-H_2 matrices. Application of a parahydrogen matrix makes it possible to obtain an IR spectrum with the narrowest (width 0.1–1 cm^{-1}) intense lines at 1431.9, 1184.41, 578.24 and 529.77 cm^{-1} (6.98, 8.44, 17.3, and 18.9 μm, respectively) belonging to isolated C_{60} and additional lines due to $(C_{60})_n$ associates.[185] An attempt to obtain a rotationally resolved spectrum of C_{60} in *p*-H_2 was unsuc-

cessful.[185] Electronic spectra of C_{60} in Ar and Ne, as well as *p*-H_2 matrices, were studied in several works.[29, 185–188] Detailed assignment of fluorescence spectra of C_{60} in Ar and Ne matrices has also been reported.[29]

Cation C_{60}^+ has D_{5d} symmetry, and more than ten vibrational bands of C_{60}^+ in Ar and Ne matrices are known at present.[186, 188, 189] The spectral region characteristic of C_{60}^+ absorptions (from 350 to 1560 cm^{-1}) partially overlaps with C_{60} and C_{60}^{2+} absorption regions. However, the positions of individual absorption bands differ considerably for the identification of these species in astronomical spectra. The bands at 6.43, 7.13, 8.1, and 10.53 μm were tentatively assigned to C_{60}^+ in some interstellar objects.[188] More definite identification of C_{60}^+ in extraterrestrial space was made on the basis of laboratory electronic spectra of the cation.[181, 182] The two DIBs at 963.2 and 957.7 nm correspond to the most intense electronic absorption bands of C_{60}^+ in the Ne and Ar matrices.[186, 188] The absorption spectra of C_{60} and C_{60}^+ in the UV region are very similar, the corresponding spectra were measured in the Ne matrix, and the features of the two species were separated in experiments with electron scavengers.[188]

The quantum chemical calculations predict D_{5h} symmetry for the C_{70} molecule.[190] Investigations of C_{70} neutral (as well as C_{70}^+ and C_{70}^- ions) ions in noble gas matrices are very limited. The characteristics of C_{70}, C_{70}^+ and C_{70}^- were studied by electronic absorption spectroscopy in solid neon.[191] The fluorescence spectrum of C_{70} is also known in a Ne matrix.[192] IR spectra of C_{70}, C_{70}^+ and C_{70}^- were recently measured in Ne and Ar matrices.[190] It should be noted that EPR spectroscopy was first applied for studying C_{60} and C_{70} fullerenes in a low-temperature toluene matrix in the 1990s,[193] and recent investigations have demonstrated EPR spectra of excited triplet C_{70} molecules in solid argon.[194] One may suggest that EPR studies may serve as a primary experimental tool for the detection of fullerene radical ions and triplet states that could provide a reference basis for IR and UV spectroscopic identification.

2.5. Complexes of astrochemically relevant molecules

It is obvious that chemical synthesis of a new molecule requires contact of reagents and removal of excess energy in case of a radiation-induced or photochemical reaction. The average density of substances in the Universe is extremely low, and cosmic ices may serve as chemical reactors for the synthesis of various molecules.[113] As mentioned in the Introduction, cosmic ices are predominantly composed of water, CO and CO_2 molecules (abundances of CO and CO_2 in different icy objects vary from 1 to 80% relative to H_2O ice column density).[113, 114, 195–198] Among other abundant components are CH_3OH (1–30% relative to H_2O ice column density in CO-rich ices), HCOOH, CH_2O and NH_3.[113, 114, 195–198] It is worth noting that the estimated mass of PAH molecules in interstellar media is comparable to the mass of icy dust particles.[113] Large PAH molecules may play a role as absorbents for small molecules and provide specific "media" for chemical reactions.

Generally, an ice matrix absorbs radiation and transfers absorbed energy to the less abundant molecules dispersed in solid media. Considering the extreme rigidity of ice media at cryogenic temperatures, one could suggest an important role of pre-existing intermolecular complexes as "templates" in these processes. Although such complexes have not yet been directly detected in space objects, spectroscopy of the complexes including the most abundant astrochemical molecules should be significant for laboratory modelling of extraterrestrial chemistry, and this is one more contribution from matrix isolation, often missing in traditional consideration. Here, we present a brief overview of the matrix isolation works devoted to spectroscopy of complexes of H_2O, CO, CO_2, CH_3OH, CH_2O, and NH_3 with different molecules detected in extraterrestrial space. For a broader consideration, one may refer to the review.[35] The common method for preparing matrix-isolated complexes is codeposition of studied molecules with matrix substances from the gas phase. This is a rather simple technique; however, the yields of complexes are usually low in highly diluted samples, and the composition of the resulting complexes is often unpredictable in the case of more concentrated systems. Another way is direct synthesis of complexes in a solid matrix by photolysis or radiolysis of an appropriate precursor molecule.[199–201] The advantages of this method are the opportunity to prepare complexes with a fixed ratio of components and to control the yield during irradiation. On the other hand, possibilities of direct synthesis are limited since the required precursor must exist and be able to dissociate during photolysis or radiolysis. Almost all the complexes in rare gas matrices were identified by IR spectroscopy due to characteristic complexation-induced shifts in the vibrational spectra.

2.5.1. H_2O complexes

One of the most important and most extensively studied components of intermolecular complexes is H_2O. Normally, association results in a redshift of the OH stretching bands in the IR spectra of isolated water molecules ranging from 2 to 68 cm^{-1}.[199, 202] A number of complexes with water were obtained and studied by the matrix isolation technique. First, it is worth mentioning that water forms dimers and larger aggregates in matrices. Spectroscopy of various isotopic forms of these associates was extensively investigated using matrix isolation.[203] The $H_2O\cdots CO_2$ complex was an object of several experimental and theoretical works, one may refer to recent studies on the IR spectroscopy of this complex in noble gas matrices for the state-of-art summary.[204, 205] The $H_2O\cdots CO$ complexes are also well known and obtained in matrices by both codeposition of CO and H_2O [206] and photolysis of HCOOH.[21] In addition, a number of complexes of water with inorganic (for example, N_2,[202] NO,[207] HCN,[199] NH_3,[208] CS_2,[35] and OCS [35]) and organic (for example, glycine,[209] HCOOH,[210] CH_3COOH,[211] CH_2O,[212] $(CH_2)_2O$,[213] CH_3OH, and C_2H_5OH [214]) molecules of potential astrochemical interest were spectroscopically characterized in noble gas matrices. Specific matrices such as parahydrogen and helium nanodroplets were also applied to study H_2O complexes.[215, 216]

Although the water complexes in matrices are usually prepared by the codeposition method, some of these caged species were obtained by photolysis (one could mention $HCN\cdots H_2O$ and $HNC\cdots H_2O$ complexes produced from formamide [217] or formaldoxime.[199]

In addition to water complexes with stable closed-shell molecules, several radical-molecular complexes with H_2O are also known. Such complexes were mostly generated in a solid matrix by photolysis of the precursor molecular complexes ($H_2O\cdots O$ from H_2O_2,[22] $H_2O\cdots C_3O$ from HC_3OOH).[218] Additionally, certain complexes (such as $HCO\cdots H_2O$ [219] and $H\cdots H_2O$ [215]) may result from H atom reactions. In recent years, attempts at laboratory modelling of atmospheric and astrochemical processes, including PAH

molecules, have led to increasing interest in spectroscopy of water-PAH complexes.[220–222]

2.5.2. CO complexes

The carbon monoxide molecule readily forms dimers [223] and associates with other molecules, such as N_2,[224] NH_3,[224] CO_2,[225] CH_3OH,[226] H_2O_2,[227] HNCS [228] and HCN,[229] during codeposition with matrix gas. All these species demonstrate complexation-induced shifts of CO stretching vibrations (Table 4) and corresponding shifts of the stretching and bending vibrations of other partners, which could be reasonably interpreted on the basis of quantum chemical calculations.

