Translated from *Uspekhi Khimii*, **57**, 1273-1296 (1988) U.D.C. 541.117.543.422.46

Spectroscopy of Molecules and Molecular Complexes Dissolved in Liquefied Gases: Structure and Reactivity

Ya.M.Kimel'fel'd

The application of the absorption spectroscopy (IR and UV) of solutions in liquefied elemental gases (N_2, O_2, Ar, Kr, and Xe) to the study of reactivities and reaction mechanisms is examined. The design of cryostats and the method of preparation of solutions are described and data on the solubilities of molecules in liquefied gases are presented. The characteristic features of the spectra of diatomic and polyatomic molecules in cryosolutions are analysed. The possibilities of the method in the investigation of unstable molecular complexes and in the elucidation of the nature of the spectra of the hydrogen-bonded complexes formed are demonstrated. The specific features of the non-linear absorption of IR radiation by molecules in the cryosolutions are discussed and a number of photochemical reactions in cryosolutions are described. It is shown that the method is promising for the solution of problems of laser chemistry in the condensed phase.
The bibliography includes 101 references.

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I. INTRODUCTION

Liquefied noble gases are transparent in the range from the vacuum ultra-violet region to the far infrared, while liquefied oxygen and nitrogen have only weak absorption bands in the middle infrared region. For this reason, solutions of molecules in liquefied gases have been traditionally investigated by methods of absorption optical spectroscopy. The latest review devoted to the IR spectroscopy of solutions in liquefied gases was published in 1973 by Bulanin[1] and describes fairly completely aspects such as the solubility of the simplest molecules in O_2, N_2, and Ar and the design of optical cryostats. It is emphasised that the low solubility is compensated by the possibility of studying very thick layers of solutions, up to 10 metres. The review reaches conclusions about the characteristics of the IR spectra of solutions of molecules in liquefied gases: the frequency shifts relative to the frequencies in the gas phase are smaller (on average down to 5 cm^{-1}) than in any other environment, for example, in matrices; the integral band intensities are close to those in the gas phase; the widths of the bands of polyatomic molecules are usually less than 5 cm^{-1}; as a result of the narrowing of the band, the IR spectrum at 90 K contains much more information than that at low temperature in a traditional solvent, for example, in CCl_4. The presence of particular groups in the molecule, the stoichiometry of the molecule, its symmetry, and even its geometry can therefore be determined from the IR spectrum.[2]

During the last one and a half decades, numerous studies have been published in which krypton and xenon were also used as solvents. At elevated pressures (up to 50–60 atm), it is possible to carry out experiments over a wide temperature range, up to 0 °C. Naturally, this made it possible to dissolve more complex molecules, such as, for example, decamethylferrocene.[3] It became possible to investigate not only molecules but also complex formation reactions, photochemical processes, etc. Studies on the effect of laser radiation on molecules in cryosolutions began to be prosecuted on a broad front. Finally, the wave length range in which spectra are obtained has been extended—from far to near infrared and further to the vacuum ultraviolet region of the spectrum. Overall, the specific features of a simple cryosolution made it possible to obtain new information about intramolecular and intermolecular processes.

II. METHODS

It has been noted[4] that the spectroscopy of solutions in liquefied elemental gases has much in common with the familiar low-temperature matrix isolation method. However, the latter method is not suitable for the investigation of weak absorption bands because of the difficulties in the preparation of specimens with a fairly large thickness and due to the light scattering by the matrix; also this procedure does not yield quantitative information about the concentration of the impurity molecules and hence about the intensity of the spectral bands. Furthermore, the solution is in a high-pressure cell and the reacting gases cannot leave the reaction space, as happens in the matrix isolation method where the measurements are performed under high vacuum. Furthermore, in the matrix experiment there is a spectroscopic problem—the band splitting associated with the positions of the molecules in the matrix. It arises because the isolated molecules can exist in different environments in the solid matrix and the IR bands are frequently split. It is therefore sometimes impossible to distinguish the matrix splittings from spectral effects associated with changes in the molecule. The

essential feature of the method of preparation of solutions in liquefied elemental gases, including N_2 and O_2, is that the solute is introduced into a closed volume cooled as a rule with liquid nitrogen (we shall designate the word liquid by the symbol L, e.g. LN_2), and the solvent gas is condensed. Bulanin[1] described two types of optical cryostats—with horizontal and vertical optical axes. A cryostat of the second type (Fig.1), developed at the Institute of Physics at the Leningrad State University, which makes it possible to carry out experiments with thicknesses of absorbing layers up to 40 cm as a result of the double passage of the IR radiation through the solution, is particularly effective. Since the cryostat window is not in contact with the cold solution and its temperature is always close to room temperature, it can withstand high pressures (up to 60–70 atm), which permits the coverage of the temperature range 80–270 K using liquefied N_2, O_2, Ar, Kr, and Xe (Fig.2).[5]

Rebiai et al.[6] used a fairly effective design of a cryostat with a horizontal optical axis. It was made almost entirely of brass in order to reduce the effect of thermal stresses. An additional shielding chamber was placed over the chamber with the specimen. It can be filled with a cooling agent, which permits the maintenance of a constant temperature in the test solution without its boiling. The specimen chamber as well as the shielding chamber are attached to the upper lid of the cryostat via stainless steel tubes having a low thermal conductivity.

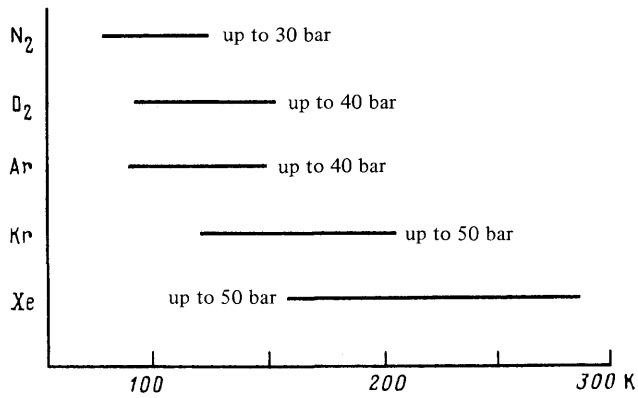


Figure 2. Region of the existence of the liquid phase of cryosolvents.[3]

In order to be able to investigate the largest possible number of substances in such solutions, their inadequate solubility must be compensated by the large thickness of the layer investigated. A novel design of multipass cell has been developed by Jeannotte and

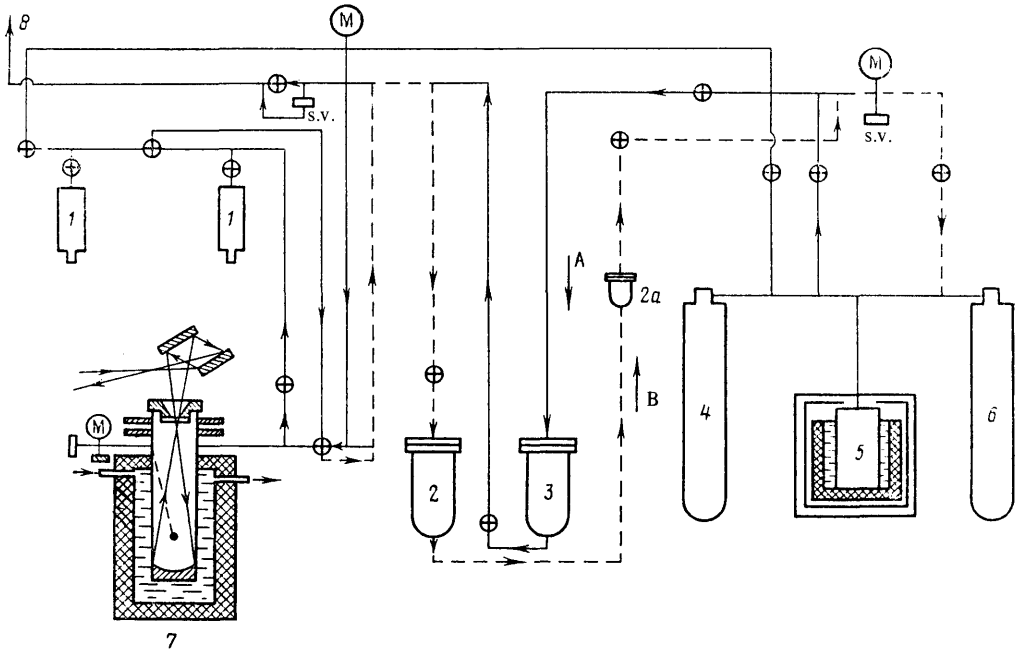


Figure 1. Schematic illustration of the apparatus for cryospectroscopy:[11] (1) vessels for the storage of the test compounds; (2), (2a), and (3) absorber systems; (4)–(6) vessels for the collection and storage of the inert gases; (7) cryostat; (8) forced evacuation; s.v.—safety valves; M—manometers; ⊕—valves; A—forward flow of the condensible gas admitted into the cryostat; B—reverse flow of the condensible gas being collected in the gas collector.

Overend.[7] The path length was varied from 0.3 to 2.1 m in 0.6 m steps. Since there are difficulties in sealing the windows under conditions where the temperature is reduced repeatedly, a cell was produced with a single window through which both the incoming and outgoing beams pass. As in the previous versions, the familiar White cell design was used. The internal 1.5 litre volume of the cell was surrounded with gaseous helium by altering the pressure of which it was possible to regulate the cooling with liquid nitrogen in the outer volume. For an optical path length of 1.5 m, LAr is entirely transparent and the transmittance of the cell over the entire IR range investigated in not less than 95%.

A design has been proposed[8] in which a change in the thickness of the optical layer by an order of magnitude is achieved without interfering with White's scheme by rotating plane illuminating mirrors placed outside the limits of the volume with the liquefied gas.

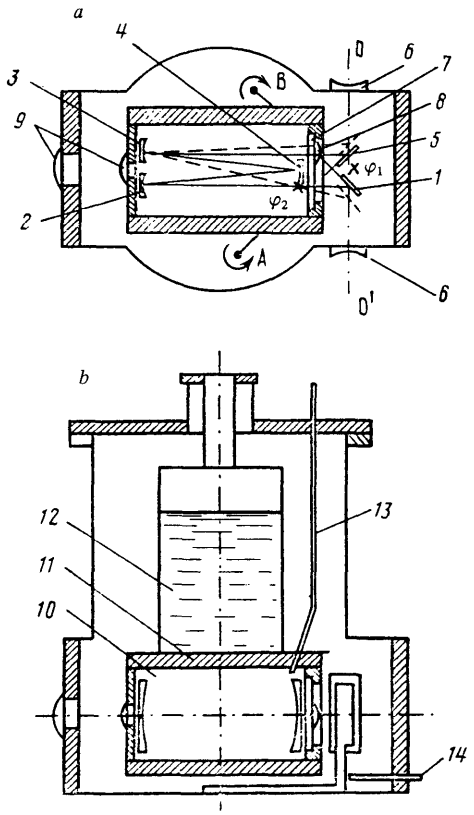


Figure 3. Schematic diagram of the cryostat:[8] (a) horizontal section: (1) and (5) plane mirrors; (2)–(4) spherical White cell mirrors; (6) scattering lenses; (7) window; (8) collector; (9) lenses; (b) vertical section: (10) cell with specimen; (11) copper jacket; (12) cooling vessel; (13) inlet for test substance; (14) component controlling the mirrors (1) and (5).

