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EPR spectroscopy and partial orientation ordering of formyl radicals stabilized in CO and Ar polycrystals at helium temperatures

© *Yu.A. Dmitriev*

Ioffe Institute, St. Petersburg, Russia

e-mail: dmitriev.mares@mail.ioffe.ru

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EPR spectra of formyl radicals DCO and HCO stabilized in solid CO and Ar, respectively, were recorded and investigated. The radicals were obtained by gas condensation on a substrate at the liquid helium temperatures. Partial orientation ordering of the radicals in the polycrystal matrices was revealed using spectrum simulation. In the carbon monoxide solid, the C=O bond of the formyl radical was directed parallel to the deposition surface of the substrate and, at the same time, perpendicular to a plane formed by the gas flows. In the Ar matrix, such a preferred direction was the normal to the deposition surface. Thus, observed for the first time with the stabilized formyl radicals, the partial ordering was estimated to be 4% and 17%, for the DCO/CO and HCO/Ar systems, respectively.

Keywords: electron paramagnetic resonance, matrix isolation, cryodeposits, formyl radical, powder spectrum, partial orientation ordering.

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Introduction

The formyl radicals HCO (DCO), which are intermediate particles in thermal and photochemical processes that play an important role in combustion of hydrocarbon flame [1], in chemistry of the terrestrial atmosphere and interstellar space [2,3], acting, in particular, as a source of atomic hydrogen in dissociation of the molecule [4].

The most important role in studying the formyl radical is played by EPR spectroscopy, which has sensitivity and selectivity in relation to the particles with unpaired electrons. The majority of such particles are chemically highly-reactive and short-lived in a gas phase. A combination of the EPR spectroscopy with matrix isolation at low temperatures makes it possible to stabilize the radicals in relatively big quantities for obtaining spectra with a high signal-to-noise ratio being sufficient for thorough study of the radical structure [5], its dynamics [6], line intensities in the spectra of absorption and radiation [7].

The investigation of specific features of parameters and a line shape of the EPR spectrum of the matrix-insulated (stabilized) radicals HCO and DCO in the main electron state makes it possible to obtain information about the dynamics of molecule atoms, tunnel orientation motion of the molecule (which is possible due to its extremely small moment of inertia in relation to one of its main axes, which is close to the C=O bond), and about possible mechanisms of spin-lattice relaxation and the influence of radical's orientation motion on it [8]. Complexity of simulation of the EPR spectra of the small radicals stabilized at the cryogenic temperatures is related to these spectra exhibiting substantially quantum dynamics of both the very paramagnetic molecule and the particles of a matrix environment. It can be exemplified by such effects as the temperature-dependent anisotropy of the tensor of the line width of the radical CH_3 in the matrices CO, N_2O, CO_2, which is related to superslow angular precession of the radical [9] and the matrix molecules [10]; and the CH_3 spectrum exhibiting weak satellite lines of the „stopped“ methyl radical in the E-symmetrical state in the matrices of CO_2, N_2O and in the melanophlogite [11–14]; and the change of the symmetry of a small impurity molecule (freely built into the matrix crystal lattice) as compared to the symmetry of this molecule in the gas phase [15], which is exemplified by CH_3 in CH_4 and CD_4 via specific features a shape of the EPR spectrum line shape that is seen through an unexpected relative intensity of the A-symmetry quartet and the E-symmetry doublet [16,17].

The present paper presents the experimental EPR spectra of the formyl radicals in CO and Ar matrices with their analysis based on spectrum simulation and demonstrates that partial orientation ordering of the trapped paramagnetic particles is observed. The partial orientation of the impurity paramagnetic centers in polycrystalline films or in glasses produced by deposition of the molecules with predominant Van der Waals interaction (physical adsorption) reflects the partial orientation of the very structure of the film. Without epitaxy, this condensate property is often a consequence of a big difference of linear dimensions of its molecules along the three coordinates [18]. We can talk both about partial translational ordering of the sample and preferred orientation of its molecules. It can be exemplified by liquified crystals, oriented polymers and biopolymers. It should be noted that the said note about the geometry of the molecule is not strictly necessary for creation of such orientation. Thus, it has been found that argon condensed from vapor at 4.2 K (a spherically symmetrical particle) was oriented with the plane (111) in parallel to a surface, on which it is condensed [19]. It often happens that the experiment conditions resulting in the growth of the partially oriented films are not obvious. Dalal et al. [20] have discovered that the molecular orientation in the organic glasses and, therefore, their orientation anisotropy could be governed by changing a set experimental factor that is a ratio of the substrate temperature during deposition to the temperature of substance conversion to the glass phase. The insufficient sensitivity to the partial orientation of the structures in such the methods as the spectroscopy of X-ray and Raman scattering compelled researchers to propose EPR of paramagnetic impurities as a method for detection and investigation of this orientation phenomenon [18,21]. This field is based on development of the method of simulation of the experimental EPR spectra [18,22] and determination of the parameters of the orientation order from comparing the results of the experiment and the calculations.