Table 4. Complexation-induced shifts of the CO stretching vibrations observed for complexes of CO isolated in Ar matrices.

Complex	Shift ($\nu_{complex} - \nu_{monomer}$), cm^{-1}	Ref.
$CO\cdots H_2O$	+11	206
$CO\cdots NH_3$	+7	224
$CO\cdots CO_2$	+5/−3 (different configurations)	225
$CO\cdots H_2O_2$	+14.5	227
CO···HNCS	+15.9	228
CO···HCN	+20	229

The CO molecule may coordinate with another molecule in complex through both C and O atoms. Most commonly, C-bonded configurations are detected in matrices. However, both C- and O-bonded conformers of complexes in rare gas matrices were observed for associates of CO with CO [223] and CO_2.[225] Photolysis of the precursor in the matrix was also successfully applied to prepare different complexes of CO. For instance, CO···HF and OC···HF are products of HCOF decomposition in the matrix,[230] and formic anhydride produces CO···HCOOH,[231] $NH_3\cdots CO$ was obtained by formamide photolysis,[232] and $H_2S\cdots CO$ appears during photolysis of HCSOH.[233] The $CO\cdots H_2O$ and CO···CO complexes obtained by photolysis of CH_2O were studied by Raman spectroscopy.[201] As found recently, the HNC···CO complex is formed upon X-irradiation of HCN···CO complex in noble gas matrices.[229] The chemistry of radical-molecular complexes $OH\cdots CO$ [200] and $CH_3\cdots CO$ [234] studied by matrix isolation IR spectroscopy is discussed in Chapter 3.3 of this review.

2.5.3. CO_2 complexes

Carbon dioxide forms T-shaped dimers in noble gas matrices.[235] Complexes of CO_2 with astrochemically relevant molecules (H_2CO,[236] NH_3,[237] NO,[238] and HCN [239]) were prepared by the codeposition method. The complexes of carbon dioxide are identified by characteristic shifts of the vibration bands corresponding to antisymmetric stretching and bending of the CO_2 molecule. However, in many cases, the shifts are rather small (within 4–6 cm^{-1}), and the corresponding satellites are poorly resolved, so the complexation-induced shifts for the other partner of the complex are even more informative (see, *e.g.*, Ref. 239). Photolysis of oxalic acid in the noble gas matrix results in $CO_2\cdots HCOOH$ complex.[240] Photodecomposition of propiolic acid (HC_3OOH) leads to the formation of $C_2H_2\cdots CO_2$ complex [218] and, as shown later, the radical-molecular $C_2H\cdots CO_2$ complex also appears.[241] Reaction of H atoms with matrix isolated $HCN\cdots CO_2$ results in another radical-molecular $HCNH\cdots CO_2$ complex.[239] In addition, $HO_2\cdots CO_2$ was obtained by codeposition from the gas phase.[242]

2.5.4. HCOOH complexes

Formic acid tends to form strong hydrogen-bonded associates. This molecule may exist in cis and trans conformations, which form complexes with different spectroscopic characteristics and chemical properties. Several types of HCOOH dimers were detected in noble gas matrices.[243] The formic acid molecule is able to produce spectroscopically detectable associates with different species, in particular, with H_2,[244] N_2,[245] CH_3CN,[246] $(CH_3)_2O$,[247] C_6H_6,[248] and C_2H_2 [249] molecules, as well as O atom.[250] All these complexes were obtained in noble gas matrices and characterized by FTIR spectroscopy. The complexation leads to a measurable redshift of the strongest C=O stretching vibrations in HCOOH, ranging from −6 to −40 cm^{-1} (except for HCOOH···O complex, where the C=O band is blue-shifted by +63 cm^{-1}), as well as other fundamentals of formic acid.

2.5.5. Complexes of NH_3, CH_3OH and CH_2O

Matrix isolation studies on intermolecular complexes of ammonia, methanol and formaldehyde complexes are relatively limited. In addition to the abovementioned complexes with H_2O and CO, the NH_3 complexes with CH_3OH,[251] CH_2O,[252] HCN,[35] HC_3N,[35] HNCO,[253] and HO_2 [254] were characterized in noble gas matrices. The ν_2 umbrella vibration band of NH_3 undergoes large shifts from 33 to 118 cm^{-1}. Except previously described $CH_3OH\cdots H_2O$,[214] $CH_3OH\cdots CO$,[226] and $CH_3OH\cdots NH_3$,[251] the associates of CH_3OH with C_2H_5OH [214] and N_2 [226] were studied in solid argon. The largest shift (−266 cm^{-1}) of the OH stretching band of methanol was observed in $CH_3OH\cdots NH_3$ complex.[251] In addition to complexes of CH_2O with H_2O,[212] CO_2,[236] and NH_3,[252] $CH_2O\cdots H_2S$ [255] and $CH_2O\cdots CH_3CN$ [252] complexes and $(CH_2O)_2$ dimers [236] were obtained by codeposition under matrix isolation conditions. In complexes of CH_2O, both symmetric and asymmetric CH_2 stretching vibrations shift for +3 to +11 cm^{-1} when the C=O stretching mode shifts for −5 to −12 cm^{-1}.

3. Modelling of astrochemical processes through studying chemical reactions in low-temperature matrices

As stated in the Introduction, cold astrochemical processes are typically initiated by UV light or ionizing radiation of different kinds. Thus, studies of photochemical and radiation-induced transformations of matrix-isolated molecules may present considerable interest for astrochemistry. In fact, molecular photochemistry in matrices has been extensively investigated, and many reviews on this topic are available.[8,256–258] On the other hand, the radiation chemistry of matrix-isolated molecules is much less studied (the status of this field was discussed in Refs 12, 259. Considering the applications of these works to astrochemistry, one should address two basic questions: (1) the astrochemical importance of the studied species and (2) relevance of the radiation spectrum used in model studies to the space conditions (as will be shown below, the latter point is crucial for photochemistry, but not so much for the reactions induced by ionizing radiation). In this chapter, we will mainly focus on the investigations that can be related to

cold astrochemistry in these two aspects and discuss their implications. In addition to photo- and radiation-induced reactions, low-temperature "in dark" chemical reactions may also occur in cold space environments (interstellar, cometary and planetary ices), in particular those driven by quantum tunneling. Applications of matrix isolation in the investigations of such processes will also be considered below.

3.1. UV- and VUV-induced photochemistry

The spectrum of non-ionizing (UV and VUV) radiation in space is characterized by a wide energy distribution.[260, 261] Photochemical transformations mainly occur due to direct photon absorption by the target molecules. It is worth noting that small molecules of astrochemical interest often show considerably strong absorption only in the VUV region ($\lambda < 200$ nm), so the action of VUV light is typically considered the most relevant choice for astrochemical modelling. Meanwhile, in the case of more complex heteroatomic astrochemically relevant species (*e.g.*, carbonyl compounds) and PAH-related aromatic molecules, absorption in the UV region ($\lambda = 200-350$ nm) may become important, so this part of photochemistry also presents certain interest. A brief overview of the status of matrix photochemistry of astrochemically significant species of different classes is given below.

