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## Microwave spectroscopy of molecular Van der Waals complexes in astrophysical studies

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The study of the composition of galactic molecular clouds is one of the most exciting problems of radio astronomy. In these clouds, which represent the remnants of protostellar matter, some hundred different molecules have already been found, including quite complex ones. However, molecular Van der Waals complexes, which are formed at the very first stage of condensation of matter and are very sensitive to the parameters of interstellar matter, have not been found so far. The reason is that reliable data on the millimeter spectra of the R-CO complexes (where  $R - H_2$ , He) most widespread in space are absent so far.

These complexes have a quite small bonding energy (20-30 K), and therefore, their production at a concentration sufficient for spectral measurements under laboratory conditions is a difficult problem. A comparatively high concentration of molecular complexes can be achieved upon expansion of a gas mixture to vacuum through a supersonic nozzle (a supersonic molecular jet). This method was used to obtain the millimeter spectra of Ar-CO [1]. However, because of the small dimensions of a supersonic molecular jet, the sensitivity of conventional single-pass radio spectrometers is insufficient for measuring complexes of CO with lighter rare gases <sup>1</sup>.

At the Institute of Spectroscopy, RAS, a molecular spectrometer based on a highly stable generator of millimeter waves, an orotron [2, 3], was developed. The basic feature of the spectrometer is that an absorbing cell with the gas under study is located inside a multipass resonator of the orotron, thereby providing a great absorption length. This results in a substantial increase in the sensitivity of absorption measurements compared to single-pass schemes.

In 1996, we began the development of a similar instrument with a supersonic molecular jet passing through the orotron resonator. Researchers of the Institute of Spectroscopy, RAS, the Institute of Metrology of Time and Space (VNIIFTRI), and the First Physical Institute of Cologne University are engaged in the project. To provide high pumping out of a residual gas, the orotron was located, together with a focusing magnet, inside a vacuum chamber near the molecular jet source (Fig. 1). In the orotron body, large holes were made through which the jet passes and the remaining gas is pumped out. Because the vacuum chamber was pumped out with a comparatively small diffusion pump (the pumping rate was approximately  $1000 \text{ l s}^{-1}$ ), the jet source operated in a pulse regime (the pulse duration  $\tau_p \approx 1.5-2$  ms and the repetition rate was 10-15 Hz). To increase the sensitivity of absorption measurements, the frequency of orotron radiation was modulated, and the output signal from the detector was amplified with a phase-sensitive amplifier tuned to the second harmonic of the modulation frequency. The time constant of the output filter of the amplifier was approximately  $0.5\tau_p$ . Signals from successive pulses from the jet were summed with a stroboscopic integrator. The radiation



Figure 1. Orotron with a molecular jet passing through its resonator [4].

frequency was continuously varied and measured during experiments.

The sensitivity of the spectrometer was measured from the value of the absorption signal on the J = 1-0 rotational transition of rare isotopomers of the CO molecule ( $^{12}C^{17}O$ ) in a natural isotopic mixture and was found to be two orders of magnitude higher than that of single-passage schemes.

Figure 2 shows a second derivative of the absorption spectrum recorded in the region of the J = 1-0 transition of the  ${}^{12}C^{17}O$  molecule. Upon measuring this spectrum, the radiation power and the frequency modulation amplitude were chosen in such a way that the narrow spectral holes



Figure 2. Second derivative of the absorption signal at the J = 1-0 transition in the <sup>12</sup>C<sup>17</sup>O molecule; *F* is the hyperfine quantum number [4].

 $<sup>^1</sup>$  The bond energy of the complex and its concentration in a jet decrease with decreasing mass of the atom R because of lower polarizability. The same is true for N<sub>2</sub> and H<sub>2</sub> molecules.

caused by the hyperfine splitting of the transition due to the interaction with a spin of the <sup>17</sup>O nucleus were observed. The width of the holes ( $\approx 50$  kHz) was close to the inverse time of flight of the molecules through the region of the electromagnetic field in the resonator, which determines the limiting spectral resolution of the spectrometer.