Experiment procedure

The experimental setup and the experimental technique were described in detail previously in [23] and briefly in [8]. The main moments of this description are repeated below for convenience.

The samples were produced by condensation of two gas streams on a cold substrate: one of them was molecular H_2 or D_2 passed through an electrodeless discharge at the frequency of 15 MHz, and the other — the matrix CO supplied to the substrate bypassing the gas discharge. Both the discharge and the matrix gas were cooled to the temperature of liquid nitrogen. The sample was formed on the surface of a quartz finger located in the center of a cylindrical resonator tuned to the mode TE_{011}. The finger was cooled with liquid helium, whose temperature was adjusted within the range of 1.2–4.2 K by pumping vapor from a tank with liquid He. High purity gaseous Ar and CO were used. In carbon monoxide hardly separated N_2 contributes at 1%. The molecular hydrogens, H_2 and D_2 were purified by passing the source gas through the heated wall made of the Pd–Ag alloy. The formyl radicals were formed in the matrix in a tunnel reaction of addition of atomic hydrogen to the CO molecule:

$$\mathrm{H} + \mathrm{CO} \rightarrow \mathrm{HCO}, \quad \mathrm{D} + \mathrm{CO} \rightarrow \mathrm{DCO}.$$

The flows were calculated from measured gas consumption from storage glass balloons taking into account the geometry of the cooling system. The VHF power of 15 mW was supplied from a klystron throught an attenuator, which made it possible to adjust the amplitude of the resonance magnetic field in a resonant cavity within a wide range. The Ar matrix experiment included supply of argon through the matrix channel and — the mixture of argon with methane CH_4 through the discharge channel. The main radical products of methane dissociation were atomic hydrogen and methyl radicals. The formyl radicals were formed in the above-mentioned tunnel reactions due to the presence of residual CO in the setup. The typical time of sample deposition — about 40 min.

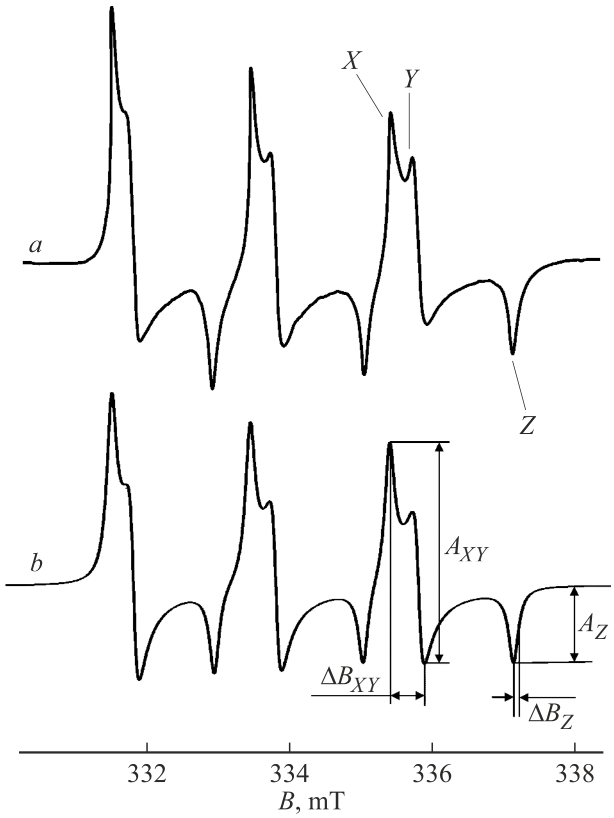

Figure 1. EPR spectrum of the radical DCO stabilized in the solid CO matrix. The sample is produced by gas condensation to the substrate at 1.4 K. (*a*) Experimental spectrum recorded at the sample temperature of 3.7 K. Resonance frequency of the spectrometer $f_{\mathrm{res}} = 9354.77$ MHz. (*b*) Simulated spectrum plotted using the magnetic tensor parameters in the inertia frame (Table 1).

Experimental results and discussion thereof

DCO in the solid CO matrix

Fig. 1 shows the experimental, *a*, and calculated, *b*, EPR spectra of the radical DCO in solid CO. The sample is produced by deposition to the substrate at 1.4 K. With the rate of matrix supply to the substrate being 0.45 mmol/h, the estimated thickness of the film on the substrate of an area about 1 cm^2 is 0.1 mm.