3.1.1. Small inorganic molecules

Small inorganic molecules, primarily H_2O and CO_2, form bulk extraterrestrial substances capable of photochemical reactions.[113, 114, 195–198] Other abundant molecules, such as NH_3, N_2O, SO_2, and H_2S, attract interest as nitrogen- and sulfur-containing precursors for the photochemical synthesis of a variety of astrochemical species.[113, 114, 195–198]

Photolysis of one of the most abundant cosmic molecules — H_2O was studied in different noble gas matrices.[262–264] Water dissociates to OH and H radicals under VUV irradiation, and thresholds of dissociation are blue-shifted in the Ar, Kr and Xe matrices (near 180, 182 and 194 nm, respectively) in comparison with the gas phase (242 nm) because of the cage effect.[264] Prolonged 193 nm photolysis of H_2O results in the appearance of O atoms.[265] Hydrogen peroxide is another source of photoinduced oxygen atoms in low-temperature media. H_2O_2 demonstrates two main photodecomposition channels in matrices.[22] The first results in formation of $H_2O\cdots O$ complex or $H_2O + O$ pair, when O escapes a cage. The second is dissociation to OH radicals. It is important, that in 193 nm photolysis experiments, the yields of $H_2O\cdots O$ complex and OH radicals are higher in the Ar matrix than in Kr and Xe. Reaction pathways for H_2S are similar to those for water. HS, H and S were detected in noble gas matrices after 193 nm photolysis of H_2S.[266] Photolysis of ammonia (NH_3) was studied in Ne, Ar, Kr, Xe and *p*-H_2 matrices at different wavelengths (121.6 and 149–164 nm for Ar, 149–164 nm for Ne, Kr, Xe and 193 nm for *p*-H_2).[162, 267, 268] The main photolysis products were NH_2, NH and H atoms. Inorganic oxides are known to produce oxygen atoms under photolysis in matrices. Carbon dioxide photolysis causes formation of $CO\cdots O$ geminate pair stabilized in matrix.[259] Sulfur dioxide dissociates to SO and O atom and O_2 and S atom and isomerizes to SOO peroxide under 193 nm photolysis in an Ar matrix.[269] The main products of N_2O 193 or 125 nm photolysis in different noble gas matrices are N_2 and O atom.[265, 270] Thus, small inorganic molecules serve as sources of free H, O and even S atoms in matrix-isolation photochemistry. A further fate of these atoms depends on potential barriers of cage escape and potential minima existing in a matrix doped with other reactive centers.

3.1.2. Hydrocarbons

Photochemistry of the simplest hydrocarbon CH_4 has been studied for decades. In their classic work, Milligan and Jacox investigated photolysis of methane in argon and nitrogen matrices by VUV (122 nm) irradiation.[271] CH_3 was identified as a main product of photolysis by UV and IR spectroscopy. Small amounts of CH, C_2, C_3, and C_2H_2 were also detected after photolysis in the matrices. Although CH_2 was not observed directly, the formation of CH_2N_2 occurred in the N_2 matrix. A recent investigation revealed the appearance of CH radicals as a product of the dissociation of excited CH_3 radicals in CH_4/Ar ices.[272] Acetylene effectively absorbs VUV light with wavelengths shorter than 200 nm, producing C_2H and C_2 in noble gas and nitrogen matrices.[273–276] In addition, the neon matrix allows the detection of stabilized anion C_2^-.[275] The C_2H radical is considered an important reagent in the formation of larger astrochemical carbon clusters. Photolysis of C_2H_4 (120 nm) in the Ne matrix results in acetylene and vinyl radical (C_2H_3) formation.[85] The main product of C_2H_4 121.6 nm photolysis in a nitrogen matrix was C_2H_2.[276, 277] Small amounts of nitrogen-containing products (CN, C_2N_2, HCN, and HNC) were also detected after photolysis of C_2H_4 and C_2H_2 in N_2 matrices. In general, small aliphatic hydrocarbons tend to eliminate hydrogen under VUV photolysis in matrices, which in perspective leads to the formation of highly unsaturated compounds and carbon clusters.

The photochemistry of benzene under matrix isolation conditions has been investigated in a few works. It was demonstrated that the aromatic C_6H_6 molecule undergoes isomerization rather than dehydrogenation under 253.7 nm photolysis in an argon matrix, forming benzvalene, fulvene and Dewar benzene.[278] In addition to these three isomers, cyclohexadienyl radicals were recently detected as a product of benzene photolysis with 193 and 253.7 nm light in a parahydrogen matrix.[279]

VUV photolysis of polycyclic aromatic hydrocarbons in argon matrices was studied in several works; for instance, cations of naphthalene ($C_{10}H_8^+$),[280] fluorene ($C_{13}H_{10}^+$),[281] anthracene ($C_{14}H_{10}^+$),[282, 283] tetracene ($C_{18}H_{12}^+$),[282] pentacene ($C_{22}H_{14}^+$),[282] coronene ($C_{24}H_{12}^+$),[283] anthracoronene ($C_{36}H_{18}^+$),[283] fluoranthene ($C_{16}H_{10}^+$),[284] and all isomers of benzofluoranthene ($C_{20}H_{12}^+$)[284] were experimentally obtained from isolated neutral precursors and identified by IR spectroscopy. In most studied systems, photoinduced electrons are stabilized in the matrix; however, some PAH molecules (such as anthracoronene,[283] pentacene,[282] benzo[*a*]fluoranthene,[284] and benzo[*j*]fluoranthene[284]) can accept electrons forming corresponding anions. Authors of work[281] supposed that VUV photolysis of fluorene results in several cationic species ($C_{13}H_n^+$, $n = 5-8$) in addition to $C_{13}H_{10}^+$. Hence, polycyclic aromatic hydrocarbons tend to form cations ($PAHs^+$) and rarely anions ($PAHs^-$) under VUV photolysis in noble gas matrices, while photofragmentation common to gas-phase reactions[281] was not directly observed in matrices.

3.1.3. Oxygen-containing organic molecules and corresponding sulfur-substituted species

Jacox studied the photolysis of methanol (CH_3OH) with 147 nm VUV irradiation in Ar and N_2 matrices.[285] The main photolysis products were CH_2OH, H_2CO, HCO, and CO. According to another work, CH_3OH produces OH under VUV photolysis in a matrix.[286] The experimentally measured thresholds of OH formation are 174 and 175 nm for the Ne and Ar matrices, respectively, which are significantly higher than the value for the gas phase (313.9 nm) because of the cage effect. A sulfur-substituted analogue of methanol — CH_3SH produces H_2CS, CS, CS_2, and CH_4 under VUV photolysis in an argon matrix.[287] Noticeably, the appearance of significant amounts of CS_2 and CH_4 requires dissociation of the C – S bond of CH_3SH and escape of the S atom from a cage.

The main product of H_2CO photolysis in a noble gas matrix is CO, which may be formed directly from formaldehyde or through HCO.[201,288] Vaskonen and Kunttu studied the photochemistry of formaldehyde in noble gas matrices using 308, 248, and 193 nm light sources.[288] The most prominent efficiency of H atom formation was achieved in the Xe matrix under 193 and 248 nm photolysis. Photolysis of formaldehyde dimers occurs effectively at all studied wavelengths, resulting in $CH_3OH\cdots CO$ complex.