A schematic horizontal section through the cryostat with a representation of the path followed by the beam is illustrated in Fig.3*a*. The retuning of the optical scheme for two passes is achieved by rotating the plane mirror *1*, whereupon light falls immediately on the exit White cell mirror *3* (dashed line) and then, by rotating the plane mirror *5*, it is directed on to the OO′ axis.

The vertical section through the cryostat is shown schematically in Fig.3*b*. The test solution is in cell *10*, which consists of a tube with an internal thread for the attachment of White cell mirrors.

Melikova[8] noted the advantages of the cryostat compared with previous designs.[1,7] Firstly, a thick optical layer is ensured for a small volume of the specimen (300 ml), achieving thereby not only economy as regards expensive solvent gases (especially xenon), but also a uniformity of temperature in the cell. Secondly, there is a possibility of adjusting the optical layer in the same specimen by an order of magnitude without the need to move any optical components in the liquefied gas. Thirdly, it is possible to work with standard spectroscopic apparatus without additional illuminating devices.

The preparation of solidified optically transparent solid solutions is of special interest, since the dissolved molecules are then in a field of known symmetry. Solid specimens, obtained by freezing liquefied noble gases, can be more crystalline than those obtained by the direct condensation of the gases. Fairly thick specimens of dilute solid solutions are sufficiently transparent for absorption spectroscopy. If the solid solutions are contained in a cell where it is possible to maintain an excess pressure of solvent vapour, the temperature can be raised up to the melting point of the solid specimen, in contrast to the matrix isolation method. The design of the corresponding cryostats has been developed by Maier.[9] In order to obtain a solid solution in xenon (it will be designated by SXe), the bottom of the cell with an optical path length of 1.3 cm is cooled to −117 °C, which is approximately 5 °C below the freezing point of pure xenon, and the top of the cell is maintained near −107 °C. Since the crystal grows upwards, the temperature of the top of the cell is slowly reduced until the crystal fills the cell. This solidification process usually lasts 4 h. The solid specimen obtained is transparent without any visible defects. Depending on the purpose of the experiment, the solid specimen is kept either several degrees below the melting point of the xenon or is cooled to lower temperatures.

Spectroscopic studies on liquid cryosystems using large optical path lengths impose extremely severe requirements on the purity of the liquefied gases.[10]

For systematic studies using expensive gases such as xenon and krypton, it is essential to make provision for a closed solvent circulation cycle (Fig.1). The purification of the gas involving the removal of the substance dissolved in the previous experiment is carried out in zeolite-filled columns and the transfer of the gas, without losses, from the cryostat to the storage compartment is achieved by recondensation in the vessel *5* cooled with liquid nitrogen.[11]

The simplest method of separation of the solutions involves the filling of the cryostat volume in the 1 : 1000 or 1 : 10 000 gas mixture, its subsequent condensation, and the addition of the solvent gas. In the measurement of the band intensities,[12] solutions of known concentration, known beforehand to be below that corresponding to saturation, were prepared by liquefying in the cryostat reference gas mixtures with the test substance.

The experiments with solutions in elemental gases are performed in the same way as those with traditional solutions. When nitrogen oxides were dissolved in LXe, the solution was constantly agitated with a magnetic stirrer, which actuated a Teflon-coated rod placed at the bottom of the cell.[13] The NO concentration in the solution depends on temperature and the NO partial presure over the

solution. In order to obtain the required concentration, an elevated NO pressure was used.

An interesting method of preparation of ozone solutions in LAr has been proposed.[14] Ozone was obtained directly in a cryostat with BaF_2 windows by irradiating LO_2 with light from a mercury lamp. The solutions in LAr were prepared by condensing AR in the cryostat after slow distillation of oxygen from a solution of O_3 in LO_2. This method makes it possible to transfer O_3 almost completely to LAr.

Cryostats with a vertical optical axis are specially convenient for the preparation of solutions of solid compounds:[3] the powder is poured into the cryostat in a stream of dry argon, the upper flange with a window is attached, argon is evacuated whilst cooling, the solvent gas condenses, and the solution is repeatedly caused to boil by releasing the pressure. One can assume that the specimen taken for the experiment dissolved if the spectrum did not change as a result of the subsequent ebullition of the solution. To accelerate the dissolution, the solution is vigorously bubbled with the gaseous medium.

III. THE SOLUBILITY OF MOLECULES IN LIQUEFIED GASES

The solubilities x of various compounds in cryogenic liquids are of independent interest for many technological problems. For example, CO_2, hydrocarbons, and NO_2 solidify during the liquefaction of air. A method has been proposed[15] for the calculation of the solubilities of solids in cryosolvents. The decisive factors in the approach described are the interaction of solute with the solvent and the melting point of the solute, its fugacity, and activity coefficient. The calculated solubilities in LO_2 [16] of different classes of compounds are given below in mole fractions (m.f.): alkanes (from methane to hexane) from 1 to 1×10^{-4}, alkenes (from ethylene to hexene) from 1 to 2×10^{-2}, acetylene 5×10^{-2}, benzene 1×10^{-4}, methanol 6×10^{-2}, CO_2 1×10^{-3}, H_2S 1×10^{-3}, NO 1×10^{-2}, NO_2 2×10^{-6}, and Kr 3×10^{-1}. The calculated solubilities of solid hydrocarbons, with the exception of methane, are higher by one and a half to three orders of magnitude than those obntained experimentally.[16] The regularities found in the solubilities of homologous series can be seen. The solubilities of alkanes and alkenes decrease with increase in molecular weight. The solubility of acetylene, which tends to form associated species, is lower than those of ethylene and isobutene. The solubilities x of olefins in LN_2 were determined by IR spectroscopy.[17] The analytical bands selected were those of ethylene ($\nu = 2168$ cm^{-1}; $\nu_{1/2} = 9.5$ cm^{-1}), propene (2034 cm^{-1}; 1.5 cm^{-1}), and but-1-ene (995 cm^{-1}; 4.0 cm^{-1}); the values of x proved to be 6×10^{-3}, 1×10^{-3}, and 1.5×10^{-4} m.f. respectively at 80 K. The solubility of olefins in LO_2 is higher by 1–4 orders of magnitude than in LN_2. Careful preparation of the saturated solution, including its bubbling with He and the measurement of the IR spectra both on heating and cooling, made it possible to determine the solubility x of linear molecules with an error in the range 15–20%: in LO_2, x is 4.3×10^{-6} for CO_2, 5.6×10^{-4} for COS, and 1.4×10^{-4} m.f. for N_2O, while x for CS_2 in LAr is 5.6×10^{-7} m.f.[18] The solubilities x of alkynes are much less satisfactorily reproducible. The following values of $10^6 x$ (in m.f.) have been obtained in LAr at 90 K: 5.4 for $HC{\equiv}CH$, 2.3 for $CH_3C{\equiv}CH$, 2.2 for $C_2H_5C{\equiv}CH$, 0.25 for $CH_2{=}CH{-}C{\equiv}CH$, and 0.16 for $HC{\equiv}C{-}C{\equiv}CH$.[19] The solubilities x of hydrocarbons containing between 5 and 8 carbon atoms in LAr have been determined[20] and have been found to lie in the range $0.3-30 \times 10^{-6}$ m.f. The parameters x in LAr and LO_2 proved to be similar. In practice this is important, since solutions in LO_2 are explosive.[4]

The values of x for certain substances have been determined from electronic absorption bands.[21] The high absorption coefficient in the UV region makes it possible to carry out measurements at lower concentrations and hence to determine x for a wider range of compounds. The list of substances and the values of x (in m.f.) found for them are as follows: 4×10^{-9} for pyrimidine in LKr, 3×10^{-10} for pyrazine in LKr, 1.4×10^{-8} and 7×10^{-10} for pyridine in LKr and LAr respectively; 5×10^{-7} for NH_3 in LAr and LKr; 5×10^{-6} and 2.2×10^{-7} for acetone in LKr and LAr; 1.1×10^{-6} for CH_3I in LAr; 7×10^{-6} and 4.5×10^{-8} for toluene in LAr and LN_2; 9×10^{-6} and 2.2×10^{-7} for benzene in LKr and LAr. A mole fraction of 2.4×10^{-3} has been quoted for I_2 in LXe.[22] Since the mole fraction x varies exponentially with temperature ($\lg x = a - b/T$), the heat of solution can be found. For the series of substances investigated, it varies from 2 to 7 kcal mole^{-1}. The solubility of toluene in LKr exceeds by more than an order of magnitude that in LAr and the solubilities of CS_2 and CH_3I in LN_2 are at least an order of magnitude lower than in LAr. Agreement between the values of x calculated by the method of Preston and Prausnitz[15] and the experimental values on the assumption that there is no interaction is achieved only for simple systems, while for solutions of toluene in LN_2, for example, the discrepancy amounts to several orders of magnitude. This makes it possible to determine the parameter characterising the interaction in solution.

Unusually high solubilities x of water in LN_2 (1×10^{-5}) and LO_2 (1×10^{-5}) have been reported.[6] Particles of ice were ground in the liquid solvent and the solution was then filtered into the cell, the degree of saturation of the solution being deterined by the intensity of the grinding. According to the authors, spectroscopic data confirm that solutions of monomolecular water were obtained. However, the frequencies quoted for the stretching vibrations of water $\nu_1 = 3605$ and $\nu_3 = 3707$ cm^{-1} are very close to those known for CO_2 in solution in LN_2 (see Section V), while the D_2O frequencies differ fairly considerably from the frequencies of this molecule in the gas phase.