The spectrum consists of three hyperfine lines, which are related to interaction of the unpaired electron with the

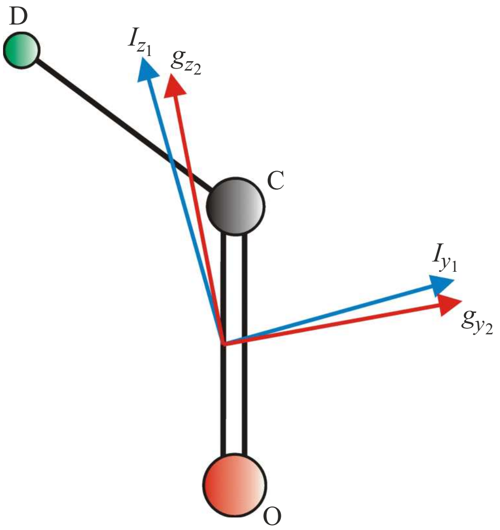

Figure 2. Structure of the planar molecule of the formyl radical DCO indicating the main axes of the tensor of the inertia (x_1, y_1, z_1) and the g-tensor (x_2, y_2, z_2). The axes x_1 and x_2 are perpendicular to a figure plane.

deuterium nucleus, whose spin is $I = 1$. The distance between the hyperfine components is about 2 mT. The tensor of hyperfine interaction, the A-tensor and the g-tensor are orthorhombic, thereby causing a quite complex shape of the EPR spectrum.

The spectrum simulation using the software *EasySpin* (available at the address http://www.easyspin.org, version 5.2.33), Fig. 1, *b*, included the use of the empirical values of the magnetic parameters and the results of the theoretical calculations [6]. These parameters are calculated in the inertia frame and given in Table 1. Fig. 2 shows the structure of the flat molecule of the formyl radical DCO with directions of the main axes of the tensor of inertia and the g-tensor [6].

When comparing the experimental and simulated spectra, it is worth to note the big relative amplitude (in comparison to the amplitude of the XY-component) of the Z-component of the experimental spectrum. This nature of the lines' shape is not temperature-dependent and is recorded within the entire investigated range of 1.4–4.2 K. The observed specific feature in the relative amplitudes can be explained by the anisotropy of the tensor of line width — the presumed width of the individual line of the Z-component is less than the corresponding widths for the X- and Y-components.

Using the WinEPR SimFonia software (Bruker WINEPR-System, version 1.25), we have simulated the spectrum for the powder samples taking into account the second order of the perturbation theory with the values of the angular parameters θ and ϕ, being 100 and 30, respectively, and assuming an axial symmetry of the tensor of the width of the individual line:

$$\Delta B_X^{\mathrm{ind}} = \Delta B_Y^{\mathrm{ind}} \neq \Delta B_Z^{\mathrm{ind}}.$$

The values of the tensor were selected so as to obtain the relative amplitude of the Z-component, A_Z/A_{XY} and the distance in a magnetic field between the extrema of the XY-component, ΔB_{XY} being close to the experimental values of 0.45 and 0.507 mT, respectively. At the same time, the magnetic parameters were determined in the g-tensor frame, Table 1. The best result is obtained at $\Delta B_X^{\mathrm{ind}} = \Delta B_Y^{\mathrm{ind}} = 0.095$ mT, $\Delta B_Z^{\mathrm{ind}} = 0.071$ mT. However, as shown by comparison of the simulation result with the experiment, the narrowing of the Z-component turns out to be overestimated. Indeed, the half-width of the Z-component of the high-field hyperfine line of the simulated spectrum $(\Delta B_Z)^{\mathrm{anis}} = 0.062$ mT turns out to be much less than the experimental value, $(\Delta B_Z)^{\mathrm{exp}} = 0.096$ mT.

Another possible mechanism resulting in the specific feature observed in the relative amplitudes of the components is that the paramagnetic centers DCO are oriented not chaotically in the CO polycrystal in relation to the axes of the laboratory system of the coordinate, but they demonstrate a certain degree of ordering.

