

PARAMAGNETIC RESONANCE OF FREE ATOMS OF THE ALKALI METALS Na, K, AND Rb, STABILIZED IN A MOLECULAR MATRIX AT LIQUID-NITROGEN TEMPERATURES

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The condensation method has been used to produce stabilization of free Na, K, and Rb atoms in benzene at liquid-nitrogen temperatures. A study has been made of the paramagnetic resonance spectra of these atoms. The maximum temperatures have been found up to which these atoms can exist in a matrix of benzene. The hyperfine structure splitting and the g-factors of the stabilized atoms have been determined.

In previous papers [1-4] studies were made of free Ag, Au, and Cu atoms stabilized in various molecular matrices at liquid-nitrogen temperatures. The present paper deals with similar studies of alkali metal atoms.

The alkali metal atoms previously investigated in [5, 6] were stabilized in matrices of noble gases at helium temperatures.

The studies of stabilized alkali metal atoms described below were made at liquid-nitrogen temperatures using molecular matrices.

1. Experimental Method

The samples containing stabilized alkali metal atoms were prepared right in the spectrometer resonator by simultaneous condensation of a beam of atoms and benzene vapor on a surface cooled with liquid nitrogen. The equipment and the method of preparing the samples are described in [7]. The Rb and Cs atoms were obtained from the bromides of these metals mixed with calcium and heated to 600°C. The Li, Na, and K atoms were obtained by evaporating the pure metals. It usually took several minutes to prepare a sample with the ampule containing the benzene at a temperature of about -50°C. Pure grade benzene was used in the experiment.

During evaporation, the nitrogen in the operating Dewar was pumped down to freezing on the sur-

face to lower the temperature of the substrate, which makes the capture process more efficient, and increases the rigidity of the matrix. Consequently, it was found possible to stabilize Na, K, and Rb atoms in a matrix of benzene. In the most successful experiments the number of stabilized Na and K atoms was about 10^{15} , and the number of Rb atoms was $(2-3) \cdot 10^{15}$. Assuming uniform distribution over the volume of the sample, the concentration of stabilized atoms was of the order of 10^{17} cm^{-3} .

Attempts to stabilize Li and Cs atoms in benzene were unsuccessful, which is probably due in the case of Li to diffusion, in the case of Cs possibly to a reaction with the material in the matrix. Nor was it possible to stabilize alkali metal atoms in the other matrices that we investigated - undecane and ethyl alcohol. In ethyl alcohol the alkali metal atoms can apparently be annihilated by the hydrogen substitution reaction, while the reasons why there is no stabilization in undecane are less clear.

The paramagnetic resonance spectra of the stabilized atoms were recorded on a RE-1301 three-centimeter band spectrometer, using the method described in [3].

The hyperfine structure splitting and the g-factors of the stabilized atoms were calculated from the edge lines of the spectra by means of the Breit-Rabi equation [1-4].

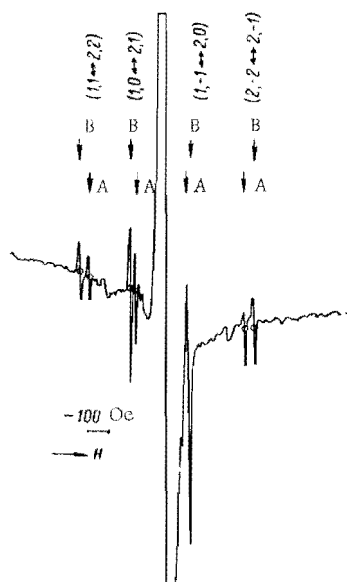


Fig. 1. Paramagnetic resonance spectrum of Na atoms stabilized in benzene at liquid-nitrogen temperatures ($\nu = 9141.5$ Mc).

2. Experimental Results

1. Sodium Atoms. After preparing the sample, pump-off of the nitrogen in the Dewar was stopped, which did not interfere with the stabilization of the sodium atoms.

Sodium has one stable isotope Na^{23} with the nuclear spin $I = 3/2$. The paramagnetic resonance spectrum of sodium atoms in benzene is shown in Fig. 1. The figure shows two spectra, designated as A and B, each consisting of four lines. The doubling of the number of lines in the spectrum is due to the fact that there are two types of capture locations with different environments for the atoms in a matrix of benzene. The letter A designates the capture location which occurs more often than the capture location B (in some experiments stabilization at the locations B did not occur, and the spectrum consisted of the lines of spectrum A

TABLE 1. Hyperfine Structure Splitting and g-Factors of Stabilized Atoms

Atom	$\Delta\nu$, Mc	$\frac{\delta(\Delta\nu)}{\Delta\nu_{\text{free}}}$, %	g_J
Na^{23}	1438.8 ± 5.7	-18.8	2.0029 ± 0.0006
Na^{23} (B)	1615.9 ± 5.7	- 8.8	2.0036 ± 0.0006
K^{39}	363.4 ± 1.0	-21.3	2.0024 ± 0.0008
Rb^{85}	2450.4 ± 10.8	-19.3	2.0046 ± 0.0012