In spectroscopic studies, special measurements of x frequently were not made, but the solubilities can be inferred by comparing the intensities of the IR bands and the optical path lengths. If cells 1 cm long are used, then x is as a rule higher than 10^{-3} m.f., while for cells 10 cm long the solubilities are $\sim 10^{-4}$ m.f.; smaller values of x require greater optical path lengths. Thus a solution of monomeric formaldehyde in LXe with a concentration of $\sim 10^{-2}$ m.f. has been observed in a cell 1.3 cm^{-1} long;[23] the solidification of Xe does not alter greatly the solubility x. We may note that the preparation of such formaldehyde solutions makes it possible to observe the spectra of its monomeric form, although the molecular density of CH_2O in the solution is equivalent to a vapour pressure of 30 mmHg, while in the gas phase at a pressure in excess of 4 mmHg of CH_2O, polymerisation takes place rapidly.[23] The vapour pressures of comparatively heavy molecules are usually low. Thus it is only 7 mmHg for OsO_4 and, in order to obtain the IR spectrum of the gas, it is necessary to use cells with a large optical path length. On the other hand, the intensity of the IR bands of OsO_4 in solution in LXe in a cell 2.7 cm long is equivalent to a vapour pressure of 400 mmHg, i.e. the preparation of solutions of substances with a satisfactory solubility makes it possible to achieve a high molecular density. This facilitates the analysis of molecular impurities. Thus the IR spectrum of OsO_4 shows a fairly intense ν_3 band of the isotopic form, containing ^{18}O, at a concentration of only 4×10^{-6}.[23] The

high sensitivity of the cryospectroscopic method has found practical applications in the analysis of liquefied gases, for example, of liquid O_2, for molecular impurities. The sensitivity of the absorption spectroscopic analysis of cryosolutions actually achieved at the present time has reached the level approaching a mole fraction of 10^{-10}.[4]

IV. INFRARED SPECTRA OF SOLUTIONS OF DIATOMIC MOLECULES

The changes resulting from the transfer from the gas phase to the cryosolution can be seen in relation to the IR spectra of hydrogen halides in LXe.[24] The rotational branches are well manifested in the spectra of HCl, HBr, and HI in LXe. The *Q* branch has a high intensity, as in gases under high pressure. The distance between the rotational *P* and *R* branches is greater than expected. According to the authors, this can be associated with the superposition of induced *S* and *O* branches, which are not resolved from the *P* and *R* branches in the spectrum. The selection rules characteristic of the liquid are probably associated with the anisotropic fields, which induce a shift of the *J* states. In this sense, the rotational movements of HX in LXe are assumed to be not free. One can imagine that the diatomic molecules execute unhindered rotation in the course of a significant proportion of the rotation period and that, on collisions, random changes take place in the molecular angular momentum. Frequent changes in rotation caused by collisions usually lead to the suppression of the rotational structure. Compared with the gas phase, the initial sections of the HCl, HBr, and HI bands in LXe shift by 34, 29 and 17 cm^{-1} respectively, which amounts to ~1% of the energy of the level. The strongest effect involves an increase in the integral intensity of the bands compared with the free molecule: by a factor of 2.8 for HCl, 3.1 for HBr, and 44 for HI. According to the calculation carried out by the authors,[24] the effect of the dielectric medium can explain an increase in intensity only by a factor of 1.22 and they therefore sought an explanation in terms of an increase in the amount of ionic character of HX and assume that approximately 1/16 of an electron moves from the proton to the halogen when the molecule is dissolved even in LXe. However, it follows from Iogansen's studies that the strength of the intermolecular interaction is characterised by the intensity increment, i.e. not by the ratio but by the difference of the intensities in two different states. The increments for HI and HCl are similar. The low intrinsic band intensity of free HI is the reason for the increase in its intensity by a large factor on dissolution. The relative intensities of the components depend on the solvent. Thus, whereas the *Q* branch is not manifested at all as an individual maximum in the spectrum of the HCl solution in LAr, on passing to the solutions in Kr, Xe, and O_2, its intensity increases successively. On raising the temperature, weakening of the *Q* component and the strengthening of the *P* and *R* components are observed, while the integral intensities hardly change under these conditions. The integral absorption coefficients ($\times 10^8$ in $cm^2\ s^{-1}\ mol^{-1}$) of the bands of the principal vibrational transitions of HCl in the solutions are as follows: 19.4 in the gas phase; 48 (80 K) and 34 (120 K) in LN_2; 27 (90 K) in LAr; 34 (126 K) in LKr; 53 (165 K) in LXe; 47.2 (293 K) in CCl_4.[25] Analysis of the spectra of diatomic molecules in various solvents showed that LAr and LO_2 are spectroscopically the most inert and perturb the spectra of the solutes to a minimal extent.[4]

The second moments of the bands of hydrogen halides found from the experimental data, which have a bearing on the band width, have been compared to the theoretical values. A satisfactory agreement has been obtained for solutions in noble gases, oxygen, and CCl_4, which confirms the dominant role of the rotational movement of the hydrogen halide molecules in the above systems in the formation of their absorption band contours. Thus the temperature and not the medium determines the second moments of the hydrogen halide bands in solution and liquefied noble gases or simple molecules exhibit no unusual features compared with the usual solvents. This is also seen from the integral intensities of the bands due to simple molecules. On the other hand, the solvent influences the frequencies significantly. The HCl frequency in CCl_4 (2833 cm^{-1}) is significantly lower than in LXe (2850 cm^{-1}, 200 K). Bearing in mind that the frequency depends on temperature (~2 cm^{-1} for 20 K), the frequency in LXe is very close to that in the gas phase (2861 cm^{-1}).

Chesnoy[26] investigated the IR absorption spectra, fluorescence excitation spectra, and fluorescence spectra of HCl in LXe and SXe near the melting point of xenon. The main band and overtone in the excitation spectrum have similar contours: the *Q* branch is present for the liquid phase and absent for the solid phase. However, there are also differences: the rotational structure begins to appear in the overtone for the liquid phase and the *Q* branch for the solution has a lower intensity than in the main band. The author interprets the vibrational spectrum of HCl in LXe by postulating the existence of limitations to the free rotation of HCl and by regarding them as a perturbation. The disappearance of the *Q* branch from the spectrum of the solid solution indicates a high symmetry (the presence of a centre of symmetry) of the immediate environment.

In a more careful study of the band contours of hydrogen halides in liquefied noble gases as well as liquid SF_6, discrete rotational structure of the vibrational bands has been observed not only for the transition $(0 \rightarrow 2)$[26] but also for the fundamental.[27-29] A distinctive structure has been observed in the spectrum of an HF solution in LXe in the experimental temperature range (230–250 K). Numerous rotational components are also present on the wings of the HCl band. The latter become more explicit with increase in the concentration of the solution or in the optical path length. The attempt by the authors[29] to observe the rotational structure in the spectrum of an HCl solution in LAr failed, although the purely rotational absorption was observed for this solution in the long-wavelength IR spectrum.[30] The first resolved lines in both the near and far infrared components of the spectrum of the HCl solution in LKr corresponded to $J = 4$. The frequency shifts of the rotational components as a function of the density of the medium in the purely rotational spectra are appreciably smaller than in the vibrational-rotational spectra, which apparently reflects the contribution by the vibration. The linear variation of the shift as a function of the density breaks down on passing from the gas to the liquid phase, the shift becoming much greater. The widths of the purely rotational bands of HCl in LKr and LXe are 3 cm^{-1},[30] which means that they are several times narrower than the rotational components of the vibrational band.[29] The broadening of the rotational components in LAr is in fact most likely to prevent the manifestation of the fine structure of the spectrum. The results of the above study[29] have shown that the vibrational and rotational relaxation processes, which determine the band widths, exhibit different dependences on the density and that the rate of rotational relaxation increases to a greater extent for densities corresponding to the liquid solvent.

We confined ourselves to describing, as an example, the characteristic features of the spectra of solutions of hydrogen halides and in the following sections we shall also present data on the spectra of solutions of other diatomic molecules: CO, NO, H_2, N_2.

V. SPECTRA OF SOLUTIONS OF POLYATOMIC MOLECULES

1. Infrared Spectra

The rotation of polyatomic molecules such as CO_2, SF_6, etc., placed in cryosolution, is greatly inhibited by collisions with their environment, whilst their rotational movement is best described as diffusion. This results in a considerable narrowing of the vibrational-rotational contour of the band compared with that observed in the gas phase and greatly simplifies the IR spectra. The low temperature of the solutions in the cryosolvents and their great inertness lead to further narrowing of the spectral bands and a decrease in their overlap. This makes it possible to determine not only the frequencies of the principal vibrational transitions but also those of overtones and combination bands. In such solvents, it is also easier to measure the absolute and relative band intensities and isotope effects. At low temperatures, a significantly greater proportion of molecules are in the vibrational ground state, especially in the absence of low frequencies in the spectrum, and the interpretation of the spectrum becomes simpler as a result of the weakening of the bands due to hot transitions. The spectroscopy of cryosolutions of polyatomic molecules is a valuable research technique especially in those cases where the rotational fine structure of the vibrational band cannot be resolved in the gas phase.[12,31] Initially we shall present the results of the study of the IR spectra of solutions of the triatomic linear molecules CO_2, COS, CS_2, and N_2O in cryosolvents,[12] which clearly demonstrates the great possibilities of the method.

The following bands can be observed in the spectra of CO_2 dissolved in LO_2: 665 cm^{-1} (Π_u, ν_2), 2343 cm^{-1} (Σ_u, ν_3), 2277.5 and 3702.5 cm^{-1} (Σ_u, $\nu_1 + \nu_3$) and 3601.2 cm^{-1} (Σ_u, $2\nu_2 + \nu_3$). The weak 2277.5 cm^{-1} band, located near the most intense ν_3 band, corresponds to the isotopic modification $^{13}C^{16}O_2$. The relative intensity of these bands is consistent with the natural abundance of the ^{13}C isotope (1.13%). Since the 3601.2 and 3702.5 cm^{-1} bands are components of the Fermi resonance, the distance between the non-interacting levels $\Delta = 28.4$ cm^{-1} was determined from the ratio of the relative intensities:

$$\nu_1 + \nu_3/2\nu_2 + \nu_3 = \frac{\varkappa + \Delta}{\varkappa - \Delta}$$

($\varkappa$ is the observed distance between the interacting levels); under these conditions, the $10^{\circ}1|W|02^{\circ}1$ perturbation matrix element is 49.1 cm^{-1}, which agrees well with the value obtained for the gas.

The higher solubility of COS in LO_2 made it possible to record almost all the second- and third-order bands corresponding to transitions to non-degenerate levels. Fourth-order bands have also been observed: $4\nu_2$ and $2\nu_1 + 2\nu_2$. At 90 K, it is possible to observe a series of absorption bands in the spectrum of the COS solution which can be attributed to isotopic modifications with the ^{13}C, ^{18}O, and ^{34}S isotopes. The isotopic splittings calculated in terms of the harmonic approximation are close to the observed splittings and the relative intensities agree with the abundances of the isotopes within the limits of the error.

Comparison with the gas phase spectra shows that, on passing to the solution, the vibrational frequencies undergo a bathochromic shift. The maximum shift, reaching 9 cm^{-1} for COS, is observed for the ν_3 stretching vibration bands, which have the highest intensity. The shift of the overtone bands and combination bands is approximately equal to the sum of the shifts of the individual levels. It has been stated[12] that, in determining the anharmonic potential energy terms, the spectra of cryosystems make it possible to obviate the difficulties associated with the separation of the vibrational and rotational motions and the allowance for the vibrational-rotational interactions.