The EasySpin software for simulation of the EPR spectra is designed to plot the spectrum with reflection of the partial orientation ordering of the paramagnetic molecules. We have used an embedded function *Exp.Ordering* with the ordering coefficient's value $\lambda = 0.2$. The non-zero value λ means non-isotropic orientation distribution of the molecular axes. The positive value of this coefficient indicates that the axes z of the molecules have a preferred direction along the external magnetic field (the axis z of the laboratory system of the coordinates), while the orientation distribution function $P(\theta)$ has a maximum at $\theta = 0^\circ$ and $\theta = 180^\circ$, where θ is an angle between the direction of the magnetic field and the axis Z of the molecule (the main axes of the g-tensor). The distribution function is as follows

$$P(\theta) = \exp\bigl(-U(\theta)\bigr), \quad U(\theta) = -\lambda(3\cos^2\theta - 1)/2.$$

The simulated spectrum is shown on Fig. 3, *b*. For convenience of comparison, the same figure 3, *a* shows the experimental spectrum corresponding to the spectrum of Fig. 1, *a*. The simulation used the magnetic parameters of the radical in the g-tensor frame. With $\lambda = 0.2$ and $\Delta B^{\mathrm{ind}} = 0.107$ mT, the simulated spectrum provides the relative amplitude of the Z-component as 0.45, $\Delta B_{XY} = 0.495$ mT, $(\Delta B_Z)^{\mathrm{order}} = 0.094$ mT, i.e. the values close to the experimental ones.

As in the case under consideration, the simulated spectra presented below in the paper were compared with the experimental ones, while the simulation parameters were chosen by correspondence of the relative amplitudes of the lines and their widths.

Let us approximately evaluate the degree of orientation ordering. For this, we introduce the following notation:

$$P_{\mathrm{tot}} = 2\int_0^{\pi/2} P(\theta)\sin(\theta)d\theta,$$

Table 1. Empirical values of the magnetic parameters of the radical DCO in the inertia and the g-tensor frames of the molecule. In spectrum simulation, Fig. 1, b sets an isotropic width of the individual line $\Delta B^{\mathrm{ind}} = 0.095\,\mathrm{mT}$ of the Lorentz form

Magnetic parameters		Inertia frame results			g-tensor frame results		
		x	y	z	x	y	z
g-tensor	x	2.004448	0.0000028	0.0000026	2.004448	0	0
	y	0.0000028	2.002224	0.0005632	0	2.00226	0
	z	0.0000026	0.0005632	1.9949954	0	0	1.994959
A-tensor, G	x	19.531	−0.0013	0.0011	19.51	0	0
	y	−0.0013	20.1153	−0.8135	0	19.99	−0.81
	z	0.0011	−0.8135	20.7877	0	−0.81	20.98

$$P_{\|} = 2\int_{0}^{\pi/3} P(\theta)\sin(\theta)d\theta, \quad P_{\perp} = 2\int_{\pi/3}^{\pi/2} P(\theta)\sin(\theta)d\theta.$$

Then, a part of the ensemble of the radicals oriented preferably along the magnetic field is $P_{\|}/P_{\mathrm{tot}} = 0.54$, whereas the portion of those oriented in the perpendicular direction — $P_{\perp}/P_{\mathrm{tot}} = 0.46$. Thus, the orientation anisotropy is quite small, while a deviation of distribution from the isotropic one is 4%.

Fig. 4 shows the scheme of the experimental setup's part comprising formation of the sample. The sample grows out of the gas phase on the cold bottom of the quartz finger that is filled with liquid helium and located along the axis of the vacuumed cylindrical resonant cavity of the EPR resonant cavity with the working mode TE_{011}. In the center of the resonant cavity, where the sample is placed, this mode has the maximum amplitude of the microwave magnetic field and, therefore, provides the highest sensitivity of the spectrometer. The axes of the laboratory system of coordinates of Fig. 1 are placed as follows: the axis z is directed along the external magnetic field lines of the spectrometer, the axis x — along the microwave magnetic field causing the resonance transitions. It is clear from the figure that it implements anisotropy of supply of those gas streams, whose velocities are mainly in the plane xy.

Relying on the similar structure of the HCO and CO molecules, including an almost equal length of the C=O bond 1.13 Å, it is reasonable to assume that the radicals are stabilized in substitutional cites and oriented in the same way as the matrix molecules. In this case, the anisotropy of orientation of the paramagnetic particles reflects the anisotropy of orientation of the matrix molecules. The polycrystal grows so as to implement a small predominant position of the valence C=O bond in a direction perpendicular to the plane of position of the deposited gas streams. At the same time, the EPR spectrum of the radical DCO indicates that the orientation of the radicals is isotropic for revolutions around this axis. It seems that this circumstance reflects the axial symmetry of the molecules of the matrix CO with embedded radicals.

