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EPR spectra and rotation of CH_3, CH_2D, CHD_2, and CD_3 radicals in solid H_2

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EPR spectra of CH_3, CH_2D, CHD_2, and CD_3 radicals have been observed in H_2 matrix in the temperature range 1.6–4.2 K. The radicals were obtained by condensation on a cold substrate of two gas flows: deuterium mixed with 2 mol % methane passed through a discharge and pure hydrogen avoiding the discharge. The CD_3 and CHD_2 spectra were found to be a superposition of two spectra: high-temperature and low-temperature. A transformation of the shape of CD_3 and CHD_2 spectrum with decreasing sample temperature was observed. This is attributed to a change in the populations of the lowest rotational states of the radicals. Compared to known results for deuterated methyl radicals in Ar, the present observations suggest an existence of a hindering barrier for the radical rotation in solid H_2.

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Introduction

Methyl radical (CH_3) isolated in various matrices has been extensively studied by EPR since the late 50's [1–6]. At low temperatures near 4.2 K, the EPR spectrum of the radical is well-known to consist of for lines with equal intensity 1:1:1:1, instead of the binomial intensity distribution 1:3:3:1. This effect has been first explained by McConnel [7]. The equal intensity of four lines was attributed to the symmetry requirements of the wavefunctions. According to McConnel and Freed [8], three protons are considered to move about the C_3 molecular axis in the matrix in a threefold potential well with a finite barrier height. The lowest torsional rotation energy level is split into two: the lower one of symmetry A and the upper, doubly degenerated one of symmetry E. At sufficiently low temperatures only the lowest spin-rotational A state with four symmetric nondegenerate nuclear spin functions is populated. So the EPR spectrum is a 1:1:1:1 quartet. The rotation is considered to be tunneling one and may occur even at helium temperatures. In such a tunneling rotation, not only the A state but also the E nuclear spin states appear by considering the next higher rotational levels. The EPR transitions corresponding to these states have been first observed for isolated methyl radical in Ref. 5. In contrast to CH_3, a few studies were devoted to deuterated methyl radicals (CD_3, CH_2D, and CHD_2). A spectrum of seven components with «non-binomial» distribution has been predicted for the CD_3 radical [9] at low enough temperatures. The septet has been actually registered in CD_4 matrix [10] at 4.2 K and solid Ar at 13 K [4]. Though these experimental results are consistent with the above theoretical scheme, another observation has been published [5] for CD_3 in Ar at 4.2 K showing a strong singlet superimposed on a weak septet. The authors explained their results with a new model of a three-dimensional, free quantum rotor with no hindering barrier present. They pointed out that the electronic state has to be included in the application of the Pauli principle in order to obtain correct overall exchange symmetry for bosons.

The present study is aimed at studying deuterated methyl radicals in another matrix in order to clarify whether the effect found in [5] is common to other matrices and to obtain new experimental results which would help to verify the free rotation model [5].

Results and discussion

The solid samples under study are obtained by gas condensation on the thin-walled bottom of a quartz finger filled with liquid helium. Located at the center of the microwave cavity of the EPR spectrometer, the bottom is used as a substrate. Both the radiofrequency gas discharge (channel *A*) and the matrix gas flow through a separate inlet tube to avoid the gas discharge (channel *B*) can be cooled down to liquid nitrogen temperature. The products of the gas discharge without intermediate feeding tubes are supplied directly onto the substrate in vacuum preventing their decay on the tube walls. Thus, the sample is obtained directly in the cavity of the EPR spectrometer, allowing an EPR observation of the sample during the condensation and a study of short-lived centres (e.g. free radicals) due to the gas discharge products. A scheme of the experimental set-up has been presented in previous papers [11].

