RADIOSPECTROSCOPE OPERATION UNDER CONDITIONS OF SPECTRAL-LINE SATURATION

A. V. Burenin and A. F. Krupnov

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§1. Operation of gas radiospectroscopes under conditions of spectral line saturation makes possible certain additional spectroscopic measurements. This question has been considered previously for Stark radiospectroscopes, in which the spectral-line signal is a change in intensity of radiative power passing through the specimen studied (spectroscopes of the first class, according to the classification of [2]) [1]. However, at the present time the best parameters and greatest possibilities for study of molecular rotational spectra in the millimeter and submillimeter wavelength ranges are manifested by radiospectroscopes of the second class (the line signal is a change in state of the specimen studied under the action of radiation) [2, 3], while a very important consideration from the viewpoint of attaining saturation conditions is the possibility of using sufficiently high radiation power in such telescopes. Since signal behavior with spectral-line saturation varies with the class of radiospectroscope, the present study will present a brief analysis for radiospectroscopes of the second class.

§2. We will consider the value of the signal in a radiospectroscope of the second class, connected with electrodipole interaction of an electromagnetic field linearly polarized along the z axis with purely rotational molecular motion. Considering that typically the lines studied are single homogeneously widened lines at low specimen optical thickness and uniform radiation field intensity distribution the area of the absorbing cell, we may write

$$A = LP_c(\nu, P_0); \tag{1}$$

$$P_c(\nu, P_0) = \pi \frac{(h\nu)^2}{kT} \Delta\nu_1 NfSl \sum_M \frac{\chi_M \Delta\nu_2^2}{(\nu-\nu_0)^2 + \Delta\nu_2^2(1+\chi_M)}. \tag{2}$$

where A is the signal value: L is constant characterizing the device; ν and P_0 are the frequency and power of electromagnetic radiation passing through a cell with cross section S and length l*; P_S is the power absorbed at frequency ν of a single spectral line, formed by a set of electrodipole rotary transitions $\sum_M (|J_1 \tau_1 M\rangle \rightarrow |J_2 \tau_2 M\rangle)$ [M is the magnetic quantum number, defining molecular orientation in space relative to the field; summation is performed within limits $|M| \leq J = \min(J_1, J_2)$]; ν_0 is the central frequency of spectral line; $\Delta\nu_1 = 1/2\pi T_1$ and $\Delta\nu_2 = 1/2\pi T_2$ are related to the longitudinal T_1 and transverse T_2 relaxation times, while for a molecular rotational spectrum in the gaseous phase usually $T_1 = T_2$ [4]; N is the number of molecules per unit volume; f is the fraction of molecules in energy state $|J_1 \tau_1 M\rangle$; $\chi_M = P_0/P_M$, where

$$P_M = \frac{3}{8\pi} \frac{ch^2 \Delta\nu_1 \Delta\nu_2}{|\mu_{12}|^2_M(g)} \tag{3}$$

characterizes the power necessary for saturation of the transition $|J_1 \tau_1 M\rangle \rightarrow |J_2 \tau_2 M\rangle$; and g is the index of major rotational axis of molecule.

For convenience we will introduce the following quantities:

$$\chi = \frac{\sum_M \chi_M}{\sum_M 1} = \frac{8\pi}{3} \frac{\mu_g^2}{ch^2 \Delta\nu_1 \Delta\nu_2} \frac{P_0}{S} \frac{S_{J_1\tau_1, J_2\tau_2}(g)}{\Sigma_M 1}; \tag{4}$$

*For type RAD radiospectroscopes of the second class the operating wavelength range is $\lambda \sim 1.5$-0.30 mm, S ~ 1 cm^2, $l \sim 10$ cm, which allows placement of the cell in the geometrical optics range for uniform illumination without significant power losses due to widening of the beam area.