The absolute intensities (integral absorption coefficients) of the $\nu_3(CO_2)$ and $\nu_1(N_2O)$ bands have been measured in the spectra of solutions in LO_2. The observed values $A(\nu_3) = (35 \pm 2) \times 10^{-7}$ cm^2 s^{-1} and $A(\nu_1) = (29.5 \pm 1.0) \times 10^{-8}$ cm^2 s^{-1} do not differ from the data for the gas phase within the limits of the scatter of the literature values. Owing to the smallness of the refractive index of liquid oxygen ($n = 1.22$), the correction of Polo and Wilson, which takes into account the influence of the solvent on the absorption coefficient, is about 10%, i.e. does not exceed the error of the measurements of the band intensities in the spectra of gases.

The data obtained by Bertsev et al.[12] provide for the first time the initial information for a large number of compound and overtone bands essential for a rigorous formulation of the electro-optical problem.

Despite the inertness of LXe, the latter induces the (02^20) CO_2 transition with a frequency of 1324 cm^{-1} as a consequence of its interaction with CO_2.[10]

In connection with the study of the selective action of laser radiation on matter, there has recently been a growth of interest in the determination of data concerning the highest vibrational state of polyatomic molecules.[32] A reliable interpretation of the structure of the IR spectra of CF_3I involves considerable difficulties because of the existence of several low-frequency fundamental vibrations of this molecule. At room temperature, about half of the CF_3I molecules are in excited states, so that a series of bands due to hot $\nu_i \rightarrow \nu_k + \nu_i$ transitions are superimposed on each absorption band. The results of the study of the IR absorption spectrum of a solution of CF_3I in LAr at 90 K in the frequency range 200–4000 cm^{-1} have been published.[33] The frequencies, half-widths, and relative integral intensities of 70 vibrational bands have been determined and interpreted. The doublet in the region of 530 cm^{-1} has been interpreted as due to the Fermi resonance of two vibrational states, ν_5 and $2\nu_6$, which lead in its turn to the appearance of several other Fermi diads, namely ($\nu_5 + \nu_6$, $3\nu_6$), ($\nu_2 + \nu_5$, $\nu_2 + 2\nu_6$), ($\nu_3 + \nu_4$, $\nu_4 + 2\nu_6$) [This should be ($\nu_3 + \nu_5$, $\nu_3 + 2\nu_6$) or ($\nu_4 + \nu_5$, $\nu_4 + 2\nu_6$) (Ed. of Translation)], and ($\nu_2 + \nu_4 + \nu_5$, $\nu_2 + \nu_4 + 2\nu_6$). For the pairs of states enumerated above, the matrix elements of the interaction depend on the same cubic constant K_{566} in the expansion of the potential energy of the molecule in series in terms of the normal coordinates, the average value of the constant being $K_{566} = 9.0 \pm 0.1$ cm^{-1}. The resonance of the four fully symmetrical states ν_1, $2\nu_5$, $\nu_5 + 2\nu_6$, and $4\nu_6$, the matrix elements of the interaction of which are determined by the two cubic constants K_{566} and K_{155}, has also been observed. The cubic constant $K_{155} = 4.6$ cm^{-1} has been estimated. Certain anharmonicity constants have been found from the vibration band frequencies with a unique interprettion (in cm^{-1}): $X_{22} = -0.2$; $X_{23} = -1.6$; $X_{33} = -1.0$; $X_{24} = -6.3$; $X_{34} = -0.2$; $X_{25} = -1.0$; $X_{36} = -0.3$; $X_{26} = -0.5$; $X_{44} = -6.8$; $X_{56} - g_{56} + r_{56} = -3$; $X_{66} = 0.7$; $g_{66} = 0.2$; $g_{44} = 4.1$; $X_{46} + g_{46} = -0.9$. The analysis of the CF_3I spectrum at a low temperature led to the conclusion that the real band structure of the gas phase at room temperature is very complex. The spectrum in the region of the $\nu_1(CF_3I)$ vibration, in resonance with the radiation of the CO_2 laser with the aid of which it is possible to perform the selective dissociation of CF_3I with formation of the CF_3 radical is of special interest. The results of the study of Bulanin et al.[33] have shown that the number of energy states involved in the anharmonic interaction

increases rapidly with increase in the quantum number v_1 and, furthermore, transitions to degenerate states, among which the $v_1 + 2v_5$ transition should be the source of the intensity, are superimposed on the same region. Thus the strong interaction of the v_1, v_5, and v_6 vibrational modes combined with the low anharmonicity constants leads to the formation in the CF_3I spectrum of energy zones with a high density of states, promoting an effective excitation of this molecule by the laser radiation up to the dissociation limit.[33] The IR absorption spectra of $^{12}CH_4$ and $^{13}CH_4$ in solution in LAr have been interpreted similarly.[34]

The simultaneous IR transition, arising from $v_3(SF_6)$ and the fundamental O_2 vibration in SF_6 solution in LO_2 at 78 K, has also been observed.[35] The frequency of the 2490.6 cm^{-1} band is independent of the SF_6 concentration, while the absorption coefficient and the band half-width increase linearly with increase in the SF_6 concentration. The calculated frequency, obtained by adding together $v_3(SF_6)$ and the intrinsic frequency of O_2, is 2492.1 cm^{-1}. The observed value differs somewhat from the calculated ones since the latter are based on binary interactions and the low gas pressure limit, which are not fully legitimate for solutions in liquids.

The spectra of not only organic but also organometallic compounds in cryosolvents have been interpreted.[36] The structure of a molecule such as $Ru(CO)_5$ has not been reliably established from the IR spectra either in solution in n-hexane or on matrix isolation of solid N_2 even in the study of the ^{13}CO-enriched compounds, since the IR spectrum of the solution always consists of two broad bands and the complex character of the spectrum of the matrix-isolated $Ru(CO)_5$ is due to the matrix splitting. The IR bands of the $Ru(CO)_5$ dissolved in LXe at −60 °C are narrowed. Thus $v_{1/2}$ for the a_2'' band of the solution in LXe is 2.0 cm^{-1}, while that of the solution in n-hexane is 6.8 cm^{-1}. In the IR spectrum of $Ru(CO)_5$ enriched in ^{13}CO to the extent of 26.5%, 16 bands have been observed. The monosubstituted specimen, containing ^{13}CO in the equatorial position, should have the comparatively low C_{2v} symmetry and all its bands should be resolved in the IR spectrum. Gregory et al.[36] assigned the following bands to this isotopic specimens: a_1—2120.7 cm^{-1}, b_2—2038.9 cm^{-1}, a_1—2032.2 cm^{-1}, b_1—2001.6 cm^{-1}, and a_1—1964.0 cm^{-1}. The overall character of the $Ru(CO)_5$ spectrum is fully consistent with the D_{3h} molecular symmetry. The presence of 16 frequencies made it possible to determine all the force coefficients of $Ru(CO)_5$ (in N m^{-1}): K_{ax} = 1728.38; K_{eq} = 1653.28; $K_{ax,eq}$ = 27.57; $K_{eq,eq}$ = 34.82; $K_{ax,ax}$ = 48.09. The band intensities in the spectrum of $Ru(CO)_5$ in LXe have been calculated in terms of the local C−O dipole approximation, the results being in good agreement with experiment. The spectrum of ferrocene in solution in LXe has been interpreted similarly.[37]

Holland et al.[9] published IR spectra demonstrating the isotopic splitting of the BCl_3, SeF_6, OsO_4, MoF_6, and $TiCl_4$ bands in solid solutions and carried out a comparison of the results obtained in sputtered matrices, in the gas phase, and in liquid solutions. As an example, we may quote the data for BCl_3. In SKr (116 K) and SAr (84 K), the BCl_3 spectrum contains narrow bands of the split v_3 vibration and the doublet due to the degenerate v_3 vibration, which can be unambiguously assigned to $^{10}B^{35}Cl_3$ (983.2 and 985.6 cm^{-1}) and $^{11}B^{35}Cl_3$ (944.6 and 947.0 cm^{-1}) respectively. The frequencies of these bands decrease with decrease in temperature by approximately 0.04 cm^{-1} K^{-1} and can readily coincide with the CO_2 laser lines in the study of its selective action on BCl_3. Comparison with the gas phase spectrum indicates a much greater information content: $v_3(^{11}BCl_3)$ has 7 components in the solid phase and only two in the gas phase.

2. Ultraviolet Spectra

The influence of the solvent on the UV spectrum of the molecules has been demonstrated in relation to the $^1\Sigma_g^+ \leftarrow {}^1\Sigma_g^+$ absorption band of carbon disulphide in four solvents.[38] Compared with the solution in LAr, the band in LN_2 has undergone a hypsochromic shift by 75 cm^{-1} and the maximum of the continuous background envelope reaches 40% of the band maximum (instead of the 30% for the solution in LAr at the same temperature); consequently the vibronic maxima are broadened to a greater extent. The pattern for the solution in LXe is completely different: the band is very diffuse and its maximum has undergone a bathochromic shift by 1200 cm^{-1} and is located in approximately the same position as for the solution in hexane at room temperature. The complete disappearance of the vibronic structure in solution in hexane and its partial retention in LXe are noteworthy. This explains the possibility of the selective action of UV radiation on certain molecules dissolved in LXe and other elemental liquefied gases but not in molecular liquids. Clearly, from the standpoint of selectivity, LAr and LN_2 are preferable to LXe.

The vibronic structure of bands in the spectra of solutions in liquefied elemental gases is not retained for all molecules. Thus, on passing to the condensed phase, the vibronic band structure in the spectrum of acetone in the region of 195 nm becomes completely diffuse, the band positions being virtually the same in LAr, LXe, and hexane. Marked broadening of the vibronic components also occurred after the addition of gaseous Ar at a pressure of 130 atm. Such behaviour of the 195 nm acetone band shows that the upper state of this transition is mixed: Rydberg orbitals are also involved in it. Overall, the use of cryosolutions for the investigated $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ bands for a large series of compounds makes it possible to improve significantly the resolution of the fundamental vibrational structure.[39] On the other hand, although most of the structure characteristic of the gas is retained in the UV spectrum of OsO_4 solution in LXe,[23] it is also retained in other solvents (Ar, Kr, N_2O, CH_4, C_5H_{10}, CF_4, CF_3Cl, and BF_3). The frequencies of the band maxima are displaced by 2−10 nm compared with the spectrum of the gas phase, the shift depending on the type of solvent.

Fine structure has not been observed in the UV spectrum of CH_2O in the vapour phase, and the width of the spectral bands for the cryosolution is somewhat greater. Nevertheless, the UV spectrum of the CD_2O solution shows a major isotope shift compared with CH_2O used for the photolytic isotope separation.[23]

The vibronic structure of the ^1L_b absorption band of benzene dissolved in liquefied Ar (from 138 to 148 K), CF_4 (from 151 to 190 K), and Kr (from 122 to 160 K) has also been investigated.[40] Since the vibronic components of the band in the argon and Freon solutions are fairly narrow, while the majority of the "hot" transitions are frozen, it is possible to carry out a detailed analysis of the vibrational band structure and to refine the assignment of certain vibronic components.