TABLE 2. Hyperfine Structure Splitting and g-Factors of Free Atoms

Atom	I	$\Delta\nu$, Mc	g_J
Na^{23}	$3/2$	1771.63	2.00231
K^{39}	$3/2$	461.72	2.00231
Rb^{85}	$5/2$	3035.74	2.00241

alone), Spectrum B never occurred without spectrum A). The lines corresponding to the transition $(1, -1 \leftrightarrow 2, 0)$ are somewhat masked by the wing of the spectrum of the free radicals formed during condensation of the sample. This spectrum is more than an order of magnitude more intense than the sodium spectrum.

The hyperfine structure splitting $\Delta\nu$ and the g-factors of the stabilized atoms g_J are given in Table 1. The errors shown in Table 1 are the maximum deviations from the mean values in the series of experiments from which the values were obtained. The results for sodium were obtained from five experiments.

The relative shift $\delta(\Delta\nu)/\Delta\nu_{\text{free}}$ is found by comparison with the splittings $\Delta\nu_{\text{free}}$ of the free atoms, the data for which are given in Table 2 [8]. The value of $\delta(\Delta\nu)$ is calculated from the formula $\delta(\Delta\nu) = \Delta\nu - \Delta\nu_{\text{free}}$.

For sodium atoms periodic recordings of the spectra while raising the temperature showed that up to 100°K the spectrum did not exhibit any intensity changes (when held for about a half hour). When the temperature was raised above 100°K the spectra disappeared, with the lines corresponding to the capture location B disappearing at a higher temperature than the A lines. No detailed study of the destruction kinetics was made, but, since the spectra A and B disappeared at different temperatures, the following conclusions could be drawn: 1) the spectra A and B are due to the fact that there are different capture locations with a different environment for the captured atoms in the matrix, and 2) the stabilized Na atoms disappear with increase in temperature as a result of diffusion, rather than by reacting with the material in the matrix (since when diffusion starts depends on the type of capture location, while a reaction would apparently start at the same temperature in different capture locations).

The paramagnetic resonance line widths of stabilized Na atoms measured between the extrema of the derivative of the adsorption line are

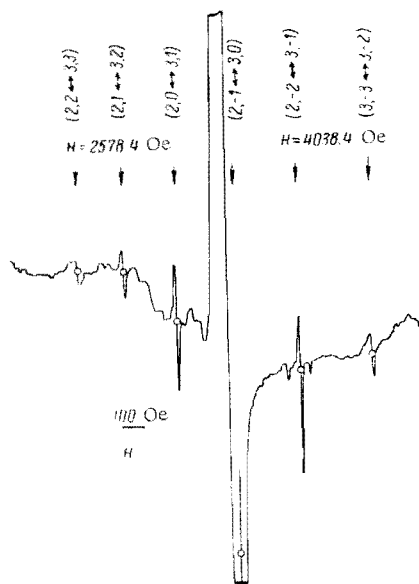


Fig. 2. Paramagnetic resonance spectrum of Rb atoms stabilized in benzene at liquid nitrogen temperatures ($\nu = 9368$ Mc).

equal to approximately 8 and 7 Oe respectively for the transitions $(1, 1 \leftrightarrow 2, 2)$ and $(2, -2 \leftrightarrow 2, -1)$. If the temperature was raised above 100°K , the lines narrowed appreciably, which may be due either to unfreezing the motions of the benzene molecules, or to changes in the structure of the matrix of the nature of phase transitions. No detailed study of this question was made.

2. Potassium Atoms. Natural potassium contains 93% of the isotope K^{39} with the nuclear spin $I = \frac{3}{2}$. Spectra of stabilized atoms of this isotope alone were observed. The spectrum of potassium atoms stabilized in benzene consisted of four lines. The distances between the edge lines of the spectrum was about 200 Oe (for free atoms this distance is about 250 Oe at a frequency of 9400 Mc), so that the whole spectrum was located near $g = 2$, where there was an intense radical spectrum. The transitions $(1, 0 \leftrightarrow 2, 1)$ and $(1, -1 \leftrightarrow 2, 0)$ were located in the wings of the radical spectrum, but the edge lines of the spectrum of the potassium atoms were recorded very clearly, and were used to calculate the hyperfine structure splittings and the g -factors given in Table 1. These results were obtained in a series of 5 experiments. The spectrum of the K^{39} atoms disappeared in about 10 min time when the temperature was raised from 63 to 77°K .

The potassium atoms observed in our experiments were only stabilized in one capture location. The widths of the edge lines were about 6 Oe.

