Indirect NMR detection of ^{235}U in gaseous uranium hexafluoride

I. Ursu, D.E. Demco, M. Bogdan, P. Fitori, A. Darabont

► To cite this version:

I. Ursu, D.E. Demco, M. Bogdan, P. Fitori, A. Darabont. Indirect NMR detection of ^{235}U in gaseous uranium hexafluoride. Journal de Physique Lettres, 1985, 46 (11), pp.493-497. 10.1051/jphyslet:019850046011049300 . jpa-00232549

HAL Id: jpa-00232549

<https://hal.science/jpa-00232549>

Submitted on 1 Jan 1985

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification
Physics Abstracts
33.25

Indirect NMR detection of ^{235}U in gaseous uranium hexafluoride

I. Ursu

National Center for Physics, P.O. Box MG-6, Bucharest, Romania

D. E. Demco

Polytechnical Institute, 3400 Cluj-Napoca, Romania

M. Bogdan, P. Fitori and A. Darabont

Institute for Isotopic and Molecular Technology, P.O. Box 700, 3400 Cluj-Napoca, Romania

(Reçu le 24 janvier 1985, accepté le 15 avril 1985)

Résumé. — On discute la possibilité d'utiliser la résonance magnétique nucléaire pour la détection indirecte du noyau ^{235}U dans le UF_6 gazeux. L'examen de la raie d'absorption du ^{19}F appartenant au UF_6 gazeux isotopiquement enrichi a révélé la dépendance de la largeur à mi-hauteur dans la concentration de ^{235}U . Le mécanisme de relaxation responsable de cet effet d'enrichissement est le couplage scalaire indirect ^{19}F - ^{235}U modulé par la relaxation quadrupolaire de ^{235}U .

Abstract. — The possibility to use nuclear magnetic resonance in indirect detection of the ^{235}U nucleus in gaseous UF_6 is discussed. The ^{19}F absorption spectra linewidths in gaseous UF_6 was investigated as a function of ^{235}U enrichment, revealing a dependence on the isotope concentration. The ^{19}F - ^{235}U indirect scalar coupling modulated by ^{235}U quadrupole relaxation is the relaxation mechanism responsible for this enrichment effect.

Recent measurements [1-7] showed that the nuclear magnetic resonance may provide a method to determine the presence of ^{235}U in liquid uranium hexafluoride.

The first proposed indirect method [2-4] consists in measuring the transverse relaxation time of ^{19}F , which is dominated by ^{19}F - ^{235}U indirect scalar interaction modulated by ^{235}U quadrupole relaxation, and therefore depends on the ^{235}U isotope enrichment. The ^{235}U isotope has a relatively high value of electric quadrupole moment (6.4 barns) [8], and consequently small dynamic distortions of the UF_6 octahedral symmetry represent an efficient relaxation mechanism.

The ^{235}U nuclear magnetic resonance signal has a poor signal-to-noise ratio as a consequence of a small magnetogyric ratio and short spin-lattice relaxation time. Despite this, a direct observation of ^{235}U NMR signal in liquid UF_6 at $B = 11.747$ T has been recently reported [7].

The aim of this Letter is to investigate the effect of the ^{235}U enrichment on the ^{19}F NMR spectra in gaseous UF_6 . Using this indirect method, it is not possible to detect the Larmor resonance frequency of the ^{235}U isotope and consequently no pseudo-enrichment effect related to the presence of impurities could be detected. Based on physical properties of uranium hexafluoride molecule in the gas phase it is possible to predict [9] the existence of a dependence for

^{19}F NMR parameters on the ^{235}U concentration. It is possible to elaborate *a priori* two distinct models for such an enrichment effect. These are based on the following considerations.

(i) In the gas phase as in liquid phase of UF_6 a ^{19}F - ^{235}U indirect scalar coupling mediated by molecular electrons is present.

(ii) The indirect scalar interaction could be thermally modulated by rapid ^{235}U quadrupole relaxation. Since this isotope has a relatively high value of the electric quadrupole moment, the small dynamic distortions induced by molecular collisions of regular octahedron UF_6 molecule in the gas phase, should be an efficient relaxation mechanism.

(iii) Our recent results [10] show that in the UF_6 gas with ^{235}U in natural abundance, for relatively small density values, the prevailing relaxation mechanism is represented by the spin-rotation interaction modulated by molecular collisions.

The dependence of the relaxation rates on gas temperature T and density ρ , acquires the form,

$$1/T_1 = 1/T_2 = A \frac{T^{1.5}}{\rho} \quad (1)$$

where A is a constant which depends on the physical parameters of the molecule.