The high sensitivity of the spectrometer made it possible to measure a number of transitions in the rotational spectra of the R-CO complexes in the 100–140 GHz range, where R = Ne, He, N<sub>2</sub>, and H<sub>2</sub>. So far, only spectra of Ne-CO have been observed in the microwave region (in the centimeter wavelength region). Figure 3 shows the recording of the Jjl = 110-000 transition (J is the total rotational moment, j is the rotational moment of CO, and l is the rotational moment for CO retarded) in the H<sub>2</sub>-CO complex. The transition frequencies were determined with an accuracy of 50-100 kHz, which is sufficient for the search for spectral lines of these complexes in space. Preliminary experimental results were published in [4].



**Figure 3.** Second derivative of the absorption signal at the rotational transition of the H<sub>2</sub>-CO complex.

Note that spectroscopy of these complexes is of great interest for the study of Van der Waals forces, because it permits the measurement of the inertia moment and, hence, the distance between monomers with high accuracy. At present, these experiments are being continued.

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# Infrared spectroscopy of new spin-Peierls compounds

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The paper presents a review of studies of the quasi-onedimensional crystals  $CuGeO_3$  and  $NaV_2O_5$  with the spin-Peierls transition, performed during two last years in the Department of Solid-State Spectroscopy of the Institute of Spectroscopy, RAS.

First, we briefly explain the meaning of the spin-Peierls transition and consider its features of interest. The spin-Peierls transition represents a phase transition in a system of Heisenberg antiferromagnetic chains of half-integer spins interacting with a three-dimensional phonon field [1]. After the phase transition, magnetic atoms in the chain come close together in pairs and form nonmagnetic dimers. In this case, the magnetic susceptibility tends to zero isotropically over all directions. A gap appears in the spectrum of magnetic excitations, which separates the ground singlet state from the first excited triplet state. The gain in the magnetic energy  $\Delta E_{\rm mag} \sim -u_0^2 |\ln u_0|$  (here,  $u_0$  is the amplitude of atomic displacements along the chain) can exceed the loss of the elastic energy  $\Delta E_{\text{latt}} \sim u_0^2$  caused by the lattice deformation. Such a transition represents a magnetic analog of the Peierls transition induced by the electron - phonon interaction in quasi-one-dimensional conducting crystals.

The concept of the spin-Peierls transition was suggested as early as 1962, and later the theory was developed. However, attempts to detect this transition were not successful for a long time, although a great number of quasi-one-dimensional magnetics are known. The reason was a competing interchain magnetic interaction resulting in three-dimensional antiferromagnetic order. The spin-Peierls transition was experimentally detected only in 1975 in a complex organic compound TTF-CuS<sub>4</sub>C<sub>4</sub>(CF<sub>3</sub>)<sub>4</sub> containing chains of  $Cu^{2+}$  ions (S = 1/2). Attempts to obtain this compound in the form of sufficiently large single crystals have failed, and its study involves difficulties. The same is true for several other organic spin-Peierls compounds discovered later. For this reason, the first observation of the spin-Peierls transition in a comparatively simple inorganic compound CuGeO<sub>3</sub> reported in 1993 [2] aroused great interest. Note that the study of lowdimensional magnetism in oxides of transition metals became especially urgent in those years in connection with the problem of high-temperature superconductivity. The matter is that, first, an important element of the structure of new high-temperature superconductors is copper-oxygen planes and chains and, second, magnetism and superconductivity are strongly related in them.

In 1996, a second inorganic compound, NaV<sub>2</sub>O<sub>5</sub>, with the spin-Peierls transition was found [3]. Both CuGeO<sub>3</sub> and NaV<sub>2</sub>O<sub>5</sub> can be obtained in the form of large stable single crystals of good quality and can be studied by different methods. The Table presents the transition temperature  $T_c$ ,

Table. Energy parameters of CuGeO3 and NaV2O5.

Crystal	$T_{\rm c}, {\rm K}$	<i>J</i> , K	$\Delta$ , meV
CuGeO <sub>3</sub>	14	140	2.1
NaV <sub>2</sub> O <sub>5</sub>	35	560	9.8