Photolysis of formic acid (HCOOH) with 193 nm light in noble gas matrices results in the formation of two intermolecular complexes: $H_2O\cdots CO$ and $H_2\cdots CO_2$, whereas the reaction pathway ratio strongly depends on the matrix.[289]

3.1.4. Nitriles and other nitrogen-containing molecules

Highly unsaturated nitriles are an important class of astrochemical molecules that may also play a role in the formation of carbon clusters. The photochemistry of HCN is well described. According to IR[290] and EPR[45] studies, VUV photolysis of HCN in an argon matrix produces HNC isomers as well as CN radicals and H atoms. Small amounts of methyleneimino radicals (H_2CN) were also detected by EPR among the photolysis products. Photolysis of cyanoacetylene (HC_3N) under VUV irradiation ($\lambda > 120$ nm) was studied in an argon matrix.[151] Three isomers were observed in photolyzed samples by IR spectroscopy: HCCNC, HNCCC and CCNCH. In addition to these isomers, several anions (CN^-, CCN^-, and C_3N^-) and radicals (CCNC and CCCN) were detected after 193 nm photolysis of HC_3N in argon and krypton matrices.[291] Obviously, elimination of a single H atom and CN group isomerization are major channels of photolysis of unsaturated nitriles. Molecules such as acetonitrile (CH_3CN) or methanimine (CH_2NH) demonstrate some additional reaction pathways. Jacox reported CN, CNC and CCN radicals, CH_3NC isomer and HCCN as products of 121.6 nm photolysis of CH_3CN in argon matrix.[292] CH_2NH photolysis with a medium-pressure mercury arc in an argon matrix resulted in the appearance of HNC as the main product, whereas only traces of HCN were observed.[39]

The addition of a strong C=O bond into a molecule increases the chance to find CO molecules among photolysis products. Formamide ($HCONH_2$) dissociates under 193 nm photolysis, forming different types of complexes: $NH_3\cdots CO$ and $NH_3\cdots OC$ in Ar and Kr matrices and $HNCO\cdots H_2$ in Xe.[232,293] Urea ($(NH_2)_2CO$) demonstrated similar behavior under 160 nm photolysis in an argon matrix, and destruction of the C – N bond resulted in the formation of HNCO, NH_3, and $CO\cdots N_2H_4$ complexes.[253] In addition, isourea $H_2N(OH)C{=}NH$ appeared in VUV-irradiated $(NH_2)_2CO$/noble gas samples.

3.1.5. Polyheteroatomic molecules

Some polyheteroathomic molecules of astrochemical interest were studied in noble gas matrices. The HCNO molecule isomerizes to HNCO under VUV photolysis ($\lambda = 193$ nm) in rare gas matrices, and elimination of H atoms also occurs, resulting in NCO and CNO radicals.[294] Additionally, $NH\cdots CO$ complex was detected after HNCO photolysis ($\lambda = 150 – 165$ nm) in matrices.[295] Photolysis of HNCS was studied at $\lambda < 290$ nm in an argon matrix.[296] HSCN and HSNC isomers, CS, NH, and $S\cdots HCN$ complex were detected as products. Hence, the studied molecules demonstrate H atom elimination, isomerization of the CN group and dissociation of the C – N or C – S bond.

3.1.6. Intermolecular complexes

Studies devoted to the photochemistry of complexes in matrices are often motivated by the synthesis of new complexes containing very active compounds (such as radicals or unstable molecules) or the building of more complicated molecules from simple species. Several examples of investigations of this type are mentioned below. VUV photolysis experiments in argon matrix demonstrate that $CO_2\cdots NH_3$ complex produces rich set of products: $NH_2OH\cdots CO$, $CO\cdots H_2O$, $CO\cdots NH$, and $CO\cdots NH_3$ complexes as well as HCO and HCOO radicals.[237] Photolysis of $HN_3\cdots HCN$ results in $HN\cdots HCN$ complex.[297] Recently, different complexes of HCN with HCNO, HNCO, and HOCN were produced in an Ar matrix by 220 nm photolysis of 1,2,5- and 1,3,4-oxadiazoles. Subsequent 121.6 nm photolysis generated HNC complexes with CNO, HNCO, and HOCN isomers.[298] VUV photolysis of the HCOOH/CH_3CN/Ne mixture during deposition results in the formation of $NC-CH_2-COOH$ molecules in addition to $HCOOH\cdots CH_3CN$ complexes in a matrix.[246] Dissociation under UV irradiation is typical for halogens. For instance, three isomeric complexes ($HO\cdots OF$, $FO\cdots HF$, $FH\cdots FOH$, $FH\cdots HOF$, and $FH\cdots FOH$) appear after 220 – 1000 nm photolysis of $H_2O\cdots F_2$ complex in argon matrix.[299] The $CH_3\cdots HF$ was produced in matrices by photolysis of a mixture of CH_4 with HF.[300] The $NH_2\cdots HF$ was obtained by reaction of F atom with NH_3.[301] While H atom reaction allows to obtain $OH\cdots O_3$ complex.[302] VUV photolysis of $H_2O\cdots CO$ complex leads to $OH\cdots CO$ complex and *trans*-HOCO radical formation.[303] Photochemistry of a radical-molecular complex $HO_2\cdots CO$ was studied in an argon matrix, and irradiation at 266 nm led to its transformation to $HO\cdots CO_2$ complex.[242] The photochemistry of complexes of PAHs with other molecules is rather poorly studied. However, some authors reported oxidation of PAHs (namely, coronene and pyrene) to hydroxy and keto derivatives, respectively, *via* UV photolysis of $PAH\cdots H_2O$ complexes.[220,222]

3.2. Radiation chemistry

Ionizing radiation in space is represented by electromagnetic radiation over a wide range of energies (from tens eV to GeVs), energetic electrons, protons, and heavy ions.[304,305] Simulation of the actual spectrum of space radiation under laboratory conditions is an extremely difficult task, so model studies in ice astrochemistry usually make use of one specific kind of ionizing radiation (*e.g.*, electrons,[277,304,306,307] X-ray photons,[308–310] or particular

ions [306, 311 – 314]). Meanwhile, one should bear in mind that the action of primary energetic radiation of different kinds (except for low-energy heavy ions) on condensed matter produces a large number of secondary electrons, which are mainly responsible for ionization and excitation of medium molecules. This means that the chemical processes are expected to be qualitatively similar for different kinds of ionizing radiation.

3.2.1. Basic features of radiolysis in matrices

In the case of matrix isolation, ionizing radiation is primarily absorbed by the matrix, and the guest molecule is mainly affected due to positive holes and excitation transfer (and sometimes due to interactions of isolated molecules with low-energy electrons). A common scheme of radiation-induced chemistry under the conditions of matrix isolation was discussed in a number of review papers:[12, 13, 315]

Primary ionization:	$M \rightsquigarrow M^{+\bullet} + e^-$	(1)
Hole transfer:	$M^{+\bullet} + RH \rightarrow (RH^{+\bullet})^* + M$	(2)
Relaxation:	$(RH^{+\bullet})^* \rightarrow RH^{+\bullet}$	(3)
Reactions of excited ions:	$(RH^{+\bullet})^* \rightarrow$ products	(4)
Ion-electron recombination:	$RH^{+\bullet} + e^- \rightarrow RH^*$	(5)
Dissociation of excited molecules:	$RH^* \rightarrow R^\bullet + H^\bullet$	(6)
Other reaction channels RH^*:	$RH^* \rightarrow$ nonradical products	(7)

The two most important basic features of radiation chemistry in matrices (in contrast to photochemistry) are the high yield of ionized species and the population of optically unattainable excited states (particularly triplet states) by ion-electron recombination.[13] It should be stressed here that the matrix plays a crucially important role in radiation-induced processes (more important and versatile than that in the case of direct excitation of molecules under photolysis). Indeed, in the case of high-energy radiation, the matrix acts as a "transport system" (charge and excitation transfer to a target molecule), "cooling bath" (relaxation of the ionic and neutral excited states primarily produced by positive hole and excitation transfer), and sometimes even "reagent" (particularly applicable to ionic species in more polarizable media).[259] On the one hand, it means that direct comparison between processes occurring in "classic" matrices (solid noble gases) and astrochemically relevant media is somewhat questionable. On the other hand, matrix effects provide new opportunities for model mechanistic studies and discrimination between different reaction routes.[12, 13] As mentioned above, the applications of matrix isolation to the radiation chemistry of astrochemically important molecules are rather limited. Earlier studies were mainly focused on spectroscopic aspects, whereas more recent works were devoted to detailed product analysis and elucidation of the corresponding mechanisms.