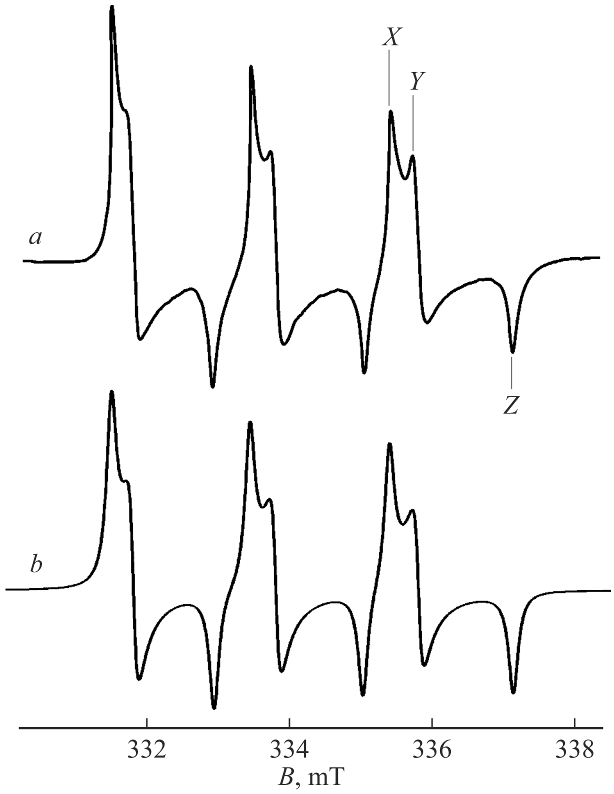

Figure 3. Experimental spectrum corresponding to the spectrum of Fig. 1, a. Fig. 3, b shows the simulated spectrum of the radical using the magnetic parameters in in the g-tensor frame (Table 1) and taking into account the preferred partial orientation.

HCO in the solid Ar matrix

Fig. 5, a shows the experimental EPR spectrum of the radicals HCO in Ar. The temperature of the substrate during sample deposition and in spectrum recording is 4.2 K. With

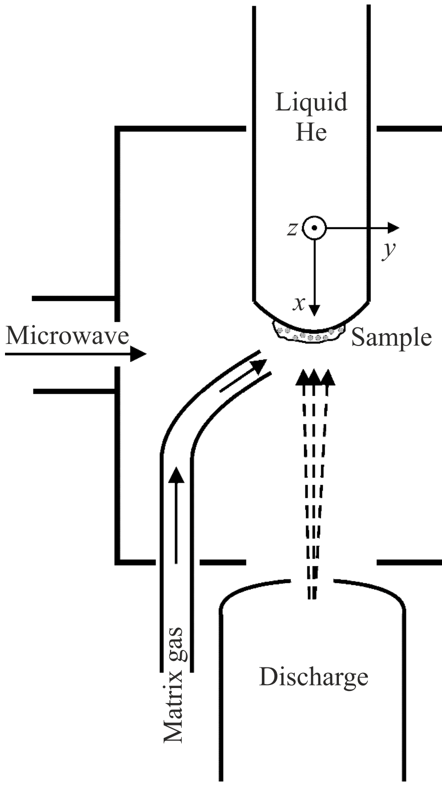

Figure 4. Scheme of the deposition system including: the cylindrical resonant cavity of the spectrometer with a waveguide path, the quartz finger filled with liquid helium, with a sampled being formed on the bottom thereof, the discharge tube and the tube for supply of the matrix gas. The figure shows the axes of the laboratory system of coordinates: z — along the lines of force of the constant magnetic field of the spectrometry, x — along the lines of force of the VHF magnetic field of the spectrometer, causing transitions between the magnetic levels of the radical.

the rate of matrix supply to the substrate being 1 mmol/h, the estimated thickness of the film on the substrate of an area about 1 cm^2 is 0.23 mm. For comparison, Fig. 5,*b* shows the experimental spectrum of HCO in CO, also recorded at 4.2 K for the sample produced at the same temperature. Let us not that the radicals DCO in CO (Fig. 1,*a*) and HCO in CO (Fig. 5,*a*) were stabilized in different experiments.

As for the concentration of the radicals, we can provide only its upper estimation — at most 10^{-4}. It is concluded based on that the line widths in the different experiments are approximately equal despite the significantly different intensities of the spectra, i.e. the concentration broadening of the line does don exceed the value about 0.01 mT.

Fig. 5,*c* shows the spectrum of HCO in CO (simulated in *EasySpin*) using the empirical values of the magnetic parameters listed in Table 2. The spectrum has been calculated without taking into account the partial orientation of the radicals to well reproduce the experimental result. The spectra of HCO plotted at the various values of the parameter λ for the preferred orientation of the axis z of the molecule are compared to show that these spectra are not so „sensitive“ to the change of λ as the spectra of DCO. As a result, the spectrum simulated at $\lambda = 0.2$ for the oriented system HCO/CO has almost (taking into account the error of reading of the experimental spectra) no difference with the spectrum for the chaotic orientation of the radicals in this system. This circumstance makes it impossible to match the degrees of orientation of the investigated isotopomers in the matrix CO and to discuss the possible influence of the degree of the „quantum nature“ of rotation motion of the formyl radical in relation to the axis z on its orientation behavior in the matrix in sample formation.