VI. SPECTRA OF SOLUTIONS OF MOLECULAR COMPLEXES

The low temperature which can be attained in liquid elemental gases should permit the observation, under the conditions of infinite dilution, of the association of molecules which does not occur under

the usual conditions because the initial components are gases and the complex formation constant is small. The high inertness of liquefied noble gases is of decisive importance for the synthesis of weak complexes. The interaction of dissolved molecules with the environment under these conditions is significantly weaker than in traditional solvents. Naturally the components of the complex must dissolve effectively in the cryosolvent. By selecting the concentrations of the initial molecules, it is always possible to achieve a situation such that the equilibrium in the complex formation process can be observed under the experimental conditions and by altering the temperature its influence not only on the spectroscopic characteristics but also on standard thermodynamics can be determined.

The first study of this kind[41] dealt with the investigation of the system comprising $CHF_3(CDF_3)$ and $N(CH_3)_3$ in LAr and LKr. When the amine was added to the CHF_3 solution, the intensity of the ν_1 (3038 cm^{-1}) and ν_4 (1373 cm^{-1}) bands diminished and the bands disappeared in the presence of a large excess of the amine and were replaced by two other bands, at 3016 and 1404 cm^{-1}, which are associated with the corresponding vibrations in the hydrogen-bonded complex (HBC). The equilibrium constants of the association process in the temperature ranges 90–130 K for LAr and 120–160 K for LKr as well as the thermodynamic parameters $\Delta H^0 = 3.5 \pm 0.2$ kcal mol^{-1} and $\Delta S^0 = 15 \pm 2$ cal mol^{-1} K^{-1} were determined from the integral intensities of the ν_1 and ν_4 bands for CHF_3 and the ν_1 band for CDF_3. We may note that in the matrix isolation method the frequencies of the complex frequently cannot be obtained and the equilibrium cannot be observed. Studies on the HBC in cryogenic solutions have been prosecuted in two directions. The first[42,43] dealt with the study of the parameters of the bands of weak complexes which as a rule do not exist under the usual conditions. By virtue of the inertness of the liquefied noble gases, interactions which occupy an intermediate position between typical van der Waals interactions and a weak hydrogen bond can be studied in them. In the second direction,[11,43] the influence of the cryogenic solvent on the spectroscopic characteristics of moderately strong HBC, whose spectra are known both in the gas phase and in a traditional solvent, was investigated.

The results of measurements of the HCl, DCl, and HBr spectra in mixed solvents consisting of LAr with added N_2 or CO have been described.[42,44] In these systems, a narrow symmetrical band appears against the background of the broad band characteristic of solutions of hydrogen halides HX in LAr (see Section IV). The narrow band was assigned to the complexes of hydrogen halides with N_2 or CO, the intensity of the bands due to the free HX molecules decreasing with increase in the N_2 and CO concentrations. Thus, whereas HCl in LAr has a band at a frequency of 2869 cm^{-1} with a half-width of $\sim$100 cm^{-1}, for the HCl–N_2 complex the frequency is $\nu = 2864$ cm^{-1} and $\nu_{1/2} = 11$ cm^{-1} and for the HCl–CO complex the frequency is $\nu = 2835$ cm^{-1} and $\nu_{1/2} = 9$ cm^{-1}. The narrowing of the HX bands has been explained by the rotation being hindered due to the greater moment of inertia in the complex. Complex formation influences the spectra of the molecules in the gas phase in a similar manner. The spectral parameters show that the interaction of the above diatomic molecules is local. The interaction between CCL_4 and HCl in LXe and LKr turns out to be similar. A narrow band appears in the IR spectrum at $\sim$2840 cm^{-1} and it may be that it is in fact the local interaction which determine the contour of the HCl band in liquid CCl_4.[44]

Wek complexes of proton donors such as HBr, HF, $HC\equiv CH$, $CH_3C\equiv CH$, and HCN have also now been investigated.[45,46] the same behaviour has been observed as for the HCl complexes.

The complexes of olefins with HCl were classified as thermally unstable systems or systems unstable as regards their reaction (for example, with isobutene). Cooling to LN_2 temperatures makes it possible to investigate these complexes either as a result of suppressing the reaction or due to a sharp increase in the complex formation constant. The shift of the HCl bands on going from the complex with eithylene to that with trimethylethylene increases from 100 cm^{-1} to 260 cm^{-1}.[47,48] If the first can be assigned to weak HBC, then the second is due to moderately strong HBC. Together with the bathochromic band shift, another property of the band due to the HCl in the HBC is its higher intensity, by more than an order of magnitude compared with free HCl. The complex formation constants were determined at 77 and 95 K. The ΔH were calculated for this temperature range from the van't Hoff equation (Table 1). It was found that the experimental results satisfy well the relations between ΔH and $\Delta A^{1/2}$ and between ΔH and $\Delta\nu$, especially the latter. Thus the spectroscopic characteristics observed in the complex formation process make it possible to classify the complexes between HCl and olefins as typical HBC and to conclude that the interaction proceeds via the hydrogen atom. The entropy ΔS of complex formation amounted to 11 cal mol^{-1} K^{-1}. These characteristics of the olefin–HCl complexes in solution in LN_2 were found to be close to those obtained later[49] in solution in LAr: ν(HCl) = 2774 cm^{-1}, $\nu_{1/2} = 15$ cm^{-1}, and $\Delta H = 1.5 \pm 0.1$ kcal mol^{-1} for C_2H_4–HCl, ν(HCl) = 2732 cm^{-1} and $\nu_{1/2} = 20$ cm^{-1} for C_3H_6–HCl, and $\nu = 2679$ cm^{-1} and $\nu_{1/2} = 28$ cm^{-1} for C_4H_8–HCl. The HCl frequency is also somewhat higher for the solution in LAr compared with that in LN_2 and the band half-width is somewhat smaller.

Table 1. Parameters of the IR spectra and the enthalpies of complex formation for HCl–olefin systems in solution in liquid N_2.[47]

Proton acceptor	ν, cm^{-1}	$\Delta\nu$, cm^{-1}	$\nu_{1/2}$, cm^{-1}	$10^{-4}A$, litre mol^{-1} cm^{-2}	K_p(77 K), litre mol^{-1}	K_p(93 K), litre mol^{-1}	ΔH, kcal mol^{-1}: authors data (Ref. 47)	calc. from ΔA	calc. from $\Delta\nu$
—	2870	—	—	0.4	—	—	—	—	—
Ethylene	2770	100	25	2.2	30	8	1.4	2.3	1.6
Propene	2720	150	35	2.7	$3.2\cdot10^2$	35	2.2	2.7	2.2
Isobutene	2660	210	30	3.4	$1.5\cdot10^3$	$1.3\cdot10^2$	2.6	3.5	2.7
Trimethylethylene	2610	260	30	4.3	$3\cdot10^3$	$6\cdot10^2$	3.5	4.1	3.2

The data for complexes of HCl with olefins in solution permit a more correct comparison of the electron-donating properties of olefins and aromatic compounds, especially since the frequency of HCl (2685^{-1}) in the complex with hexamethylbenzene was determined in solution in LXe.[50] Comparison of the frequencies of the complexes with trimethylethylene and hexamethylbenzene shows that the decrease in frequency for the olefin is greater despite that the fact that its ionisation potential is higher (8.67 eV) than that of hexamethylbenzene (7.85). An intermediate case obtains for complexes of ferrocene and its methyl derivatives with HCl.[3]

Whereas the small width of the band of HCl in the weak C_2H_4–HCl complex is understandable, the fact that the band of the moderately strong $(CH_3)_2{=}CHCH_3$–HCl complex remains narrow despite its significantly greater shift is unusual. This result led to the hypothesis that the marked broadening of the stretching vibration bands of the XH bond, observed in traditional solvents, is

not a universal property of the hydrogen bond but depends on the nature of the solvent. A study was therefore made in LKr and LXe of a series of HBC whose parameters were known for traditional solvents.

We selected the $CH_3CN-HCl$ complex as the principal object of study because of its adequate stability and high symmetry.[51] According to literature data, the HCl band half-width for the solution of this complex in CCl_4 is 275 cm^{-1}, while for the solution of HCl in CH_3CN it is 350 cm^{-1}. On the other hand, the spectrum of the gas phase complex consists of the principal HCl band with a half-width of 100 cm^{-1} and a weaker difference band, separated from the principal band by ~ 100 cm^{-1}. The band half-width for the HCl in the complex was estimated as ~ 70 cm^{-1} in solution in LXe ($T \simeq 165$ K) at HCl and CH_3CN concentrations of 3×10^{-4} and 6×10^{-3} M respectively,[51] i.e. much lower than in solution in CCl_4 and somewhat lower than in the gas phase. An even smaller value of $\nu_{1/2}$ (HCl) = 40 cm^{-1} has been obtained by Muradov and Tokhabze for $CH_3CN-HCl$ in solution in LXe.[44] The study of this complex in LKr showed that the HCl band becomes narrower ($\nu_{1/2} \simeq 35$ cm^{-1}) at the same temperature (165 K) and that cooling of the solution in LKr from 165 to 130 K leads to further narrowing of the band to 30 cm^{-1}. These data have been confirmed.[44] Thus cooling (from 290 to 130 K) and the change of solvent (from CCl_4 to LKr) narrowed the ν(HCl) band for the $CH_3CN-HCl$ complex by an order of magnitude. Previously this effect was not known. Subsequently, using CD_3CN and higher concentrations of the $CD_3CN-HCl$ complex,[11,43] it was possible to obtain for the solution in liquid Xe the overall and difference ν(HCl) $\pm$ ν_σ frequencies, where ν_σ is the frequency of the stretching intermolecular vibration of the hydrogen bond. This is a consequence of the narrowing of each band.

Table 2. The frequencies and widths of the ν(OH) bands of the binary hydrogen-bonded complexes in various media.[53]

T, K	Medium	$(CF_3)_3COH-CD_3CN$		$(CF_3)_3COH-(CD_3)_2O$	
		ν, cm^{-1}	$\nu_{1/2}$, cm^{-1}	ν, cm^{-1}	$\nu_{1/2}$, cm^{-1}
300	gas	3355	70	3190	120
	CCl_4	3250	160	3090	220
	Freon	3245	160	3100	200
270	xenon	3285	65	3135	130
	Freon	3235	160	3085	195
250	xenon	3280	65	3130	130
	Freon	3230	160	3075	185
200	krypton	3290	45	3140	115
	xenon	3270	50	3125	120
	Freon	3190	155	3055	180
150	krypton	3275	40	3127	110
	Freon	3150	150	3030	180
125	krypton	3270	35	3120	105
	Freon	3150	150	3040	180

In order to discover how general is the narrowing of the ν(XH) band on passing to an atomic solvent, a study was made[52] of a large number of heterocomplexes of methanol, trifluoroethanol, and perfluoro-t-butyl alcohol and their deuterio-derivatives with representatives of various classes of bases—olefins (C_3H_6), nitriles (CH_3CN), ethers [$(CH_3)_2O$], sulphides [$(CH_3)_2S$], ketones [$(CH_3)_2CO$], and amines [$(CH_3)_3N$] in solution in LXe and LKr in the temperature range 120–270 K. The ν(OH) frequency shifts from 70 to 500 cm^{-1} compared with the free alcohol, i.e. both weak and moderately strong complexes were investigated. Comparison with literature and own own[53] data shows that the ν(OH) band widths for the complexes of these alcohols in solution in the usual molecular solvents are greater by a factor of between 2 and 4 than in the atomic solvent at the same temperature (Table 2). On the other hand, the ν(OH) band widths of a gas-phase complex and the complex in LXe are approximately the same. Furthermore, the ν(OH) band widths of the complexes in solution in LXe and LKr are virtually the same in the same temperature range, which implies that the difference between the macroscopic parameters of the atomic solvents has little influence on the band width.