In the presents experiments, molecular deuterium, D_2, mixed with 2 mol % methane, CH_4, was prepared in a glass vessel and passed through the channel *A* with discharge on. Simultaneously, the H_2 was fed through the channel *B*. The latter flow was much larger than the discharge flow, thus providing an admixture of D_2 in H_2 matrix as small as about 1:30. A pulsed discharge has been employed with the off-duty factor of 10. The substrate temperature during the deposition was 4.2 K. Figure 1 shows the EPR spectrum of a sample of solid H_2 with trapped radicals. The experimental spectrum reveals seven strong lines of the CD_3 radical and weak lines for CH_3, CH_2D, and CHD_2 radicals. Superimposed is a record of the high-field lines with a higher gain. The outermost peak is a high-field component of the CH_3 spectrum which is composed of four lines of equal intensity and was studied in H_2 matrix earlier [6]. Three equal-spaced lines constitute a part of the CH_2D spectrum being a triple triplet due to the hyperfine (HF) splittings of two hydrogen nuclei, major triplet, and one deuterium, minor triplets. One of the peaks to the left-side of the high-gained spectrum is a purely CHD_2 component while its right neighbor is composed of the outermost left CD_3 component, CHD_2 line, and the CH_3 transition at $m_F = -1/2$. At high enough temperatures, the CHD_2 spectrum is a double quintet. Thus the spectrum in Fig. 2 is a superposition of several spectra.

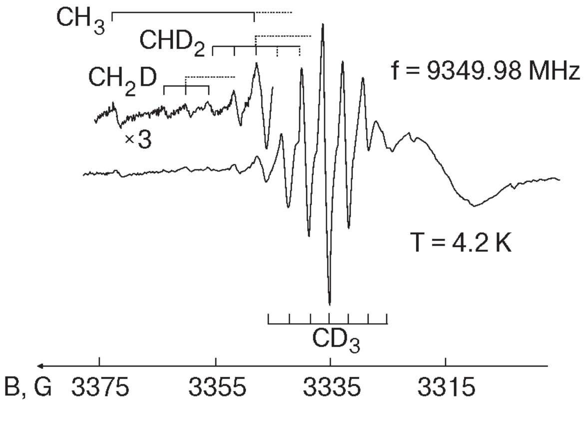

Fig. 1. The EPR spectrum of a solid H_2 sample with trapped methyl radicals. The substrate temperature during deposition T_{sub} = 4.2 K.

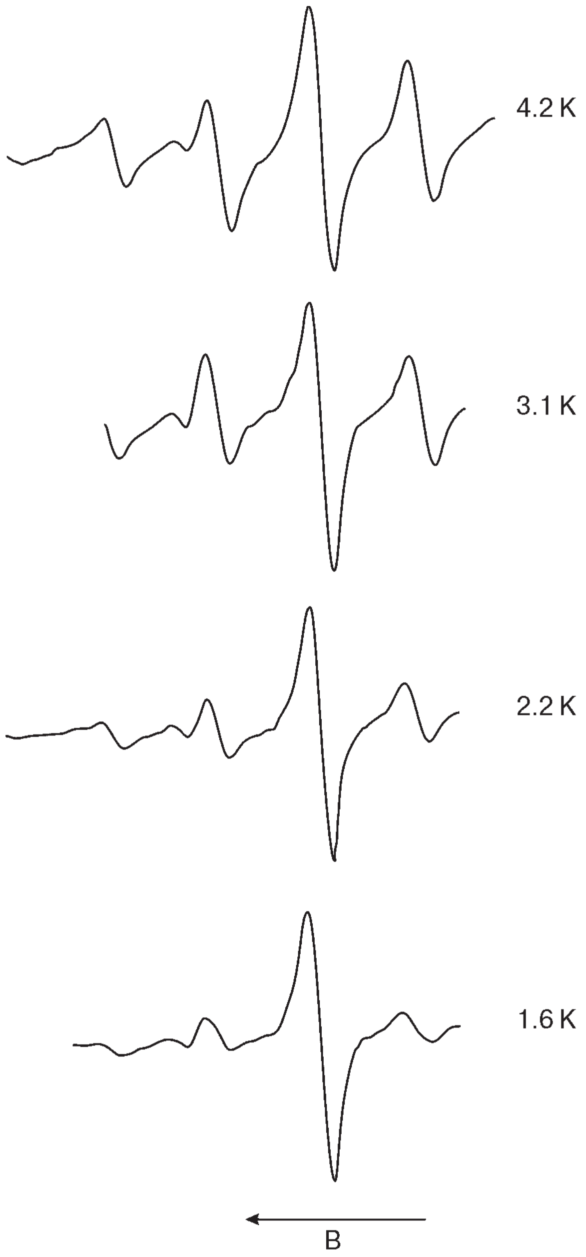

Fig. 2. The central part of temperature-dependent EPR spectra of CD_3 radical in H_2 matrix. The substrate temperature during deposition T_{sub} = 4.2 K.