3.2.2. Spectroscopic characterization of ionized molecules produced by radiolysis

Radiolysis in noble gas matrices is a useful tool to generate ionized isolated molecules because noble gas atoms usually have higher ionizing energy (IE) values than guest molecules, and positive hole transfer is quite efficient.[12] This approach makes it possible to characterize unstable radical cations produced from different species and to evaluate their stability and possible reaction routes. Taking into account that ionized molecules are very common in ISM, this kind of information may be useful for astrochemistry. Furthermore, in certain cases, it is also possible to characterize radical anions resulting from electron attachment in matrices, which may also be relevant to astrochemical issues. Small, highly reactive radical ions (including a number of astrochemically significant species) were extensively characterized by EPR spectroscopy in a solid neon matrix by Knight and co-workers.[33, 34] This group applied several different approaches for the generation of radical ions,[316] among which the X-ray radiolysis of deposited matrices was found to be particularly efficient. In this way, the EPR parameters (g- and hyperfine coupling tensors) were obtained for a number of small astrochemically important radical cations, namely, $CO^{+\bullet}$,[317] $H_2O^{+\bullet}$,[318] $CH_4^{+\bullet}$,[319] $CH_2O^{+\bullet}$,[320] $CH_3OH^{+\bullet}$,[321] and $CH_3CHO^{+\bullet}$.[322] A number of larger organic radical cations of certain relevance to astrochemistry were characterized by EPR in halocarbon (Freon) matrices (see Refs 323 – 326 for review) as well as in argon matrix.[12, 259, 327] Even though the EPR spectroscopic characteristics are not directly comparable to the data of observational astronomy, they are very important for characterization of electronic and geometrical structure of radical ions and verification of the results of quantum chemical calculations. Additionally, the hyperfine coupling constants determined by EPR provide significant information for comparison with the data extracted from rotational spectra.

Radiolysis has also been applied for the characterization of electronic and vibrational spectra of ionized molecules in matrices; however, there are still relatively few examples. Early studies of radical cations were performed by Bally and co-workers.[124, 328, 329] Recently, such an approach based on electron irradiation was used for the characterization of some radical cations [84, 330] and radical anions,[331, 332] as well as protonated aromatic molecules [333] of potential astrochemical interest. It is worth noting that charcaterization of the spectra of PAH radical cations and protonated molecules was mainly performed using other methods (*e.g.*, photoionization), and the related data are described in chapter 2.3 of this review. An attempt to apply EPR spectroscopy as a "reference" method for assigning the vibrational spectra of hydrocarbon radical cations in matrices has been reported;[315] however, this powerful combination was not still used systematically for this purpose because of experimental limitations.

It should be noted that using noble gas matrices with various electronic characteristics makes it possible to shed some light on the "hot" reactions of primary radical cations, which are usually formed in unrelaxed states;[12, 259] see the reaction scheme given above. Indeed, in the case of a low-polarizable argon matrix with high ionization energy (IE), small organic radical cations initially have significant excess energy, which can be roughly evaluated from the difference in IE energy between the matrix atom and guest molecule (IE gap, ΔIE). These "hot" cations may undergo rapid fragmentation under cryogenic temperatures, as was demonstrated by EPR studies for a number of small aliphatic molecules.[12, 259, 327, 334] On the other hand, in more polarizable matrices with smaller IE gaps (krypton and, particularly, xenon), fragmentation is often suppressed, but some radical cations may undergo prompt deprotonation of the matrix to yield the corresponding neutral radicals.[259, 335] Interestingly, almost complete switching from frag-

Table 5. The products observed upon the radiolysis of various astrochemically relevant molecules isolated in low-temperature noble gas matrices (Ne, Ar, Kr, Xe).

Molecule	Primary products	Secondary products	Matrix effect	Ref.
CH_3OH	CH_2OH, H_2CO, HCO, CO	CO	Yield of "primary" CO increases with increase of matrix IE (highest in Ne)	339
HCN	H, CN, HNC, HCN^+ (in Ne matrix only)	H, CN		337
CH_3CN [a]	CH_2CNH, CH_3NC, CH_2NCH, CH_2CN, CH_2NC	HCCN, HCNC, CCN, CNC	At low doses CH_2CNH is predominant isomer in Ne matrix (high IE), while CH_3NC is predominant Ne isomer in Xe matrix (low IE)	340
HCOOH [a]	CO, CO_2, HOCO	CO, CO_2 (in Ar and Kr matrices)	At low doses, relatively low yield of HOCO observed in Ne (high IE) and Xe (low IE) as compared to Ar and Kr matrices (moderate IE). CO_2/CO branching ratio increases in row Ne < Ar < Kr < Xe (IE decreasing, external heavy atom effect on S – T convesrsion)	210
C_2H_2 [b]	C_2H	C_2H, C_2		16
C_2H_4 [b]	C_2H_3, C_2H_2	C_2H, C_2		16
C_2H_6 [b]	C_2H_4, C_2H_5	C_2H_2, C_2H_3	Yield of C_2H_5 increases dramatically in a row Ar < Kr ≪ Xe (IE decreasing, external heavy atom effect on S – T conversion)	16
Benzene [b]	Phenyl radical, fulvene, 1,3-hexadien-5-yne (in Ar matrix only)	1,3-hexadien-5-yne	Phenyl radical to fulvene branching ratio increases in a row Ar < Kr ≪ Xe (External heavy atom effect on S – T conversion)	341

[a] No data on secondary products in Ne matrix. [b] No data in Ne matrix.

mentation to deprotonation was observed for the $CH_2OCH_2OCH_3^{+\bullet}$ radical cation by turning from argon to xenon matrix.[336] These findings provide an important basic clue regarding the basic nature of matrix effects in the ionic chemistry of icy media.

3.2.3. Model studies on the radiation-induced transformations of astrochemically important species

Recently, the radiation chemistry of a number of astrochemically important molecules in noble gas matrices was extensively characterized by FTIR spectroscopy up to a very high conversion degree (*ca* 90%), which made it possible to reveal both primary processes and subsequent radiation-induced evolution of the molecular and radical products.[13] In particular, such an approach was applied to HCN, CH_3CN, CH_3OH, HCOOH, C_2 hydrocarbons, and benzene.[16, 210, 337 – 341] The results of these studies are summarized in Table 5.