The first model for the enrichment effect in gaseous UF_6 is based on the multiplet resolved structure which is expected *a priori* to exist for gaseous UF_6 spherical molecule. The ^{235}U isotope has a magnetic moment ($S = 7/2$) which means that the ^{19}F - ^{235}U scalar coupling will generate a multiplet structure in the ^{19}F NMR absorption spectra described by frequencies of,

$$\nu = \nu_0 + JM_s \quad (2)$$

where ν_0 is the Larmor frequency of ^{19}F nucleus, M_s is the magnetic quantum number, and J is the ^{19}F - ^{235}U scalar coupling constant. Since the J coupling constant for liquid MoF_6 and WF_6 is 47 Hz and 44 Hz respectively [11] and is expected not to be essentially different for the liquid and vapour phase, it is estimated that for gaseous UF_6 , the distance between the extreme satellite lines will be of the order of 300 Hz. The multiplet resolved structure could be concealed by the mechanism of line broadening related to the spin-rotation relaxation. The efficiency of this mechanism is diminished by increasing the density of the gas (see Eq. (1)).

The second possible model which predicts an enrichment effect is related to the collapsing of the multiplet structure due to rapid fluctuation of ^{235}U magnetic moment, a consequence of the short quadrupolar spin-lattice relaxation of ^{235}U . If the fluctuation frequency is of the order of indirect scalar coupling constant J , one expects the collapse of the multiplet structure and the emerging spectrum will be a single broad line.

In order to test which of the above models is valid, NMR measurements were made at 84.754 MHz on UF_6 saturated vapours in equilibrium with the liquid phase. The Fourier transform NMR spectra of ^{19}F nucleus were recorded with a Bruker SXP pulse spectrometer using a high resolution magnet and an « Aspect 2000 » computer. The temperature was stabilized within ± 0.5 K. The spectra linewidths were measured with an accuracy of ± 0.3 Hz for non-rotating samples. The samples were specially prepared in order to minimize the presence of impurities (especially HF and paramagnetic impurities), and sealed in 5 mm o.d., 4 mm i.d. quartz tubes.

The ^{19}F Fourier transform NMR spectra were used for measuring the HF content in saturated vapour UF_6 samples. The sample with molecular concentration $\text{UF}_6/\text{HF} = 1/4$ has a linewidth at half height 1.6 times smaller than that for a sample in which no trace of HF was detected. The measurements were performed at $T = 328$ K. That is the reason why for the low density saturated vapours of UF_6 , in equilibrium with the solid phase at $T = 325$ K, the ^{19}F NMR spectra did not reveal any systematic ^{235}U concentration dependence [3]. At high temperatures,

for saturated UF_6 vapour in equilibrium with the liquid UF_6 the effect of HF accidentally present during the sample preparation is negligible because the UF_6 gas pressure is very high in these experimental conditions. Contrary to the behaviour of liquid UF_6 , the influence of paramagnetic impurities which might come from the radiolysis of UF_6 can be totally excluded for gaseous UF_6 .

The ^{19}F NMR spectrum of saturated UF_6 vapours, 93.29 % enriched in ^{235}U at $T = 393\text{ K}$ was recorded. No multiplet structure was put in evidence. The linewidth at half height is $\Delta\nu_{1/2} = 163 \pm 0.3\text{ Hz}$ and a spectral width of 1.2 kHz was used. At this temperature the UF_6 vapour pressure is 6.61 atm. and the density is 84.9 kg/m^3 . For this density value the efficiency of the spin-rotation relaxation mechanism is substantially diminished and a possible multiplet structure should be detected.

The simultaneously recorded NMR spectrum of ^{19}F in vapour and liquid UF_6 with ^{235}U in natural abundance is presented in figure 1. A chemical shift of 10.6 ppm for ^{19}F signal in the vapour phase relatively to the liquid phase was put in evidence.

The ^{19}F NMR spectra of liquid and vapour UF_6 phase, for 0.71 %, 49 % and 93.29 % ^{235}U enrichment were separately and simultaneously recorded at $T = 363\text{ K}$. The spectral width was 10 kHz and 256 scans were used. The linewidths at the half height of the ^{19}F NMR absorption line for these nonrotating samples are presented in table I.

Fig. 1. — ^{19}F NMR absorption spectrum in liquid and gaseous UF_6 (^{235}U in natural abundance) at $T = 383\text{ K}$, simultaneously recorded.

Table I. — The linewidths at the halfheight ($\Delta\nu_{1/2}$) for the ^{19}F NMR absorption line for nonrotating samples of liquid and saturated vapours of UF_6 recorded at $T = 363\text{ K}$ for different values of ^{235}U enrichment.