We have found that seven CD_3 lines are of equal linewidth, $\Delta H = 0.86(6)$ G, with HF splitting $\delta H =$ = 3.59 G. The relative intensity ratio 1:3:6.5:12:6.5:3:1, except for the central line, is close to the «binomial» intensity distribution 1:3:6:7:6:3:1. It was observed in Ref. 5 that at temperatures above 10 K the intensity distribution for CD_3 in Ar is practically «binomial» one originating not only from the population of $J = 0$ but also of higher rotational levels. With lowering temperature down to 4.1 K the central line increased while the other six lines decreased rapidly. As a result, the intensity of the central peak relative to the neighboring one reached 15. It was shown that the spectrum corresponding to the $J = 0$ rotation level is a singlet. Turning to our study, one can conclude that the spectrum of CD_3 in H_2 at 4.2 K is a superposition of the high-temperature nearly «binomial» spectrum and the low-temperature singlet. The above mentioned CH_3 spectrum of four equal lines corresponds to $J = 0$ thus being a low-temperature one. Such a difference between the appearances of the CH_3 and CD_3 spectra is not surprising because the energy gap between $J = 0$ and $J = 1$ rotational states for the free CH_3 is twice as large as the CD_3 gap. Therefore, $J = 1$ state of the CH_3 radical is not populated at low temperatures close to 4 K. We have also found that the CHD_2 spectrum is actually a superposition of a high- and low-temperature spectrum. This will become clear later when describing temperature effects. We have failed to draw conclusion about the CH_2D spectrum appearance, because the central CH_2D triplet could not be seen due to the strong CD_3 transitions superimposed on it. It is seen from Fig. 1 that the CD_3 quantity is well above the others. We have estimated the yields of the deuterated methyl radicals in reference to the CH_3 yield. These were found to be 35:1 for CD_3, 2:1 for CHD_2, and 1.3:1 for CH_2D. Thus, we conclude that methane in our discharge was almost completely deuterated through the intermediate products CH_2D and CHD_2 to the final CD_4 one. The reactions of the methyl isotopomers (CH_3, CH_2D, and CHD_2) with excess deuterium atoms have been studied earlier using discharge flow/mass spectrometry [12].

Figure 2 shows the central part of the CD_3 spectrum taken at several temperatures. One can readily see that the central peak with $m_F = 0$ increases rapidly with decreasing temperature in reference to the neighbor transitions. We have plotted saturation curves, that is intensities of the central and neighbor lines versus microwave power, and found that the high-temperature spectrum shows no saturation in the power range used at both 4.2 K and 1.6 K, whereas the central peak starts to saturate at 4.2 K, reaching a prominent saturation at 1.6 K. Such a difference in the saturation behavior between the lines is a further proof that the central peak is actually a superposition of transitions due to different states.

