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Fluorine Magnetic Resonance in Xenon Tetrafluoride

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Intrigued by the beautiful result of the Argonne National Laboratory group in synthetizing xenon tetrafluoride[1] we thought it worthwhile to look into the nuclear magnetic resonance spectra of this extraordinary compound, as no such study was announced by the authors.

It is expected that ^{129}Xe and ^{131}Xe resonances could yield important information regarding the molecular structure and bonding in XeF_4. (Such measurements are under way in the »Jozef Stefan« Institute for Nuclear Research.) However, the fluorine spectra are of interest for the same reason, and also in view of the suggestion by the Argonne group, that there are two (high- and low-temperature) cristaline modifications of XeF_4. The work reported here was made possible by the readiness and efficiency with which J. Slivnik and his group at the »Jožef Stefan« Institute kindly supplied the xenon tetrafluoride sample.

The spectra shown in Fig. 1 were recorded with a conventional bridge-type spectrometer. The low-temperature spectra were carefully taken at different RF-levels and the presented results are saturation free.

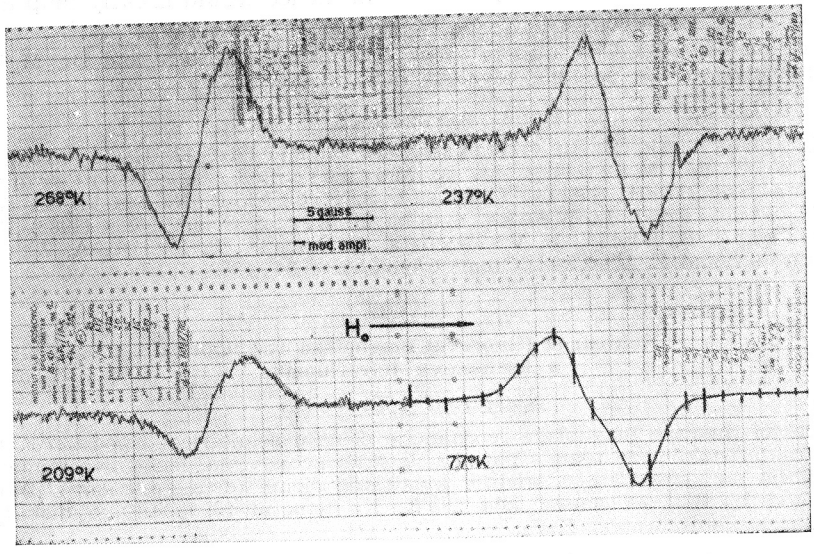

Fig. 1. Fluorine magnetic resonance spectra of XeF_4. (The line at 77°K was measured point by point.)

There are two temperature regions regarding the shape of the fluorine resonance lines: (1) between room temperature and 237°K the lines are symmetrical and, (2) below 237°K the spectra are unsymmetrical with tailing-off characteristic for substances with paramagnetic properties. This is in agreement with the findings of Slivnik *et al.*[2] in that the diamagnetic susceptibility »becomes temperature dependent« below 237°K (with decreasing negative values). It is not known if this temperature corresponds also to the change in the crystalline modification reported by the Argonne group[1]. Further experiments on the field- and temperature-dependence (including shifts if any) of these spectra which are in course will enable us to discuss the observed effect in details.

There is no appreciable change in the shape of the symmetrical lines, but the second moment at room temperature is 2.7 gauss^2 and 3.5 gauss^2 at 237 and 268°K. With an overall uncertainity in these values of 0.3 gauss^2, the diference may well be real and due to some kind of molecular reorientation, a point to be looked into yet in more detail. However, the substance is purely diamagnetic in the high temperature region (see also *loc. cit.* 2). Thus, to start with, the second moment of 3.5 gauss^2 may be used in discussing the possible molecular structure of XeF_4. This value sets an upper limit for the molecular dimensions. If any molecular reorientation does take place, then the rigid lattice value for the second moment should be greater and the following reasoning is even more substantiated.

On supposing a covalent radius for fluorine of 0.72 Å and for xenon a value close to that of iodine, 1.33 Å, the second moment of a tetrahedral XeF_4 molecule (accounting for the Xe-isotopes contribution) is 0,760 gauss^2. This is only about one fifth of the experimental value and implies an unusually high intermolecular contribution, or, perhaps suggests smaller Xe—F distances then assumed here. Other molecular configurations are also conceivable, but they are not expected to change the situation appreciably. A knowledge of at least the Xe — Xe distances in the crytal lattice would greatly help making more definite conclusions.

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IZVOD

Nuklearna (fluorova) magnetska rezonancija u ksenonovu tetrafluoridu

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Spektri fluorove magnetske rezonancije postaju asimetrični ispod 237°K s oblikom karakterističnim za tvari s paramagnetskim svojstvima. Iznad ove temperature oblici linija su simetrični, a srednje kvadratne širine (drugi momenti) iznose 3.5 gausa^2 kod 237°K i 2.7 gausa^2 kod 293°K. Na temelju tih podataka diskutira se molekularna konfiguracija XeF_4.

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