From these studies, one may derive two important conclusions. First, they demonstrated the importance of "hot" processes at the molecular level occurring in rigid media at extremely low temperatures. As an example, we could mention the prompt formation of CO from methanol,[339] which appears to be a single-step process. Most likely, this implies the formation of a primary product (formaldehyde) in a vibrationally excited state followed by its immediate decomposition. It is worth noting that such deep hydrogenation virtually does not occur in molecular media at higher temperatures because of the more efficient relaxation of excess energy. The second finding is concerned with the strong effect of the physical characteristics of the inert matrix on the distribution of reaction channels. As mentioned previously, this fact also implies an important role of intermolecular relaxation for both ionic and neutral excited states, and such a consideration should be taken into account in the radiation-induced astrochemistry of ice media with different medium polarizabilities.

A new direction of model matrix isolation studies for cold astrochemistry is related to the radiation chemistry of isolated intermolecular complexes. In this respect, the isolated 1 : 1 complexes may be considered the simplest "building blocks" in the processes of low-temperature synthetic astrochemistry. It was found that X-ray irradiation of matrix-isolated complexes $H_2O\cdots CO_2$ [205] and $H_2O\cdots CO$ [342] leads to the formation of the HOCO radical, which is supposed to be an important intermediate in prebiotic astrochemistry.[343] In the latter case, the synthesis of formic acid was also observed either directly or after annealing the sample at relatively low temperatures. Specific radiation-induced chemistry combining consecutive synthesis and degradation was revealed in the case of radiolysis of the $C_2H_2\cdots CO$ complex under the conditions of matrix isolation.[344] Another interesting example of the effect of complexation of astrochemically relevant processes was observed for the $HCN\cdots CO$ complex.[229] It was found that the rate of radiation-induced isomerization of HCN to HNC significantly increased upon the formation of complexes with CO, which may be useful for understanding the relative abundance of HCN and HNC isomers in certain space regions.

Generally, studies on the radiation-induced chemistry of matrix-isolated complexes (still very limited) may provide important clues for challenging astrochemical issues.

3.3. Low-temperature reactions "in dark"

Although the matrix isolation approach was originally based on the idea of disabling the high reactivity of the studied species, this experimental technique actually found broad use in studies devoted to chemical reactions. In addition to the photo- and radiation-induced processes, which were discussed above, many matrix isolation experimental studies deal with various thermal-induced and tunneling-driven reactions, including many of those, which are relevant in the context of astrochemistry. Low-temper-

ature conditions may only provide a low barrier (a few kJ mol^{-1}) or barrierless reactions to occur in matrices. Also, the tunneling mechanisms may be involved. Generally, the 'in dark' reactions occurring in matrices may be divided into three groups: (i) isomerization processes, (ii) bimolecular reactions between the reagents allocated in close neighborhood, and (iii) reactions involving diffusing species.

3.3.1. Isomerization reactions

There are two forms of isomerism: structural isomerism (chemical bonds in the isomers are different) and stereoisomerism (chemical bonds in the isomers are the same, but orientations of atoms differ). Structural isomerization typically requires rather high activation energy, so at cryogenic temperatures, such reactions may occur under the action of radiation (some examples are given in chapters 2.2 and 2.3 of this review) but not *via* the thermal-induced mechanism. However, some metastable species isolated in matrices may transform to more stable structural isomers even at temperatures of *ca.* 10 K due to the tunneling reactions. A remarkable paper by Schreiner and colleagues[345] reports the capture and spectroscopic characterization of elusive hydroxymethylene (H$-\ddot{\text{C}}-$OH), a carbene considered a possible intermediate in the synthesis of simple sugars in space environments. It was found that H$-\ddot{\text{C}}-$OH rearranges to formaldehyde (H_2CO) with a half-life of only 2 h at 11 K by pure hydrogen tunneling through a large energy barrier (30 kcal · mol^{-1}). Authors stated that this intrinsic instability of hydroxymethylene raises considerable problems for its astronomical detection and doubt that such short-living species may participate in interstellar chemistry at very low pressures. Peculiarities of the tunneling isomerization reactions of various carbenes isolated in low-temperature matrices have been discussed in the review paper.[346] It is important to mention that in addition to widely known hydrogen atom tunneling reactions, there are examples of heavy atom (carbon, nitrogen) quantum mechanical tunneling leading to structural isomerization in matrices.[347]

Conformational isomerism is a form of stereoisomerism, implying that isomers can be interconverted by rotations around a chemical bond. Conformational isomers (conformers) are the configurations that correspond to local minima on the energy surface, and the barrier height determines the conformational populations in a molecular system. Conformational interconversion might occur not only in a "through-the-barrier" manner (*i.e.* driven by classic thermodynamic equilibrium reactions) but also in "over-the-barrier" (induced, *e.g.*, by photoexcitation) and "under-the-barrier" (driven by quantum tunneling mechanism) ways. Photoinduced conformational switching may provide sufficient concentrations of a higher-energy conformer at low-temperature conditions. For example, the metastable conformer of formic acid, *cis*-HCOOH (which is 16.3 kJ mol^{-1} higher in energy than *trans*-HCOOH, while the barrier of trans-to-cis conversion is 57.7 kJ mol^{-1}), was detected in the Orion Bar photodissociation region.[348] Authors propose that it is photoswitching mechanism that responsible for relatively high abundance of *cis*-HCOOH (observed *cis*/*trans* ratio is *ca.* 0.36) and emphasize that less stable conformers of other molecules could also exist in the ISM.

Small carboxylic acids (HCOOH, CH_3COOH) are important in astrochemistry and astrobiology. Conformers of these molecules were thoroughly studied using a matrix-isolation technique. The trans configuration is the most stable conformer for both formic and acetic acid. Higher-energy cis conformers could be prepared in low-temperature matrices in sufficient amounts using selective narrow-band infrared excitation (the peculiarities and advantages of this approach are discussed elsewhere — see Ref. 349 and references therein). It was found that *cis*-HCOOH and *cis*-CH_3COOH isolated in noble-gas matrices quickly transform into their trans analogues even in darkness. This is due to the quantum tunneling of hydrogen atoms through the torsional barrier. The cis to trans decay becomes faster at higher temperatures, while the low-temperature limit is achieved below 10 K.[349] Additional evidence for the tunneling mechanism is the strong kinetic isotope effect (for *cis*-HCOOD and *cis*-CH_3COOD, the observed decay was slower by 3 – 4 orders of magnitude).[349] The *cis* to *trans* decay of acetic acid is faster than that of formic acid, which is in agreement with barrier height values (*ca.* 34 and *ca.* 38 kJ mol^{-1}, respectively).[350] It is important to note that the barrier height is not the only determining factor. For both formic and acetic acids, a secondary isotopic effect was observed — isomerization of *cis*-DCOOH and *cis*-CD_3COOH was faster than that of *cis*-HCOOH and *cis*-CH_3COOH.[349] This effect was explained by the difference in the vibrational state density of a trans form near the energy of the initial state (cis form, behind the torsional barrier). Importantly, environment strongly affects the rate of the unimolecular (and hence virtually intrinsic) reaction of tunneling-induced conformerization. Different matrix dependences of the *cis*-to-*trans* tunneling decay rate were observed for formic and acetic acids in noble-gas matrices, indicating that a complex set of solvation effects should be considered (changes in barrier heights, energy gaps, nature of accepting levels, reorganization energies and coupling with phonons).[349] Computational insight (using a polarizable continuum model) into how the noble-gas matrix influences these processes reproduces experimental results for *cis*-HCOOH but not for *cis*-CH_3COOH.[350] With rare exceptions, the complexation of a metastable cis conformer by other molecules leads to an increase in its stability, *i.e.*, decreasing the rate of the tunneling decay. For example, the *cis*-HCOOH$\cdots H_2O$ complex was found to be practically stable with respect to tunneling-driven *cis*-to-*trans* isomerization.[349] The relative stability of higher-energy *cis* conformers in the solid nitrogen matrix (compared to noble-gas matrices) was explained in terms of the specific 1 : 1 interaction of a surrounding N_2 with the OH group of a carboxylic acid molecule.[350]

The matrix isolation technique has also been applied to study the conformational isomerism of the simplest amino acids, such as glycine and alanine (see, *e.g.*, Refs 351 – 353). It was shown that some higher-energy conformers of these molecules prepared in low-temperature noble gas matrices transformed very quickly (with a lifetime of several seconds) to more stable ones because of hydrogen atom tunneling. Similar to the case of simple carboxylic acids (HCOOH and CH_3COOH), the use of a nitrogen matrix may provide evident stabilization of elusive conformers.