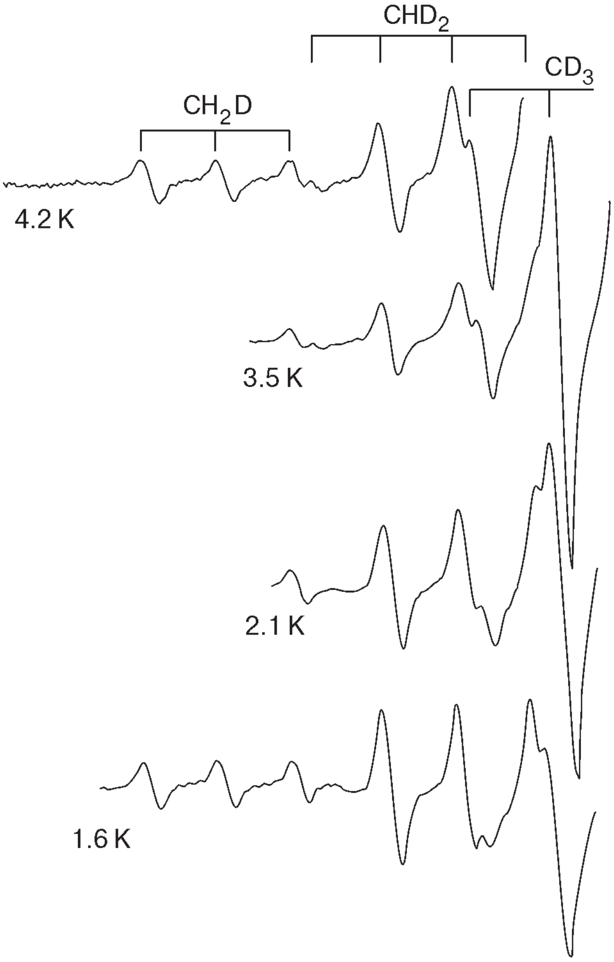

Fig. 3. Temperature-dependent high-field quintet of the spectrum of CHD_2 matrix-isolated in solid H_2. The substrate temperature during deposition $T_{\text{sub}} = 4.2$ K.

Figure 3 shows a change in the shape of the high-field quintet of the CHD_2 spectrum. The outermost left transition ($m_F(\text{D}) = -2$) of CHD_2 is superimposed on the outermost right line of the CH_2D high-field triplet. Here D stands for the splitting due to the deuterium nuclei. The transition at $m_F(\text{D}) = 0$ (the third from the left) of CHD_2 is superimposed on the high-field ($m_F(\text{D}) = -3$) CD_3 line. The next two CHD_2 peaks to the right are not seen against the strong CD_3 components. A high-temperature CHD_2 spectrum exhibits a «binomial» relative intensity ratio 1:2:3:2:1 for the quintet components. It has been found previously [5] that in argon matrix the quintet transforms into a triplet with decreasing temperature from 10 K to 4.2 K. In our experiments, the spectrum of CHD_2 in H_2 was still a double quintet at 4.2 K showing though an intensity distribution significantly different from the binomial one which was evident from the fact that the ratio of the line amplitude at $m_F(\text{D}) = -1$ to the outermost one at $m_F(\text{D}) = -2$ was well above 2. One can see from Fig. 3 that the CHD_2 transition at $m_F(\text{D}) = -2$ disappears, while the line at $m_F(\text{D}) = 1$ becomes more pronounced against decreased high-temperature CD_3 lines. Thus, in H_2 matrix as well, the CHD_2 quintet changes to the triplet with decreasing temperature. This change from high-temperature to the low-temperature spectrum for CHD_2 corresponds very well to the case of CD_3 radical in H_2.

Conclusion

The present results not only verify the effect of temperature on the shape of the CD_3 and CHD_2 spectrum first observed in Ar [5] but give new information when comparing the temperature ranges for these spectrum transformations in Ar and H_2: 10–4.2 K and 4.2–1.6 K, respectively. Since the spectrum changes we discuss are due mainly to changes in the populations of the lowest $J = 0$ and $J = 1$ states of trapped radicals, the difference in the range suggests that the energy interval between the above rotational states is larger in Ar then in H_2. In turn, a decrease of this interval for a trapped molecule in comparison with a free one is due to hindering of the rotation of the molecule in the matrix. Because the interaction energy CD_3–H_2 is lower then that of CD_3–Ar, one may expect a more free rotation of CD_3 in H_2, i.e. a smaller effect on the radical rotation than in Ar. Indeed, solid H_2 is well know to have a small effect on the parameters of various radicals in comparison with many matrices. However, the present result suggests the phonon-rotation coupling for CHD_2 and CD_3 molecules in H_2 to be surprisingly high. This unexpected conclusion requires further theoretical and experimental study.

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