E (%)	Liquid $\Delta\nu_{1/2}$ (Hz)	Saturated vapours $\Delta\nu_{1/2}$ (Hz)
0.71	20	256
49.00	50	265
93.29	85	287

Fig. 2. — Temperature dependence of the ^{19}F NMR linewidths spectra for saturated UF_6 vapours with 0.71 %, 49 % and 93.29 % ^{235}U enrichment.

The ^{19}F NMR absorption spectra linewidths in saturated UF_6 vapours in equilibrium with liquid UF_6 in the temperature range $333 \leq T \leq 363$ K, for different values of ^{235}U enrichment are presented in figure 2.

It is possible to make an order of magnitude estimation for the enrichment effect detected in UF_6 gas. The linewidth modification induced by various ^{235}U enrichments is related to the ^{19}F - ^{235}U indirect scalar interaction, modulated by rapid ^{235}U quadrupole relaxation. The contribution to the linewidth due to enrichment effect, for ^{19}F NMR spectra recorded on $^{235}\text{UF}_6$ molecules (enrichment in ^{235}U isotope, $E = 100$ %), could be described by the relation [2],

$$\Delta\nu_{1/2} \cong \frac{21}{4} J^2 \left[T_U + \frac{T_U}{1 + (\omega_F - \omega_U)^2 T_U^2} \right] \quad (3)$$

where T_U is the ^{235}U nuclear magnetic relaxation time. An order of magnitude estimation for T_U can be obtained from the measurement of ^{235}U linewidth spectrum recorded at $T = 380$ K in liquid UF_6 [7]. We suppose that for the gaseous phase the value of $T_U \cong 20 \mu\text{s}$ is valid and $J \cong 50$ Hz. Using these parameters we obtain from equation (3) for the contribution of the enrichment effect to the linewidth the value $\Delta\nu_{1/2} \cong 10$ Hz, which is in satisfactory agreement with our experimental results, $\Delta\nu_{1/2}(E = 93.29 \%) - \Delta\nu_{1/2}(E = 0.71 \%) \cong 30$ Hz.

In conclusion, an enrichment effect similar to the effect put in evidence for liquid UF_6 , was also detected for gaseous UF_6 . The linewidth modification induced by various ^{235}U enrichments is related to the ^{19}F - ^{235}U indirect scalar interaction modulated by rapid ^{235}U quadrupole relaxation.

A detailed study of the ^{235}U enrichment effect on the longitudinal and transverse relaxation times of ^{19}F in gaseous UF_6 will be published elsewhere.

Acknowledgments.

The authors are indebted to Dr. P. Rigny and Dr. J. Virlet for a critical reading of the manuscript and valuable suggestions.

References

- [1] URSU, I., *Magnetic Resonance in Uranium Compounds* (in Romanian) (Ed. Acad. R.S.R. Bucharest) 1979. *Magnity rezonans v soyedineniyah urana* (in Russian) (Energestomizdat, Moscow) 1983.
 - [2] URSU, I., DEMCO, D. E., SIMPLACEANU, V., VÎLCU, N., *Rev. Roum. Phys.* **19** (1974) 605.
 - [3] URSU, I., DEMCO, D. E., SIMPLACEANU, V., VÎLCU, N., *Rev. Roum. Phys.* **22** (1977) 705.
 - [4] URSU, I., DEMCO, D. E., BOGDAN, M., DARABONT, AL., FITORI, P., GRODESCU, R., VÎLCU, N., *Rev. Roum. Phys.* **27** (1981) 451.
 - [5] SEPPELT, K., BARTLETT, N., *Z. Anorg. Allem. Chem.* **436** (1977) 122.
 - [6] IORGA, Z. V., KUCEIAEV, A. G., LEBEDEV, V. A., *Koord. Him.* **7** (1981) 145.
 - [7] LE BAIL, H., CHACHATY, C., RIGNY, P., BOUGON, R., *J. Physique Lett.* **44** (1983) L1017.
 - [8] DORIAN, P. B., HUTCHINSON, C. A., WONG, E., *Phys. Rev.* **105** (1957) 1307
 - [9] URSU, I., DEMCO, D. E., BOGDAN, M., FITORI, P., preprint CS-8-1983.
 - [10] URSU, I., DEMCO, D. E., BOGDAN, M., FITORI, P., DARABONT, A., Proc. XXII-nd Congress Ampere, Zürich, (1984) p. 307.
 - [11] RIGNY, P., DEMORTIER, A. D., *C. R. Hebd. Séan. Acad. Sci. Paris, Ser. II* **263** (1966) 1408.
-