There are not only carboxylic acids that exhibit *cis*/*trans* tunneling-driven isomerization in low-temperature matrices. Similar processes were also investigated for some small transient species of potential astrochemical interest, such as HOCO radical[354] or HOPO molecule.[64] For the other kind of metastable compounds, heterocumulenes OSNSO and OCNSO, thermal-induced *syn*/*anti* isomerization (through

the barrier of *ca.* 1 kcal mol^{-1}) was observed in argon and nitrogen matrices.[99, 100]

3.3.2. Local reactions

In the context of general chemistry, bimolecular reactions require diffusion mobility of both reactants. While the long-range mobility of guest species embedded in cryogenic matrices is frozen, a slight temperature increase causing some short-range matrix relaxation may induce a local reaction between neighboring fragments. Because of low-temperature conditions, only low-activation-energy processes, *e.g.*, radical recombination or some radical-molecule reactions, may occur in this scenario. Low-temperature reactions involving radicals are important for understanding the chemistry of interstellar ices, particularly the mechanisms of formation of organic and prebiotic molecules.[355] Thus, model studies of these reactions under matrix-isolation conditions might help solve these problems.

Practically, the neighboring pair of reactants could be produced in matrices by photolysis or radiolysis of intermolecular complexes or relatively large molecules (see chapters 2.1 and 2.2 of this review). A radical-radical pair would rather recombine immediately (what is known as the "cage effect"), while a radical-molecule pair may be stabilized due to the reaction barrier. For example, VUV photolysis [303] or radiolysis [342] of matrix-isolated H_2O. The CO complex yields stabilized $^{\bullet}$OH/CO radical-molecule pairs in the form of OH···CO complexes. The thermally induced conversion of matrix-isolated OH···CO complexes to *trans*-HOCO radicals have been investigated in noble-gas matrices.[303, 342] Annealing of the Ar, Kr, and Xe matrices at 30 K causes "through-the-barrier" OH···CO → *trans*-HOCO transformation. The observed sharp temperature dependence of the reaction rate agrees well with the very low activation barrier (*ca.* 8 kJ mol^{-1}).[303, 342] It was also found that the OH···CO → → trans-HOCO reaction slowly occurs in the Ne matrix even at 4.5 K in darkness, which indicates some involvement of the tunneling mechanism.[303] These studies represent a case of experimentally simulating the OH + CO reaction in low-temperature ices (while most other research works related to this fundamentally important reaction deal with the gas phase [356]). The product of this reaction, the *trans*-HOCO radical, is a crucial intermediate in the synthesis of formic acid (HCOOH) in interstellar ices.[342, 343]

An attempt to activate the thermal reaction between CH_3 radicals and CO molecules was made in experiments with *p*-H_2 matrices.[234] Although photolysis of CH_3I/CO/*p*-H_2 samples at 3.2 K resulted in the formation of CH_3 radicals with excess energy higher than the barrier of the $CH_3 + CO \rightarrow CH_3CO$ reaction, and further annealing of the matrix containing CH_3 and CO to 5.1 K cause no signs of acetyl radical (CH_3CO) formation. Instead, authors detected the CH_3···CO complexes, formed in a barrierless process. This case indicated that the kinetic energy of CH_3 radicals is readily quenched in the *p*-H_2 matrix and that this kind of medium is only suitable for investigating reactions with extremely low barriers. (Notably, the calculated barrier for the $CH_3 + CO \rightarrow CH_3CO$ reaction is *ca.* 27 kJ mol^{-1}).

3.3.3. Reactions of diffusing species

The long-range mobility of small guest species embedded in cryogenic matrices or ices can be unfrozen at elevated temperatures. Atoms trapped in defects of matrix crystallites may overcome the potential barrier and diffuse through a matrix to react with other species. It should be noted that low-temperature diffusion-driven reactions in matrices show inhomogeneous kinetic behavior, which is typical for chemical reactions in solid media.[357, 358] There are detailed studies of H,[357, 359] O,[360, 361] and F [36, 362] atoms mobility in low-temperature matrices. Fluorine chemistry seems less important in the context of astrochemical evolution. Mobile hydrogen atoms might be involved in addition reactions and H-atom abstraction reactions. For oxygen atoms, insertion reactions are also possible. Atom addition reactions, especially H atom addition, play an important role in the chemistry of interstellar ices.[6] For instance, hydrogenation of CO is considered a main pathway of methanol formation, and formic acid could be formed due to hydrogenation of HOCO radical. Oxygen atoms recombine to form important astrochemical molecules — O_2 and O_3 — which further produce various hydrogen-oxygen compounds. Quantum tunneling of oxygen atoms may play an important role in the reactions occurring in interstellar ices.[363] The matrix isolation technique is a powerful approach for investigating atom addition reactions since it allows to probe atoms directly (by means of EPR, UV absorption or fluorescence spectroscopy) and to activate their reactions thermally or photochemically.[36, 364] Comprehensive reviews devoted to the studies of atom reactions in solid matrices allow one to go deeper into the mechanisms of production of free atoms, their detection, and activation, as well as the peculiarities of "matrix site effects".[358, 364]

The hydrogenation of CO, which is a first step in the synthesis of a number of organic molecules in interstellar ices, was intensively studied in matrix isolation experiments. It was found that H atoms react with carbon monoxide during deposition of matrix samples, and an additional amount of HCO appears after annealing, which activates diffusion of trapped H atoms in Ar, Kr, and Xe matrices.[365] The reaction $H + CO \rightarrow HCO$ has a very low, if any, barrier in the Ne matrix, as demonstrated by Pirim and Krim.[366] Non-energetic H atoms readily reacted with nearby CO molecules at 3 K in the neon matrix in darkness, and subsequently, thermally induced diffusion of H led to an increase in the HCO amount. The other steps of the $CO \rightarrow CH_3OH$ reaction pathway were discussed in Ref. 367, where the formation of CH_2OH by the thermally induced reaction $H + H_2CO \rightarrow CH_2OH$ was reported for the first time. Reactions of H-atom addition to many other astrochemically important molecules isolated in matrices have been widely investigated (see, *e.g.*, Refs 86, 219, 337, 342). Notably, hydrogen atoms can not only be attached to unsaturated molecules but may also abstract hydrogen from a reacting species. An example of such a reaction is presented in work devoted to the kinetics of the $C_2H_6 + H \rightarrow C_2H_5$ reaction in the Xe matrix.[368]

The *p*-H_2 matrix can serve as a source of H atoms (produced chemically, photolytically or radiolytically). In recent studies, different astrochemically important species were produced in *p*-H_2 matrices by hydrogen abstraction (a common scheme may be written as $AH + H^{\bullet} \rightarrow A^{\bullet} + H_2$), namely, H_2NCO,[369] HNCO,[369] CH_2CONH_2,[370] and $C(O)OCH_3$.[371] In contrast, reacting H atoms in the *p*-H_2 matrix produce hydrogenated PAHs by the reaction $H + PAH \rightarrow H_1PAH$.[161] Competition between H-atom addition and H-atom subtraction is an important issue. For example, the *p*-H_2 matrix reaction of hydrogen atoms with HCOOH yields HOCO radicals [372] (abstraction pathway), while in Kr matrices, H_2COOH radicals [373] (addition pathway) are the key product.

