

Magnetic hyperfine structure of the quadrupole spectrum of the CH_3I molecule

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(Submitted November 18, 1976)

Pis'ma Zh. Eksp. Teor. Fiz. **25**, No. 1, 14–17 (5 January 1977)

A new pulsed spectrometer has been developed for the observation of quadrupole spectra of molecules, the magnetic hyperfine structure of the quadrupole spectrum of the molecule $\text{C}^{12}\text{H}_3\text{I}^{127}$ has been resolved, and Fermi resonance has been observed between the levels $J = K = 3$, $F_1 = 9/2$, and $F_1 = 7/2$.

PACS numbers: 35.20.Sd

1. The absorption spectrum corresponding to transitions between levels of the quadrupole hyperfine structure of a molecule in a given rotational state (quadrupole spectrum) lies in the case of the CH_3I molecule in the decimeter band, where the Doppler broadening is less than 1 kHz, which makes it possible in principle to obtain a higher resolution than in the case of observation of the rotational spectrum in molecular beams.^[1] However, owing to the low intensity of the quadrupole spectra, they must be observed by a double-resonance method, when the simultaneous action of the strong pump field and the signal field leads to a Stark broadening of the energy levels, and the observed line width turns out to be much larger than the Doppler width.

2. We obtained an appreciable line narrowing (Fig. 1) by separating in time the action of the pump field and the signal field. The experimental setup is shown in Fig. 2(a). The investigated gas is in a coaxial resonator 1 at a pressure on the order of 10^{-4} Torr. The resonator diameter is 40 cm. The

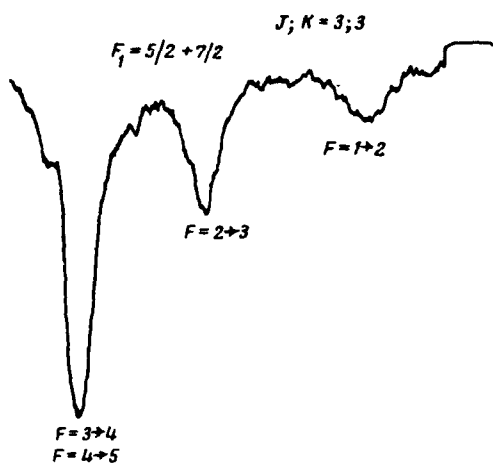


FIG. 1. Magnetic structure of quadrupole spectra. Pressure 8×10^{-5} Torr, frequency marker spacing 1 kHz.

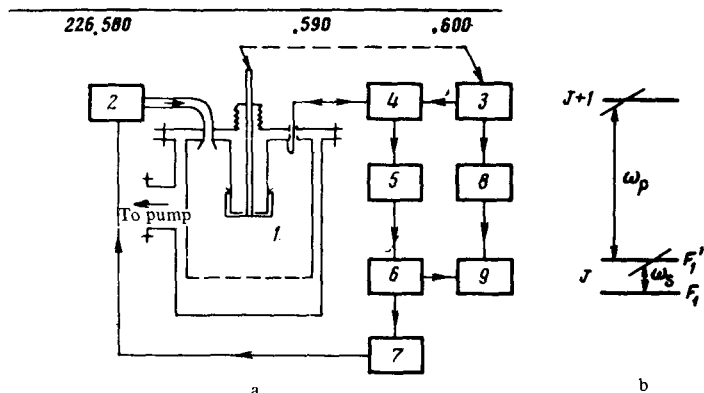


FIG. 2. a) Experimental setup: 1—resonator, 2—klystron, 3—decimeter-band generator, 4—hybrid ring, 5—superheterodyne receiver, 6—synchronous detector, 7—modulator, 8—frequency meter, 9—automatic recorder, b) working-level scheme.

resonator is the absorbing cell of the superheterodyne balanced decimeter-band radiospectrometer. The pump radiation frequency ω_p , which is close to the corresponding frequency of the rotational transition (Fig. 2b), is modulated by a sine or sawtooth wave, the deviation of the frequency being such that the inhomogeneous line widths, including the Doppler width of the rotational transition, is traversed within a time much shorter than the modulation period. Thus, the molecule is at resonance for most of the time only with a weak field of frequency ω_s close to the frequency of the quadrupole transition, and there is practically no Stark broadening by the pump field.

The output signal of the spectrometer is a periodic sequence of pulses obtained from the output of the receiver 5 and averaged by the synchronous detector 6. The pulses repetition frequency is double the modulation frequency. The pulses correspond to nonequilibrium absorption at the frequency ω_s , which takes place after each passage of the pump frequency through resonance, and which attenuates within the time between the collisions of the molecules with one another or with the resonator walls. The sinusoidal 300-Hz voltage that modulates the frequency of the pump generator 2, and the reference voltage for the synchronous detector 6 (in the form of rectangular pulses with a repetition frequency 600 Hz) are produced by a generator. When the decimeter-band generator 3 is slowly tuned mechanically and the resonator 1 is tuned in synchronism, the quadrupole-spectrum line is registered by the automatic recorder 9.