The EPR spectrum of HCO in Ar (Fig. 5,*a*) is characterized by a small relative amplitude of the Z component, a line shape similar to the Gaussian one and by a reciprocal ratio of the amplitudes of the X- and Y-components of the high-field line as compared to the spectrum of the isotropically oriented radicals (Fig. 5,*c*). The simulation in *EasySpin* has shown that the direct application of the function *Exp.Ordering* did not provide positive results. It means that the preferred orientation of the C=O bond can not be described as being implemented along the axis z of

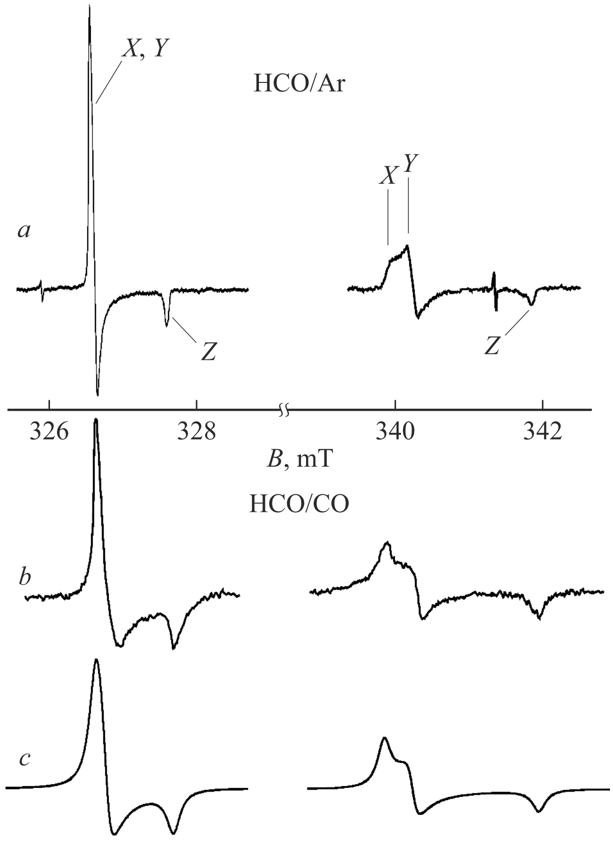

Figure 5. Experimental spectra of the radicals HCO in the matrices Ar (Fig. 5,*a*) and CO (Fig. 5,*b*), as recorded at 4.2 K. The temperature of the substrate during sample deposition is 4.2 K. Resonance frequency of the spectrometer $f_{\mathrm{res}} = 9350.87$ MHz. Fig. 5,*c* — the simulated spectrum of HCO in CO without the partial orientation ordering of the radicals. The empirical values of the magnetic parameters used in simulation are listed in Table 2.

Table 2. Empirical values of the magnetic parameters of the radicals HCO in the g-tensor frame for the molecules stabilized in the matrices Ar and CO. The spectrum of HCO/Ar is simulated for the line, which is a convolution of the Gaussian and Lorentzian functions with the widths equal to $\Delta B_G^{\text{ind}} = 0.1$ and $\Delta B_L^{\text{ind}} = 0.02$, correspondingly. The spectrum of HCO/CO is simulated (Fig. 5, b), with setting the width of the individual line $\Delta B^{\text{ind}} = 0.125\,\text{mT}$ of the Lorentzian shape.

Magnetic parameters		Matrix Ar			Matrix CO		
		x	y	z	x	y	z
g-tensor	x	2.003912	0	0	2.003994	0	0
	y	0	2.002710	0	0	2.002080	0
	z	0	0	1.995500	0	0	1.994950
A-tensor, G	x	133.530	0	0	132.074	0	0
	y	0	136.09	−5.042	0	134.011	−5.042
	z		−5.042	141.98		−5.042	142.082

the laboratory system of coordinates or isotropically in the plane perpendicular to it.