Somewhat less attention was paid to oxygen atom reactions in matrix isolation works. Danilychev and Apkarian demonstrated that thermally induced recombination of oxygen atoms $O + O \rightarrow O_2$ occurs at two different temperatures in Kr and Xe free-standing crystals, which correspond to activation of diffusion of atoms trapped in two different sites.[360] However, matrix samples (which, in contrast to free-standing crystals, are imperfect polycrystalline samples) demonstrated somewhat different temperature dependences of the O atom diffusion mobility.[265] Geminate recombination of O atom with molecular oxygen ($O + O_2 \rightarrow O_3$) was studied in the Xe matrix.[374] Reactions of O-atom addition (*e.g.*, $HO + O \rightarrow HO_2$ and $CO + O \rightarrow CO_2$) occur in Kr and Xe matrices under annealing at temperatures lower than that required for activation of H atom mobility.[205] Oxygen atoms may also be involved in the insertion reactions. For instance, vinyl alcohol was obtained by reaction of a thermally mobilized O atom with ethylene in an Ar matrix ($C_2H_4 + O \rightarrow H_2C{=}CHOH$).[375] A non-trivial transformation of acetylene into ketene caused by thermally activated O atoms was observed in solid Ar ($C_2H_2 + O \rightarrow H_2CCO$).[376] The reaction between vinyl radicals and molecular oxygen $C_2H_3 + O_2 \rightarrow C_2H_3OO$ occurring in the Ar matrix after 25 K annealing[377] is also mentioned here, although the authors did not describe the mechanism of reagent mobility, and we cannot clearly assign this reaction to long-range diffusion or local processes.

Recent studies have revealed that nitrogen might be abundant in interstellar ices. In this regard, investigations of low-temperature reactions of N atoms should be mentioned here.[378, 379] It was shown that thermalized (non-energetic) N atoms remain unreactive at 3K but cause isomerization and fragmentation of CH_3CN at 10 K in mixed acetonitrile/N_2 ice.[378] Another investigation demonstrated that N atoms readily formed HNCO molecules when CO ice with embedded H_2O molecules and N atoms was heated from 3.5 to 10 K.[379] Hence, the possibility of thermally induced reactions of N atoms in low-temperature molecular matrices was proven, although the experimental design of both studies was different from "classic" matrix-isolation investigation.

Speaking of different atoms reacting in matrices, one should notice an exotic case of sulfur atoms. The thermally induced reaction of S atoms with the CS fragment yielding CS_3 was detected in an Ar matrix under annealing at 28 K.[58] Keeping in mind that CS is one of the sulfur-bearing species detected in the interstellar medium, this matrix-isolation work is evidently relevant for laboratory astrochemistry.

Finally, we would like to mention somewhat different example of utilizing a matrix isolation method for studying thermally induced reactions. Ref. 367 is devoted to the synthesis of quite large astrochemical molecules, namely, glycolaldehyde ($HOCH_2CHO$) and ethylene glycol ($HOCH_2CH_2OH$). H_2CO/Ng ices were preliminarily photolyzed at 12 K to produce HCO radicals and then annealed at 30 and 50 K (for Ng = Ar or Xe, respectively) to activate hydrogenation of HCO by H atoms and formation of CH_2OH radicals trapped in the matrix. Since HCO and CH_2OH radicals are too large to diffuse in rare gas solids, matrices were slowly sublimated, and residual $HOCH_2CHO$ (glycolaldehyde), $HOCH_2CH_2OH$ (ethylene glycol), CH_3OH (methanol), and tentatively OCHCHO (glyoxal) were detected as the reaction products. The study demonstrates pathways of glycolaldehyde and ethylene glycol formation *via* recombination reactions $CH_2OH + HCO \rightarrow HOCH_2CHO$ and $CH_2OH + CH_2OH \rightarrow HOCH_2CH_2OH$.

4. Conclusion

In this review, we have mainly focused on recent applications of matrix isolation to the rapidly developing field of molecular astrophysics and astrochemistry. In fact, such applications cover two major aspects. The first is related to matrix isolation spectroscopy. This tool is a classical and somewhat "old-fashioned" method that has been applied to some astrophysical issues for several decades. As shown by the examples presented in this review, it is still an efficient and powerful approach for assigning freshly observed spectroscopic manifestations of different species in space objects and predicting new possible candidates. It is based on versatile opportunities for the generation and stabilization of unstable and exotic ionic and neutral species under the conditions of matrix isolation. Recent progress is associated with the elaboration of new experimental procedures, the use of specific matrices (such as parahydrogen) and the improvement of detection methods.

Meanwhile, we have to draw attention to another aspect, which deals with using matrix isolation as a specific tool for simulations of mechanisms involved in key processes of cold astrochemistry. It should be noted that the term "simulation" is used here in different contexts compared to typical meaning in astrochemistry. Indeed, matrix isolation experiments do not provide realistic simulation of the complex processes occurring in icy extraterrestrial media because noble gases and other inert matrix materials are not common in space. However, using matrix isolation gives unique opportunities for step-by-step modelling of key mechanistic stages, which cannot be directly identified in ice studies. In our view, this is a very important intermediate step between extensive theoretical predictions (usually made for the gas phase) and experimental results obtained in realistic complex ices. Matrix isolation may provide a specific molecular design for the simulation of elementary radiation-induced or photochemical reactions in building blocks presumably involved in synthetic astrochemistry, such as intermolecular complexes or small aggregates. We have shown herein a number of examples of recent studies of various groups in this direction, and this is still the beginning of the story. Additionally, matrix isolation allows one to directly observe the transformations induced by reactions of free atoms slowly diffusing in a cold inert medium and to study the effects of tunneling, which may be important for cold astrochemical processes. Finally, model investigations of the effects of the matrix environment on the radiation-induced processes in matrices may help to better understand the relation between gas-phase and solid-state radiation chemistry, which is crucially important for proper interpretation of the results of ice experiments. We believe that the development of such approaches will be very useful to unravel the unresolved issues of modern astrochemistry (as a complement to realistic ice simulations) and bring new knowledge significant for other fields, including chemical physics, photochemistry and radiation chemistry.

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5. List of used acronyms

DIBs — diffuse interstellar bands,
EPR — electron paramagnetic resonance (spectroscopy),
FTIR — Fourier-transform infrared (spectroscopy),
IE — ionization energy,
IR — infrared,
ISM — interstellar medium,
PAHs — polycyclic aromatic hydrocarbons,
UIR — unidentified infrared (bands),
UV — ultraviolet,
UV/vis — ultraviolet-visible (spectroscopy).

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