The influence of the solvent on the ν(OH) frequency is noteworthy: for all the complexes investigated, the frequency in LXe at 250–270 K is lower by 40–70 cm^{-1} than in the gas phase and higher by 30–40 cm^{-1} than in solution in CCl_4. In LKr, the ν(OH) frequency is higher by 10–20 cm^{-1} than in LXe at the same temperature.

The parameters of the ν_σ band, due to the intermolecular vibration of the (A...B) hydrogen bond itself, which is located in the far infrared, have also been investigated for a series of complexes of HCl with fluoro-alcohols in LXe and n-pentane at identical temperatures (165–250 K).[54,55] The band width proved to be ~ 30 cm^{-1} and was independent of the type of solvent. Such different types of influence of the atomic solvent on the ν(XH) and ν_σ band widths can be described by the theory developed by Sakun.[56] According to this theory, the broadening of the above band is due to different factors. The ν_σ band is formed under the influence of the oscillatory component of the motion of the A...B bond, while the width of the ν(XH) band and its structureless character are determined by the dissipative component of the A...B mode. The approximate equality of the ν(XH) band widths of the HBC in liquid noble gases and in the gas phase at similar temperatures indicates a weak interaction of the HBC with the atomic solvent. Presumably, in the atomic solvents, as in the gas phase, the ν(XH) band width is determined mainly by the contribution of the "hot" transitions of the ν_β deformation vibration. The principal difference in band shape should be the "smearing out" of the fine structure of the spectrum by the solvent. A decrease in temperature in LXe and LKr leads to the partial freezing out of the "hot" transitions and a decrease in their contribution to the ν(XH) band width with a temperature contaction coefficient of 0.1–0.3 cm^{-1} K^{-1}. More intense cooling, which is attainable in the matrix isolation method, leads to the almost complete freezing out of the "hot" transitions and in certain cases to a sharp narrowing of the band. For example, the width of the ν(OH) band of the complex of perfluoro-t-butyl alcohol with acetonitrile in the Ar matrix is only 10 cm^{-1}.[57] The observed temperature-induced shift of the ν(OH) band of the HBC investigated in LXe and LKr is 0.1–0.3 cm^{-1} K^{-1} and can be caused by a change in the contribution of the "hot" transitions as a result of cooling and hence a redistribution of the intensities within the limits of the band. the presence of the narrow ν(OH) and ν(OD) bands in the spectra of the series of complexes investigated made it possible to measure with a high degree of accuracy the isotope ratio, whose value for both weak and moderately strong HBC proved to be approximately equal to that for the free alcohol. The results obtained show that the isolated HBC do not exhibit an anomalously high anharmonicity. It is noteworthy that narrow ν(XH) bands are not always obtained in LXe and LKr, fairly broad bands remaining in the spectra of the complexes of acetone[50,52] and polymeric methanol.[50,58] Their width

can apparently be accounted for either by the presence of complexes of different composition or by their different structures.

The presence of a narrow ν(XH) band in the spectrum of the LXe solution made it possible to consider the problem of the site of coordination of HCl or perfluoro-t-butyl alcohol in complexes with a series of metallocene derivatives ranging from ferrocene to decamethylferrocene.[3,59] In principle, there is a possibility of coordination of both to the ring and to the metal atom. In both cases, the presence of only one ν(XH) band, displaced to lower frequencies, indicates the formation of a hydrogen-bonded complex of one type. the values of $\Delta\nu$ and $\Delta\nu$ for the interaction of ferrocenes with $(CF_3)_3COH$ are somewhat higher than for the interaction with HCl owing to the somewhat greater proton-donating capacity of the alcohol. In view of the similarity of the results for the HCl complexes with ferrocene,[3] olefins,[42,47] and aromatic compounds,[50] one can assume that the hydrogen bond is formed with the cyclopentadienyl ring and not with the metal atom. The same type of coordination is characteristic of the $(CF_3)_3COH$ complexes.

For carbonyl-containing cyclopentadienyl metal complexes, there are as many as three possible centres for the formation of a hydrogen bond: the π-ligand, the metal atom, and the oxygen atom of the CO group. When $(CF_3)_3COH$ is added to a solution of $CpMn(CO)_2$. .$P(iso\text{-}Pr)_3$ in LXe at 180 K, a band appears at 3415 cm^{-1}, indicating the formation of a HBC, in addition to the 3590 cm^{-1} free alcohol band.[60] The identification of the type of coordination was made on the basis of the changes in the region of the CO vibrations. The IR spectrum of a solution of $CpMn(CO)_2P(iso\text{-}Pr)_3$ in LXe contains bands at 1935 and 1873 cm^{-1}, while in the spectrum of its complex with alcohol the bands are shifted to 1931 and 1835 cm^{-1}. On the basis of the bathochromic shift of ν(CO), Lokshin et al.[60] concluded that the oxygen atoms of the carbonyl groups are involved in the hydrogen bond. When the spectrum at 180 K was subtracted from the spectrum at 165 K, two further bands become visible at 1906 and 1832 cm^{-1}; they have been assigned to a 1:2 complex in which two alcohol molecules interact with both CO groups.

Low temperatures make it possible to study also the intermolecular interaction of simple molecules, for example, those of NO and NO_2, in LXe.[13,61] In addition to the band due to the free molecule, a band at 1762 cm^{-1}, due to $(NO)_2$, appears in the spectrum of the NO solution and a band at 3594 cm^{-1} has been assigned to a combination band of the dimer. The authors were unable to conclude which form, *cis*- or *trans*-, of ON—NO exists in LXe. When NO_2 was dissolved in LXe, N_2O_4 bands were clearly manifested: at 375, 422, 743, 1251, and 1742 cm^{-1}; a large number of bands due to the combination vibrations of N_2O_4 were also observed. The authors suggest that only a planar conformation of N_2O_4 with D_{2h} symmetry exists in LXe between 163 and 233 K. One of the bands, at 1813 cm^{-1}, may be due to the asymmetric form $ONONO_2$, which has been identified in the IR spectrum of solid N_2O_4. According to spectroscopic and photolytic data, N_2O_3 exists in the form of two isomers: $ONNO_2$ and ONONO. In the spectrum of the solution of NO and NO_2 in LXe, the IR bands of the asymmetric N_2O_3 form can be clearly identified: at 244, 411.5, 768.6, 1294, 1625, and 1829 cm^{-1}. The situation with *sym*-N_2O_3 is less clear. The 375 and 1687 cm^{-1} bands clearly refer to this species and possibly also the weak 965 cm^{-1} band. The fractions of the isomers were determined from the temperature dependence of the bands. The difference between the energies of *symm*- and *asymm*-N_2O_3 was calculated: $\Delta H = 1.8 \pm 0.2$ kcal mol^{-1}.

The formation of HBC between benzene and CHF_3 in LKr has also been studied by UV spectroscopy.[62] The measurements were based on the longest-wavelength, the so called ^1L_b band due to the ππ* transition of benzene located in the region of 255 nm. In cryosolutions, the ^1L_b band has fairly pronounced vibronic structure, which makes it possible to study individual vibronic components. For the HBC with benzene, quantitative data have been obtained in the region of the σ_0^1 transition, the band undergoing a hypsochromic shift relative to the band of monomeric benzene on formation of the complex. Heating of the HBC solution in LKr from 120 to 180 K increases the band half-width from 140 to 240 cm^{-1} and decreases the distance between the maxima of the bands of the monomer and the HBC from 240 to 120 cm^{-1}. The enthalpy of complex formation has been determined as 2.0 kcal mol^{-1} from the temperature variation of the equilibrium constant.

VII. NON-LINEAR ABSORPTION OF INFRARED RADIATION AND STIMULATION OF CHEMICAL REACTIONS IN CRYOSOLUTIONS

The influence of vibrational excitation on the reactivity of molecules is nowadays being vigorously investigated. As mentioned in the previous Sections, the use of cryosystems greatly simplifies the form of the spectrum by virtue of the suppression of the hot transitions and the temperature changes are also reduced to a minimum on vibrational excitation as a consequence of the high specific heat of the condensate. The measurement of the populations of various vibrational states is thereby facilitated.

The possibility of carrying out chemical reactions, stimulated by laser radiation, in solutions is of independent interest, since it is possible to establish a higher density of molecules in solution than in the gas phase at the same temperature.

Burtsev and Bulanin[63] investigated the characteristic features of the non-linear absorption of the IR radiation from a CO_2 laser ($\nu = 936.8$ cm^{-1}) in a solution of SF_6 in LKr (at 140 K) in order to estimate the time τ of the V—T relaxation of $\nu_3(SF_6)$ in the cryosystem. Within the framework of the approximations adopted, $\tau = 9$ ns was obtained. In a subsequent study,[64] the same workers used much higher intensities of the laser radiation. An extremely strong saturation of the test solution was observed; for example, at $I_0 = 1.5$ MW cm^{-2}, the transmittance of the specimen increases by a factor of 2×10^3 compared with the transmittance in a weak field. The formalism of the two-level model now no longer ensured a complete agreement with experiment and a model based on a three-level scheme was used to interpret the experimental data. A somewhat shorter vibrational relaxation time of SF_6 was obtained: $\tau \simeq 3$ ns. In the same study, the influence of extraneous substances on the relaxation of SF_6 was investigated. The introduction into the cryosystem of several mole per cent of a molecular admixture has an appreciable influence on the saturation of the absorption, although it does not affect either the position or the width of the SF_6 absorption band. The following relaxation times have been obtained in the presence of additives: 0.15 ns for O_2, 0.06 ns for CH_4, and 0.01 ns for NO. The fast relaxation in the case of NO has been explained by the appearance of low-lying acceptor levels as a result of the dimerisation of NO in the cryosystem.

The SF_6 molecule has also been investigated in liquid O_2 and Ar.[65,66] The V—T relaxation time of SF_6 is ~37 ps in LO_2 and ~160 ps in LAr.