3. The electric and magnetic interactions in the CH_3I molecule are analogous to the same interactions in the NH_3 molecule. We therefore use the formulas of^[2], retaining the same notation (see also the erratum in^[3]).

The magnetic splitting of the quadrupole spectrum is the result of the following:

I. The I-J interaction, which is proportional to

$$S = A + C \frac{K^2}{J(J+1)}, \quad (1)$$

where I is the combined spin of the protons and the constants A and C are determined by the magnetic field of molecule and can be obtained only from experiment.

II. The spin-spin interaction of the protons and the iodine nucleus, with an interaction constant D_1 that is independent of J or K .

III. The spin-spin interaction between the protons, with a constant D_3 likewise independent of J or K . The constants D_1 and D_2 can be calculated with sufficient accuracy from the known magnetic moments of the nuclei and the structural parameters of the molecule. In the presence of magnetic splitting, the state of the molecule is characterized by the quantum numbers J , K , F_1 , and F , while the selection rules for the quadrupole spectrum are

$$\Delta K = \Delta J = 0; \quad \Delta F_1 = \pm 1 \quad \text{and} \quad \Delta F = 0, \pm 1.$$

The quadrupole spectrum of the CH_3I molecule (the spin of iodine is $5/2$) contains several pairs of levels with equal first-order energy; the distance between the levels, determined by the second-order quadrupole effect, is approximately 1 MHz. Such pairs can be subject to the effect of mutual "repulsion" of the levels, analogous to the Fermi resonance in the vibrational spectrum. Thus, for the pair of levels $J=K=3$, $F_1=9/2$, and $F_1=7/2$ (Fig. 3b), Fermi resonance is produced by all three interactions I, II, and III.

4. The use of a pulsed method has made it possible to resolve the magnetic structure of the quadrupole spectrum of the $\text{C}^{12}\text{H}_3\text{I}^{127}$ molecule at a line width 2 kHz and at a frequency-measurement accuracy ± 0.2 kHz. One of the magnetic multiplets is shown in Fig. 1. For each value $J=K=2, 3$, and 4 we measured the frequencies of 4 transitions and calculated the value of the I-J interaction S (at $D_1=0.97$ kHz and $D_3=20.4$ kHz calculated from the structure of the molecule). It turned out that at $J=K=2$ (as well as $J=K=4$), the two magnetic multiplets give practically identical values of S , Fig. 2(a). At the same time, the two multiplets with $J=K=3$:

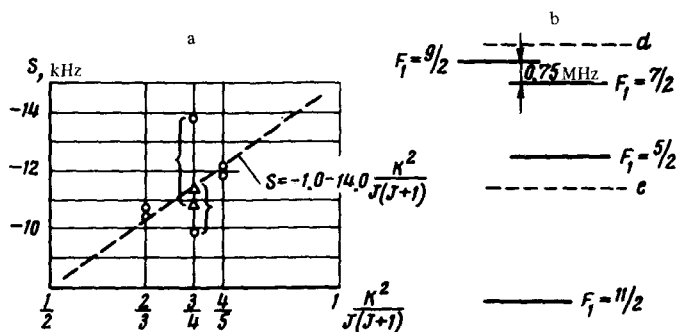


FIG. 3. Dependence of S on J and K . Accuracy along the vertical axis ± 0.3 kHz. b) Energy levels for $J=K=3$; d—position of the levels $F_1=9/2$ and $F_1=7/2$, which coincide in first-order approximation.

$$F_1 = 11/2 \rightarrow 9/2 \left\{ \begin{array}{ll} F = 5 \rightarrow 4 (444655.3; & + 1.29) \\ F = 7 \rightarrow 6 (444664.1; & 0.00) \end{array} \right. \quad \text{and}$$

$$F_1 = 5/2 \rightarrow 7/2 \left\{ \begin{array}{ll} F = 2 \rightarrow 3 (226584.1; & - 1.25) \\ F = 1 \rightarrow 2 (226595.3; & 0.00) \end{array} \right.$$

(the parentheses contain the measured frequency and the calculated corrections to them for the Fermi resonance, in kHz) yield substantially different values of S . On the other hand, inclusion of the corrections for the Fermi resonance yields the values marked by the triangle in Fig. 2(a), in good agreement with the linear dependence of S on $K^2/J(J+1)$.

¹J. Burie, D. Boucher, and J. Demaison, and A. Dubrulle, *Mol. Phys.* **32**, 289 (1976).

²S. G. Kukolich, *Phys. Rev.* **156**, 83 (1967).

³S. G. Kukolich, *J. Chem. Phys.* **57**, 869 (1972).