Thus, the task includes both clarification of the degree of preferred orientation and determination of its direction. We have written a small script, whereby the program *EasySpin* was determining a taken arbitrary orientation of the molecule not in relation to the axis z, but recalculating it into orientation in relation to the axis z' of the system of coordinates rotated in relation to the laboratory one. Respectively, the function of direction-distribution of the molecules described in the previous section was set in a new system of coordinates. The best result was obtained for the system of coordinates described by means of Euler angles $(-\pi/8, \pi/2, 0)$ and with application of the positive coefficient of the orientation degree $\lambda = 0.9$ (Fig. 6). The line is shaped as the convolution of the Gaussian and Lorentzian functions with the widths of $\Delta B_G^{\text{ind}} = 0.1\,\text{mT}$ and $\Delta B_L^{\text{ind}} = 0.02\,\text{mT}$, respectively. Thus, the valence C=O bonds of the molecules demonstrate partial orientation ordering along the axis z', which is in the plane xy and makes the angle 22.5° with the axis x and the angle 112.5° with the axis y of the laboratory system of coordinates. It means (Fig. 4) their preferred orientation perpendicular to a growing surface of the sample and partially along the gas stream of the matrix, which significantly exceeds the stream out of the discharge tube.

The present paper has not investigated the radicals DCO in Ar. It should be mentioned in this regard that implementation of the partial orientation of the radicals in the system HCO/Ar is indicated by an anomalous ratio of the amplitudes of the X- and Y-components, which can be observed only for the high-field hyperfine HCO line, where they are partially resolved. The low-field component turns out to be uninformative in this respect. As for the radical DCO - the X- and Y-components are not resolved for all the hyperfine lines of the spectrum.

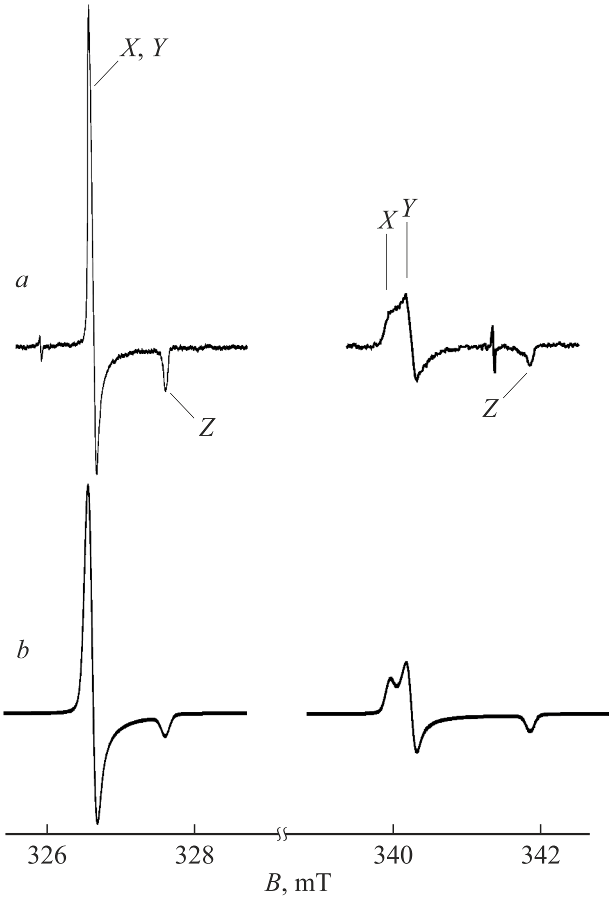

Figure 6. EPR spectrum of HCO in the Ar matrix. The experimental spectrum (Fig. 6, a) is copied from the spectrum of Fig. 5, a. Resonance frequency of the spectrometer $f_{\text{res}} = 9350.87\,\text{MHz}$. Fig. 6, b shows the simulated spectrum of HCO in Ar taking into account the partial orientation ordering of the radicals. The magnetic parameters used in simulation are listed in Table 2.

Let us note that the degree of the partial orientation of the ensemble of the radicals HCO in the Ar matrix is higher than for the DCO molecules in solid CO. For the system HCO/AR, the portion of the radicals oriented preferably along the axis $z'$is $P_{\|}/P_{\text{tot}} = 0.67$, whereas the portion of those oriented in the perpendicular direction — $P_{\perp}/P_{\text{tot}} = 0.33$. I. e., the deviation of distribution of the molecules' axes from the isotropic one is 17%.

The literature's EPR method was taken to observe and study the partial orientation ordering of the light paramagnetic molecules in the Van der Waals matrices predominantly on the example of nitrogen dioxide NO_2 and nitrogen difluoride NF_2 (of the radical's similar structure). The paper [24] has obtained the EPR spectra of these paramagnetic particles in the matrices of solid inert gases (Ne, Ar, Kr) via vapor-phase deposition to the substrate at 4.2 K. The systems NO_2/Ne, NF_2/Ar, NF_2/Kr have exhibited the preferred orientation of the axis perpendicular to the molecule plane along the normal to the sample surface, thereby meaning orientation of the molecule plane in parallel to the deposition surface. It reports the different degrees of orientation of the same molecules in the different matrices. This value is estimated only qualitatively, and at the same time it is recorded as being a significant one. The solid Kr has exhibited the degree of orientation of the radicals NF_2 below that in Ar, and it turned out to be zero in Ne. It also discusses a possible role of the direction of the gas flow in relation to the deposited surface in generating the partial orientation order of the captured paramagnetic particles.