Bertsev and Burtsev[67] chose the ozone molecule as the object of investigation, which is a suitable candidate for carrying out vibrationally-activated reactions in low-temperature condensed

systems. Solutions of O_3 in LAr and LO_2 were investigated at temperatures in the range 90–100 K: τ is ~100 ns in LAr and ~40 ns in LO_2. The result obtained was compared with vibrational relaxation data for O_3 in the gas phase, where the ratio of the efficiencies of Ar and O_2 as deactivators of the (001) state of ozone is known to be ~1:3. The populations of the vibrational states of O_3 were estimated for a specified level of pumping on the assumption that direct V–T relaxation of the (001) level is unlikely and that this state is deactivated stepwise:

$$(001) \xrightarrow{\tau_1} (010);\ (010) \xrightarrow{\tau_2} (000)\ .$$

As a result, it is possible to attain an appreciable population of the excited vibrational level of the O_3 molecules (up to 0.4) and the systems investigated are thus found to be potentially suitable for carrying out reactions involving vibrationally excited molecules in the condensed phase.

In one of the first investigations,[68] a study was made of the relaxation of the vibration of CH_3F in LAr and LO_2 from the saturation of the IR absorption and also experiments were performed on double IR–IR resonance, yielding directly the V–T relaxation time. Thus induced absorption at 1021.2 cm^{-1}, due to the $\nu_3 \rightarrow 2\nu_3$ transition, is observed in the experiment by the double IR resonance method with pumping by radiation at a frequency of 1037.4 cm^{-1}. As for O_3, the CH_3F relaxation time in LAr (1.30 μs) is several times greater than in LO_2 (375 ns) and probability of the V–T transition in the cryosystem is only an order of magnitude higher than in the gas phase for systems of the same type.

Thus the hot transition in the SF_6 spectrum in LKr at 140 K has also been observed by the double IR resonance method.[69] The maximum of this "hot" absorption is displaced by –4.5 cm^{-1} relative to ν_0, the V–T relaxation time of the $\nu_3 = 1$ level is ~3 ns, and the population of this level reaches 0.7. The absorption observed from the excited vibrational level[69] is more suitable for the study of the anharmonic structure of the $\nu_3 \geqslant 2$ states than the diffuse pattern characteristic of the gas phase. The calculation for the transition

$$v_3 = 1\,(F_{1u}) \rightarrow v_3 = 2\,(A_{1g},\ E_g)$$

shows that the anharmonic constants are $X_{33} = -1.2$ cm^{-1}, $G_{33} = 0.53$ cm^{-1}, and $T_{33} = -0.27$ cm^{-1}. According to the authors, the results show that the inversion of the populations does really occur in the optical pumping of cryosystems.

Experiments of another type have been performed with excitation of the N_2 vibrational mode with the aid of an HBr laser. The relaxation of the vibrational energy was followed from the fluorescence of the CO impurity molecule.[65] In the limit reached on decreasing the CO concentration, the relaxation time constant characteristic of pure LN_2 was obtained: ~0.018 s^{-1}. Overall, the rates of collision-induced vibrational deactivation in liquid CO–N_2 mixtures are low and the radiation-induced decomposition processes predominate as vibrational energy is lost in solution. The principal result of these measurements is that, at least for the system investigated, the kinetics of the vibrational exchange in simple cryogenic liquids do not differ greatly from those in a dilute gas; the rate constants measured in the gas phase can be simply extrapolated to the density of the liquid phase without any significant correction. Lupo et al.[70] reached an analogous conclusion having measured the rate constant for energy transfer from CO to O_2 in LAr in the temperature range 86–145 K:

$$CO(v=1) + O_2 \rightarrow CO + O_2(v=1) + \Delta E,$$

where $\Delta E = 589$ cm^{-1}. The rate constant for the quenching of the CO fluorescence in the above temperature range is higher by a factor of ~3 but remains equal to values for the gas phase within the limits of experimental error. The vibrational relaxation of CO in the presence of CH_4, CD_4, and CF_4 is several times faster than both for the solution in LAr and for the gas phase.[71] In the absence of impurities, the V–T relaxation in the CO solution in LAr is not the dominant process, the purely radiation-induced relaxation with a lifetime of 18 ns predominating.[72] With increase in CO concentration, the radiation was reabsorbed and the lifetime increased to 1 s. Isotope-enriched carbon monoxide (88% $^{13}C^{16}O$, 12% $^{13}C^{18}O$) in LAr has been optically pumped to the $v = 1$ level by means of a continuous CO laser.[73] As a result of the collision-induced redistribution of energy, some of the molecules were excited to higher vibrational states; fluorescence was recorded from vibrational levels up to $v = 20$ and the inversion of the populations of the level was noted.

A transition from an excited vibrational state to an excited electronic state is not ruled out either. When matrix-isolated $^{13}C^{18}O$ in Ar was irradiated by a colour-centre laser, the frequency of the radiation of which coincided with the first overtone of the CO band, fluorescence was observed in the visible and UV part of the spectrum.[74]

Overall, by virtue of the relatively slow V–T relaxation in solutions in liquefied monatomic gases, a high population (tens %) of the excited vibrational states of the impurity diatomic molecules in cryosolutions is readily attained. However, it seems unlikely that multiphoton IR excitation should occur in polyatomic molecules dissolved in cryogenic liquids. SF_6 dissolved in LAr, LO_2, and LN_2 has been irradiated[66] by a CO laser using a power much greater than that employed in multiphoton experiments in the gas phase, but no traces of dissociation were observed.

Processes in which single-photon IR excitation can increase the rate of reaction between an excited molecule and other molecules in the cryogenic solution are of interest. Such a process has apparently been discovered. The reactions of ozone with NO in the cryosystem stimulated by IR radiation have been investigated.[75] Preliminary experiments showed that the solutions of O_3 in NO at temperatures in the range 130–160 K are fairly stable. The character of the spectrum shows that the formation of a complex between NO and O_2 cannot be ruled out.

When the solution is irradiated by a CO_2 laser ($\lambda = 9.5$ μm), the concentration of excited O_3 molecules is about 10%. It was established that the irradiation leads to a rapid loss of O_3 from the solution: after 20 pulses, the O_3 concentration decreased by 30–50%, which corresponds to a quantum yield of the order of 3×10^{-2} molecules per photon under the experimental conditions. This result demonstrates the real occurrence of the stimulation of a reaction in cryosystems by IR radiation.

In a two-step IR–UV isotope separation process, an IR photon can be used to excite selectively the vibrational state of one of the isotope-substituted derivatives, while a UV photon can lead to the dissociation of vibrationally excited molecules. The possibility of marking molecules with the aid of an IR photon and then of the excitation of only the marked molecules by another photon has been demonstrated in measurements of double IR–IR resonance (see above).[65,69]

VIII. PHOTOCHEMICAL REACTIONS IN CRYOSOLUTIONS

The transparency of cryosolvents in the UV region facilitates photophysical studies and the weak interaction of the molecules with the solvent makes it possible to investigate molecules virtually in a free state. On exposure to a picosecond pulse (λ = 505 nm), predissociation of I_2 in LXe ($\tau \simeq 14$ ps) and the subsequent primary recombination ($\tau \simeq 40$ ps) were observed.[22] As a result of the photoexcitation of HCl in LXe (λ = 193 nm), IR fluorescence of HCl from the $v = 1$ state was noted.[76] The formation of vibrationally excited HCl molecules as a result of triple collisions of H and Cl atoms with Xe is the most probable. Emission by HCl from the $v = 2$ level appears[77] in SXe and the rate of relaxation from the $v = 1$ level diminishes. Both these effects have been attributed to the loss of mobility by HCl in the solid phase and the consequent decrease in the intensity of the interactions between the HCl molecules. It has also been shown[78] that the rate constant for the deactivation of DCl is smaller than that for HCl. It has been suggested that the rotational degrees of freedom also play a role in the vibrational relaxation of molecules in the liquid phase.

Photochemical reactions have been studied systematically by Turner and Poliakoff[2] using cryostats described previously.[9,13] Oskam's group[79,80] has been working on the same lines. The interaction of the environment in a solid matrix with the complex $Cr(CO)_5$ obtained on UV photolysis of $Cr(CO)_6$ had been investigated earlier from the position of the absorption band of the pentacarbonyl complex in the visible part of the spectrum.[81] For a series of matrices (CH_4, Xe, Kr, Ar, CF_4, SF_6, and Ne), the absorption band shifts from 480 to 640 nm. The magnitude of the shift shows that no solvent is completely inert towards $Cr(CO)_5$ and that the influence of trace impurities may be important in photochemistry.[82]

The first experiments in cryogenic solutions were performed in order to obtain complexes of metal carbonyls with N_2.[83] A band at 2236 cm^{-1}, associated with the $\nu(N-N)$ vibration, has been clearly observed in the IR spectrum of $Cr(CO)_5N_2$. A careful study[84] demonstrated that more prolonged photolysis of $Cr(CO)_6$ in LXe at a higher N_2 concentration makes it possible to obtain species with a higher N_2 content. Narrow-band photolysis at 367 nm in a solution in LXe containing N_2-substituted $Cr(CO)_{6-x}(N_2)_x$ complexes decomposes certain compounds while leaving others comparatively unaltered. At the same wavelength (corresponding to $d-d$ transitions), different isomers have markedly different absorption intensities and respond differently to irradiation. Thus the *cis*- and *trans*-isomers of $Cr(CO)_4N_2$ and the *mer*- and *fac*-isomers of $Cr(CO)_3(N_2)_3$ have been clearly separated. The introduction of additional N_2 molecules reduces the thermal stability of the complexes; it has not been possible to identify the $Cr(N_2)_6$ complex at −79 °C in solution in LXe.

Using a cell with four windows, Maier et al.[85] were able to obtain the IR spectra of the very unstable compound $Ni(CO)_3N_2$ as a result of the photolysis (λ = 286 nm) of $Ni(CO)_4$ in LKr with added N_2 at −170 °C. On switching off the UV lamp, the IR spectrum of Ni.$(CO)_3N_2$ (2267.5, 2101.0, and 2030.0 cm^{-1}) disappears fairly slowly and the kinetic parameters of the reaction

$$Ni(CO)_3N_2 + CO \rightarrow Ni(CO)_4 + N_2$$

were measured. The disappearance of the $Ni(CO)_3N_2$ bands follows first order kinetics. However, the kinetics are complicated by the dependence of the reaction rate constant both on the CO concentration and on the N_2/CO ratio. This agrees with the hypothesis of the occurrence of two competing processes in the reaction. One is dissociative in character, while the other results in CO participating in the transition state.[86]

The possibilities in the study of the kinetics of ligand substitution in liquefied gases can be seen particularly clearly in relation to the reaction of the complex $Fe(CO)_2(NO)_2$ with N_2 in LKr.[87] After UV photolysis for 4 min, the intensity of the bands due to $Fe(CO)_2(NO)_2$ fell and bands appeared at 2257.5 cm^{-1} [$\nu(N-N)$], 2046.0 cm^{-1} [$\nu(CO)$], and 1805.1 and 1761.5 cm^{-1} [$\nu(NO)$]. After further photolysis, additional bands appear at 2250.5 and 2228.0 cm^{-1} [$\nu(N-N)$] and 1796.3 and 1749.4 cm^{-1} [$\nu(N-O)$]. The experiments described indicate the stepwise substitution of CO by N_2. The primary photoproduct $Fe(N_2)(CO)(NO)_2$ is stable at −155 °C and begins to vanish only after the solution has been heated to −107 °C. Thus, in addition to the information obtained in matrix isolation experiments about the existence of complexes, in cryosolutions it is possible to obtain data concerning their stability and hence also their thermodynamic parameters.