3. Rubidium Atoms. The spectrum of Rb^{85} atoms stabilized in benzene is shown in Fig. 2. The spectrum consists of 6 lines ($I = \frac{5}{2}$). Weak lines, corresponding to the isotope Rb^{87} , which is a factor of 2.5 less abundant in the natural mixture than the main isotope Rb^{85} , were sometimes observed, but they were of too small intensity to make any quantitative treatment of the results of the measurements.

The spectra of the Rb^{85} atoms slowly disappear even with continuous pump-off of the nitrogen in the working Dewar (the intensity decreased by a factor of 2-3 in 40 minutes). The spectra disappeared in several minutes after pump-off of the nitrogen was stopped.

Stabilization of the Rb^{85} atoms occurred in capture locations of only one type. The line widths were about 23 and 16 Oe for the edge transitions $(2, 2 \leftrightarrow 3, 3)$ and $(3, -3 \leftrightarrow 3, -2)$ respectively. The interior lines of the spectrum were somewhat narrower than the edge lines, so that the amplitudes of the first derivatives were greater than those of the edge lines. The results of investigating the spectra of Rb^{85} atoms are given in Table 1. These data were obtained by averaging the results of 6 experiments.

The usefulness of the isotopic Hamiltonian and the Breit-Rabi equation that follows from it in describing stabilized atoms is discussed in [4]. Calculations using the method given in this paper, made for the Rb^{85} atom with the transition $(3, -3 \leftrightarrow 3, -2)$, and for Na^{23} atoms with all the internal transitions for both capture locations show that there are no anisotropic effects in a matrix of benzene.

3. Structure of Benzene and the Place where the Atoms are Captured

The following facts give reason to assume that the benzene matrix is, at least for the most part, crystalline:

1) The deposit builds up in the direction of the temperature gradient (along the normal to the surface of the semicircular bottom of the Dewar on which the sample is being precipitated), and has a grainy structure on cleavage, which may indicate that the sample is polycrystalline, with the grains oriented in the direction of the temperature gradient. Growth of such structures for other substances under similar conditions is indicated in [9, Chapter 9];

2) The results of an x-ray structure analysis of deposits of various substances obtained by freezing out vapors at a quite high condensation rate

show that for the majority of substances the deposits are crystalline [9, Chapter 9], and

3) The occurrence of different capture locations in benzene, and the narrowness of the lines agree with the assumption that the atoms are stabilized in a crystalline phase.

The crystal structure of benzene has the face centered unit cell P_{6ca} . At -195°C the dimensions of the cell are as follows: $a = 7.277 \text{ \AA}$, $b = 9.452 \text{ \AA}$, and $c = 6.728 \text{ \AA}$ [10].

The Van der Waals half-thickness of the benzene molecule is 1.85 \AA . The dimensions of the Na, K, and Rb atoms are such that they are found in capture locations where separation of the lattice has occurred. It is evidently impossible to take account of this lattice separation in the theory [5, 11], so that the hydrogen and carbon atoms forming the benzene molecule are at various distances from the stabilized atoms.

It may be assumed that the sodium atoms, for which two types of capture locations occur, are stabilized in a substitutional position of the benzene lattice, and in an interstitial site – in the center of a somewhat distorted octahedron, while the potassium and rubidium atoms, which are of larger size than the sodium atoms, are only stabilized in the substitutional position, where there is more room than in the octahedral position.

4. Conclusions

The results of this paper thus show that it is possible to stabilize Na, K, and Rb atoms at liquid-nitrogen temperatures, and in a molecular matrix.

The paramagnetic resonance spectra of stabilized atoms are easily recorded, so that it is possible to make quantitative calculations and interpret the results of the experiment.

An important result of the work is that there are large negative shifts $\delta(\Delta\nu)/\Delta\nu_{\text{free}}$ in the hyperfine structure splitting. For Na^{23} , K^{39} , and Rb^{85} , these shifts are -18.8 , -21.3 , and -19.3% respectively, and are of nearly the same value for atoms of the different elements. Such large negative shifts in stabilized atoms in the $^2S_{1/2}$ state are of great interest from the point of view of theory [5, 11], and show that Van der Waals forces predominate in the interaction between the captured atom and the matrix.

Within the limits of accuracy of the experiment, the g-factors of the stabilized atoms are practically the same as the values for free atoms, which shows that there is spherical symmetry in the external electron cloud, i.e., the S-state of the atom is maintained.

The fact that no monotonic character is observed in the matrix shifts on going from sodium to potassium and from potassium to rubidium is not inconsistent with the theoretical ideas of [5] and [11], since the increase in the negative shift resulting from increase in the polarizabilities in the order Na, K, Rb may be made up for by the positive contribution to the matrix shift, which increases with increase in size of the atom in the series of alkali metals.

Preliminary studies of the temperature dependence of the paramagnetic resonance spectra of stabilized atoms show that it is possible to investigate the disappearance kinetics of the atoms and obtain information on the mechanism of the disappearance, as well as on the changes in structure of the matrices with change in temperature. All these questions require special study.

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