The paper [25] has studied the EPR spectra of the NO_2 molecules captured in the matrix of dinitrogen tetroxide N_2O_4 by vapor-phase deposition to the substrate, within the range of 35−65 K. The spectra have been analyzed to show that the symmetry axis of the second order of the NO_2 molecules was oriented preferably in perpendicular to the deposition surface, thereby meaning the perpendicular position of the molecule plane in relation to the surface of the sample film. The experimental spectra were simulated by superimposing the spectra of the statistically (isotropically) oriented molecules and the molecules of the above-said preferred orientation. When depositing to the substrate at 35 K, the degree of orientation was 73%, while being only 10% at the temperature of deposition of 65 K.

For the particles stabilized in Ne, Ar and Kr at 4.2 K, the EPR spectra of another stable paramagnetic molecule — chlorine dioxide ClO_2 (which is similar in the structure to the NO_2 molecule), have demonstrated [26] the preferred orientation of the molecule plane in parallel to the deposition surface.

Using the EPR method, the Knight team's studies have discovered the preferred orientation of molecular ions and neutral molecules in the matrices of frozen gases. It can be exemplified by acetaldehyde cations CH_3CHO^+, which are oriented in the Ne matrix [27] with the plane CCHO parallel to the deposition surface. They have found a substantial dependency of the degree of preferred orientation on the substrate temperature during deposition.

Another example includes the radicals BO in the Ne and Ar matrices. The EPR spectra have been analyzed to show [28] that the axes of these molecules stay in the plane (that is perpendicular to the deposition surface) preferably in parallel or perpendicular to this surface. As for the radicals stabilized in solid Ar, they are oriented chaotically.

Conclusions

The present paper has been the first to find the partial orientation of the formyl radicals, when they were stabilized out of the gas phase, in the Van der Waals matrices, as exemplified by the radicals DOC in solid CO and HCO in solid Ar. Undoubtedly, the result is of interest, since the majority of the published papers using the technique of stabilization out of the gas phase are the EPR studies of the effect of partial orientation of the small stable molecules and the radicals with a structure similar to the structure of the NO_2molecule. The present paper has established that the same impurity molecules could have a principally different preferable orientation in relation to the deposition surface when being trapped in different matrices. This observation confirms that the opposite literature data about orientation of the matrix-isolated NO_2 molecules do not contradict to each other.

Let us note that a change in the direction of the partial orientation of the trapped NO_2 molecules went with experimental transition from the spherically symmetrical matrix particles (that is what the atoms of inert gases are) to the particles of lower symmetry in case of dinitrogen tetroxide. In the present paper, the change in the direction of the preferable orientation of the formyl radicals also accompanied the decrease in the symmetry of the matrix particles — from the spherically symmetrical Ar atom to the axially-symmetrical CO molecule. It seems that in case of the matrix of close-packed balls, Ar, the most favorable orientation of the formyl radicals is determined by the structure of the building-up layers of Ar [19], whereas in case of the CO molecules exhibiting anisotropy interaction, the contribution by orientation ordering is also substantial.

It is reasonable to assume that the observed orientation effect can be contributed by lattice relaxation around the impurity molecule. In this case, based on comparative geometrical characteristics of the particles of the matrix and the radicals, one should expect a bigger influence of such relaxation for the system of formyl radical/Ar as compared to the system of formyl radical/CO. Our search in the literature, including the optical methods of research, has shown that only a small number of the papers [29–33] compared the properties of the formyl radicals in the different matrices or took steps towards analysis of behavior of the radical in the matrix.

It is worth noting the demonstrated capabilities of the EPR spectroscopy for observing such fine effects as the partial preferable orientation of the molecules at the level of 4% of their ensemble. It can be assumed that generalizing the literature experimental data about the partial orientation of the paramagnetic molecules in cryodeposits and further targeted experimental work using EPR and matrix isolation of the various-structure radicals can result in substantial advance of the gas condensation theory. It seems that the experiments shall be planned based on the small impurity paramagnetic molecules, which can be easily embedded into the substitutional position of the lattice of the investigated polycrystal without substantial disarrangement of the nearest environment.

Conflict of interest

The author declares that he has no conflict of interest.

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