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$$\varepsilon = (\nu - \nu_0)/\Delta\nu_2; \tag{5}$$

$$P_c^{max} \approx P_c(\varepsilon = 0,\ \chi \to \infty) = \pi \frac{(h\nu_0)^2}{kT} \Delta\nu_1 NfSl \sum_M 1, \tag{6}$$

where μ_g is the molecular dipole moment component along the major axis g; $S_{J_1\tau_1, J_2\tau_2}(g) = \frac{1}{\mu_g^2} \sum_M |\mu_{12}|^2_M(g)$ is the spectral-line strength. As a result,

$$P_c \approx P_c^{max} \varphi(\varepsilon, \chi); \tag{7}$$

$$\varphi(\varepsilon, \chi) = \left(\sum_M 1\right)^{-1} \sum_M \frac{\chi_M}{\varepsilon^2 + 1 + \chi_M}; \tag{8}$$

$$\chi_M = 3\chi \begin{cases} \dfrac{J_1^2 - M^2}{J_1(2J_1+1)}, & -J_1 + 1 \leq M \leq J_1 - 1 \quad \text{(P branch)}, \\ \dfrac{M^2}{J_2(J_2+1)}, & -J_2 \leq M \leq J_2 \quad \text{(Q branch)}, \\ \dfrac{J_2^2 - M^2}{J_2(2J_2+1)}, & -J_2 + 1 \leq M \leq J_2 - 1 \quad \text{(R branch)}, \end{cases} \tag{9}$$

The form of the function $\varphi(\varepsilon, \chi)$ for the P and R branches is the same with replacement of $J_1 \rightarrow 1_2$. Therefore, it is sufficient to consider spectral lines of only the Q and R types. For $\chi \to 0$, $\varphi(\varepsilon, \chi) \to \chi/(\varepsilon^2 + 1)$; i.e., the usual Lorentz absorption line is obtained.

For transitions between rotational terms with larger values of the quantum number describing total moment of the momentum, which are typical for the submillimeter wavelength range, instead of Eq. (8) it is convenient to use the following approximate expression:

$$\varphi^*(\varepsilon, \chi) = \lim_{J\to\infty} \varphi(\varepsilon, \chi) = \begin{cases} 1 - \delta \operatorname{artg} 1/\delta & \text{(Q branch)}, \\ 1 - (\delta' - 1/\delta') \operatorname{arth} 1/\delta' & \text{(R branch)}, \end{cases} \tag{10}$$

Here $\delta = [(\varepsilon^2 + 1)/3\chi]^{1/2}$, $\delta' = (2\delta^2 + 1)^{1/2}$. Numerical calculation (performed within the limits $10^{-2} \leq \chi \leq 10$, $0 \leq \varepsilon \leq 10$, $1 \leq J \leq 25$) has shown that the maximum difference between the exact equation (8) and the approximate equation (10), naturally observed at small values of J, does not exceed several percent. We note that as $\chi \to 0$, $\varphi^*(\varepsilon, \chi) \to \chi/(\varepsilon^2 + 1)$, i.e., transforms to an exact expression.

§ 3. We will consider the possibilities of using the spectral-line saturation effect in radiospectroscopes of the second class. At large values of the saturation parameter ($\chi \gg 1$) the signal amplitude at the line center is proportional to the population of the lower level (with consideration of degeneration) and also to $\Delta\nu_1$ and ν_0^2; it is independent of the power passing through the cell. On the other hand, the width of the observed line is determined by the parameters $\Delta\nu_2$ and χ, and for $\chi \gg 1$ the linewidth is proportional to $\chi^{1/2} \sim P_0^{1/2}|\mu_{12}|$.