The photolysis of $Cr(CO)_6$ in pure LXe or LKr with 5% of added LXe gives rise to the IR bands of an intermediate compound ($\tau_{1/2} \simeq 2$ s at −98 °C), which may be due to the unstable complex $Cr(CO)_5$...Xe.[88] In the absence of Xe, these bands were not observed in the spectrum.

The simplest complex of H_2 with a d^6 metal is $Cr(CO)_5H_2$. Its existence as a reaction intermediate has been postulated and it has been the object of several theoretical studies. UV photolysis of $Cr(CO)_6$ dissolved in LXe with added H_2 [89] leads to the formation of a new carbonyl-containing compound, which was not observed in the absence of H_2. The spectrum of the compound has a broad absorption in the near UV region at 370 nm and the compound is decomposed by the UV light at this wavelength:

$$Cr(CO)_6 + H_2 \underset{367\ nm}{\overset{228\ nm}{\rightleftarrows}} Cr(CO)_5(H_2) + CO\,.$$

The IR spectrum of the compound in the region of the CO vibrations has three bands: at 2094, 1974.3, and 1971.9 cm^{-1}. When D_2 is introduced into the complex, the low-frequency band undergoes a distinct downward shift by ~ 1 cm^{-1}. The shift is not caused by a solvent effect, which led the authors to the conclusion that they had obtained a hydrogen-containing compound. The three $\nu(VO)$ bands agree with the C_{4v} symmetry of the $Cr(CO)_5$ ($2a_1 + e$) fragment. This structure was confirmed by the preparation of a hydrogen-containing complex from $Cr(^{12}CO)_5(^{13}CO)$; as expected, the decrease in symmetry leads to the appearance of additional CO bands. A comparatively broad band with a maximum of 3030 cm^{-1}, which shifts to 2241 cm^{-1} for the deuterio-derivative, was also observed in the spectrum. The shift is somewhat smaller than for the isolated H_2 molecule, but the authors believe that an interaction with the CO vibrations must be considered. These bands have been assigned unambiguously[89] to the H−H and D−D stretching vibrations of the molecular hydrogen in the complex, which proved to be entirely stable up to −35 °C even after the evacuation of a large part of the excess H_2.

A comparative study has been made[90] of the interaction of the complexes $M(CO)_6$ (M = Cr, Mo, or W) with H_2 in LXe: $M(CO)_5$.(H_2) is always formed and in the case of Cr and W *cis*-$M(CO)_4(H_2)_2$ is also produced. The complex $W(CO)_5(H_2)$ has likewise been obtained in solution in LXe.[91] The $\nu(H-H)$ frequency for the Cr complex quoted above (3030 cm^{-1}) proved to be intermediate between the values for the molybdenum (3080 cm^{-1}) and tungsten (2711 cm^{-1}) complexes. The stability of the chromium complex in

LXe is greater than that of the molybdenum complex and smaller than that of the tungsten complex. Under D_2 pressure, the exchange reaction

$$Cr(CO)_5(H_2) \rightarrow Cr(CO)_5(D_2)$$

takes place. HD is probably formed as a result of the intramolecular exchange

$$Cr(CO)_5(H_2)(D_2) \rightarrow Cr(CO)_4(HD)_2 .$$

Metals with the d^8 configuration form dihydrides and not complexes with H_2. UV photolysis of $Ru(CO)_4PPh_3$ and H_2 dissolved in supercritical Xe at room temperature leads to the formation of $Ru(CO)_3(H_2).PPh_3$—an unstable dihydride, the existence of which in heptane at higher temperatures and an H_2 pressure of 550 atm had been reported earlier. The 1892.3 and 1810 cm^{-1} bands, which are more distinct in LXe than in heptane, were assigned to Ru—H bond vibrations.

The interaction, on photolysis, of H_2 with the most active catalysts for homogeneous catalysis, namely $Fe(CO)_2(NO)_2$ and $Co(CO)_3NO$ in LXe at −104 °C and under a 10—20 atm H_2 or D_2 pressure, had also been investigated.[92] The coordinated H_2 or D_2 molecules in $Fe(CO)(NO)_2(H_2)$ and $Co(CO)_2(NO)(H_2)$ were identified from the IR bands at 2973 and 2195 cm^{-1} and 3000 and 2228 cm^{-1} respectively. The symmetrical and antisymmetric stretching vibrations of the $M-H_2(D_2)$ were also assigned. Experiments in LXe showed that the reaction proceeds via the same pathways as in the usual solvent but at the same time it is possible to follow them in greater detail. It was found that the complexes of molecular H_2 are more abundant than had been supposed and that hydrogenation reactions, especially photocatalytic reactions with metal carbonyls, can proceed via the coordinated H_2 and not via metal hydrides.

Previously unknown complexes of ethylene with $Cr(CO)_6$ derivatives, namely $Cr(CO)_5(C_2H_4)(m)$, $Cr(CO)_4(trans\text{-}C_2H_4)_2(t)$, and $Cr(CO)_4(cis\text{-}C_4H_4)_2(c)$, have also been obtained on LXe at −78 °C.[93]

Brief photolysis at very low C_2H_4 concentrations yielded the complex (*m*) (with the IR bands of the CO groups at 2078.9, 1967.4, and 1960 cm^{-1}). At a higher C_2H_4 concentration, the complexes (*c*) (2036.8, 1949.3, and 1913 cm^{-1}) and (*t*) (1953.1 cm^{-1}) were formed. Bands referring to the C_2H_4 vibrations also appear in the IR spectrum in the range 1000—1600 cm^{-1}. The structures of the complexes were established spectroscopically: C_{2v} for (*m*), C_{2v} for (*c*), and pseudo-D_{4h} for (*t*).

Similar experiments with $Mo(CO)_6$ and $W(CO)_6$ lead to the formation of not only the previously known complexes (*m*) and (*c*) but also of the unknown analogues (*t*) for Mo and W. In contrast to the unstable chromium complexes, the molybdenum and tungsten complexes are stable under the experimental conditions.

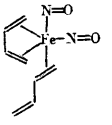
When the photolysis of $Co(CO)_3$ was carried out in LXe with added but-1-ene, it was clear from the spectrum that the photoproduct contains two CO groups and one NO group. The fourth coordination site is apparently occupied by the π-linked olefin.[2]

The photolysis of the $Fe(CO)_2(NO)_2$—but-1-ene system in LXe proceeds with formation of two photoproducts:[94]

$$Fe(CO)_2(NO)_2 \xrightarrow{h\nu} Fe(CO)(NO)_2(\eta^2\text{-}1\text{-}C_4H_8) \xrightarrow{h\nu} Fe(NO)_2(\eta^2\text{-}1\text{-}C_4H_8)_2 .$$

No signs of the decomposition of either complex in LXe were observed for 1 h at −104 °C.

A greater variety of products is attained in the reactions of the same complexes $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ with buta-1,3-diene in LXe, since the η^2-C_4H_6 and η^4-C_4H_6 derivatives are obtained.[95] Under similar photolytic conditions in LKr, $Ni(CO)_4$ affords only $Ni(CO)_3(\eta^2\text{-}C_4H_6)$, which is thermally less stable than the above iron and cobalt complexes. The compound $Fe(CO)_2(NO)_2$ forms a bis-η^2-butadiene complex, which can be regarded as an active intermediate in dimerisation reactions. The catalytic process apparently proceeds via a pentacoordinate intermediate with a bent NO group:



This intermediate, which has three coordinated C=C bonds, leads to the formation of mainly 4-vinylcyclohexene and not other possible dimers such as cyclo-octadiene. The stabilising role of the hydrocarbon ligand has been discovered in the photochemical synthesis of $(\eta^4\text{-}C_4H_6)Fe(CO)_2(N_2)$ in solution in LXe with added 1.7% N_2 at −110 °C.[96] No decomposition of the complex was observed on heating the solution to −80 °C.

The photolysis of $CpRh(C_2H_4)_2$ dissolved in LXe with added N_2 at 173 K leads to the splitting off of C_2H_4 and the formation of $CPRh(C_2H_4)(N_2)$.[97]

The experiments described here show that LXe is a solvent which yields additional information compared with low-temperature solid matrices and solutions at room temperature.

Naturally, the photochemical processes in the cryosolutions are not restricted to organoelemental compounds. It has been demonstrated for formaldehyde[23] that it is possible to carry out even isotopically selective processes (see Section V). When a mixed solution of CD_2O and CH_2O in LXe is irradiated, the concentration of each component decreases linearly with time, which indicates cross-order kinetics. the CD_2O concentration then falls somewhat faster than that of CH_2O; this is clearly indicated by the relative intensities of the IR bands of CD_2O and CH_2O. At −94 °C and −106 °C and at irradiation wavelengths of 325 and 318.7 nm, the preferential decomposition of CD_2O (by a factor up to two) was attained. The quantum efficiency of the photo-decomposition of CH_2O at 325 nm is ~0.001. The ratio of the rates of decomposition of the CD_2O and CH_2O molecules is approximately proportional to the ratio of the optical densities in their spectra at the excitation wavelength.

The dissociation of molecules in solution in simple gases has also been achieved using the UV radiation generated by the electrical breakdown of the liquid medium effected by an intense CO_2 laser:[65]

$$OCS + h\nu \rightarrow CO + S;\ C_2H_4 + h\nu \rightarrow C_2H_2 + H_2;\ O_2 + h\nu \rightarrow 2O(^3P) .$$

The construction of lasers with a tunable frequency combined with the characteristics of the cryosolutions should lead to further development of photocheistry in the condensed phase. On the other hand, in order to investigate the reaction mechanism, it is useful to apply the methods of the high-speed IR spectroscopy developing at the present time.[2,98-100] With the aid of multichannel Raman spectrometers, it is possible to record rapid processes up to the picosecond range. In experiments with solvents such as N_2, O_2, and Ar,[101] it was found that the low solubilities make the Raman method rather unpromising. However, the comparatively high solubilities of the molecules in LXe give rise to the hope that Raman

spectroscopy will find extensive application in the study of the mechanisms of photochemical reactions.

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Thus reactivity and chemical reaction mechanisms can be studied spectroscopically in solutions in liquefied elemental gases. The low temperatures and the weak interaction of the molecules with the solvents make it possible to obtain the spectra of reactive and unstable compounds with standard instruments. The absence of absorption by the solvents at wavelengths ranging from UV to far infrared ensures the possibility of investigating the effect of laser radiation on the course of reactions. The measurement of the spectra of very thick layers of solution (up to several metres) compensates for the relatively low solubility of molecules and renders the method general.

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Institute of Spectroscopy,
USSR Academy of Sciences,
Troitsk,
Moscow Region