As a result, in radiospectroscopes of the second class:

a) individual determination of lower-level population and matrix element of the transition is possible. In radiospectroscopes of the first class these values appear in the expression for observed line intensity in the form of a product [1].

b) Line identification is significantly simplified (especially for broad spectral recordings [3]) by using the equality at $\chi \gg 1$ of intensities of observed lines which have identical populations. We note that in this case the forms of lines of the Q branch and P and R branches are close to Lorentzian and the difference between them [according to Eq. (10)] is quite small.

c) Absolute calibration of sensitivity of spectroscopes of the second class is possible, i.e., determination of the constant L in Eq. (1) or determination of observed line intensity, by recording the maximum signal from a line, Eq. (6), at $\chi \gg 1$ and several additional operations, which in principle consist only of frequency measurements (for determination of the statistical sum, i.e., the structure of the molecular levels, and width and frequency of the spectral line) and measurement of the gas pressure in the cell. For example, when using lines corresponding to identical transitions of molecules into various oscillatory states (which have very similar dipole moment matrix elements), such calibration can be performed with markedly different power levels absorbed by the gas.

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THEORY OF SYSTEMS SUBJECTED TO THE ACTION OF NONDELTA-CORRELATED RANDOM FORCES

Yu. A. Ryzhov

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The kinetic equations used to describe the evolution of dynamic systems obeying systems of stochastic ordinary differential equations afford an extremely powerful tool for the solution of statistical problems [1-3]. In the present note we discuss approximate solutions of the generalized kinetic equations for systems subjected to the action of random forces that are not delta-correlated. These equations have been derived in [4] in the Bourret approximation in application to the Liouville stochastic equation.

The fundamental equation for the distribution of the solutions of the system of differential equations

$$\frac{d\xi^i}{dt} = v^i(\xi, t), \quad \xi(t_0) = \xi_0 \quad (i = 1, 2, \ldots, n) \tag{1}$$

has the form

$$\frac{\partial W}{\partial t} = \frac{\partial}{\partial x^i}\int_{-\infty}^{t} dt' \left.\frac{\partial B^{ij}(x, y; t, t')\, W(y, t')}{\partial y^j}\right|_{y=x}. \tag{2}$$

For simplicity we have put $\langle v \rangle = 0$. Here $W(x, t)$ is the probability density function for the random vector $\xi(t)$, and $B^{ij}(x, y; t_1, t_2) = \langle v^i(x, t_1) v^j(y, t_2)\rangle$ is the velocity correlation tensor. The solution of the integro-differential equation (2) is assumed to be known at the initial time t_0:

$$W(x, t_0) = W_0(x), \tag{3}$$

and is equal to zero for $t < t_0$, so that the actual interval of integration in (2) is $[t_0, t]$. In the case of a time-homogeneous process $v^i(x, t)$ $[B^{ij}(x, y; t_1, t_2) = B^{ij}(x, y, t_1 - t_2)]$ Eq. (2) is reduced by Laplace transformation to a partial differential equation in the spatial coordinates. The condition of zero net probability flow across the boundary of the domain of admissible values generally guarantees uniqueness of the solution of this equation and of the problem as a whole. In cases where the indicated approach is not applicable [due to inhomogeneity of the process $v^i(x, t)$ or because of actual computing difficulties] the following approximative method can be used. We write (2) in integral form:

$$W(x, t) = W_0(x) + \frac{\partial}{\partial x^i}\left[\frac{\partial}{\partial y^j}\int_{t_0}^{t} dt' W(y, t')\, \tilde{B}^{ij}(x, y; t, t')\right]\Big|_{y=x}. \tag{4}$$

Here $\tilde{B}^{ij}(x, y; t, t') = \int_{t'}^{t} dt_1 B^{ij}(x, y; t_1, t')$. If $B^{ij}(x, y; t, t') = F^{ij}(x, y, t)\delta(t - t')$ [i.e., if the process $v^i(\xi, t)$ is delta-correlated with respect to the time], then Eq. (4) goes over to the Einstein–Fokker–Planck–Kolmogorov (EFPK) diffusion equation. In solving Eq. (4) we rely on the solution of a certain auxiliary EFPK equation, in

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