# ASYMMETRY OF THE MAGNETIC TUNING CHARACTERISTICS OF MOLECULAR MASERS

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Molecule-reorientation processes (transitions with a change in the quantum number M) are found to affect the asymmetry of the magnetic tuning characteristics of a molecular generator with respect to the sign of the magnetic field applied to the resonator. Two possible mechanisms for the occurrence of asymmetry are suggested and are confirmed by experiment.

The modulation of the spectral-line Q by a magnetic field is a widely-used method for tuning a molecular generator to the center of the spectral line. In the case of a resonator inaccurately tuned to the line center, calculations show that the oscillation frequency depends quadratically upon the value of the magnetic field applied to the resonator. This dependence of the oscillation frequency upon the magnetic field vanishes in the case of exact tuning [1].

However, experimental magnetic tuning characteristics differ from the theoretical ones by the fact that a linear dependence is present in addition to the quadratic dependence, i.e., there is asymmetry with respect to the magnetic-field sign. The linear dependence is not removed even when the resonator is exactly tuned (Fig. 1) [2]. This fact leads to a loss in tuning accuracy. Such an effect may ultimately be accounted for by unequal intensity of the transitions for $\Delta M = +1$ and $\Delta M = -1$ in the resonator, the frequencies of these transitions being shifted by the magnetic field in the opposite directions. The predominance of one transition type must lead to a linear displacement of the over-all line-center frequency in a magnetic field.
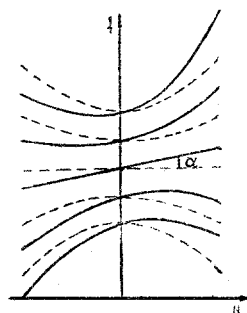


Fig. 1. Theoretical (dashed curves) and experimental magnetic tuning characteristics of a molecular generator for various detunings of the resonator.

Oraevskii [1] points out that such an effect could arise owing to the presence of circular polarization of the rf wave in the resonator, leading to predominance of one type of transition even for equal populations of levels differing in the sign of M, at the resonator input. Note

that sorting does not lead to population inequality of levels differing in the sign of M [1].
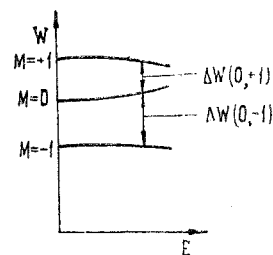


Fig. 2. Stark effect of linear-molecule levels preliminarily split in a constant magnetic field. The E and H fields are parallel.

The authors have established that the asymmetry of the characteristics is dependent upon known reorientation processes (i.e., transitions with variation of the quantum number M) of molecules in weak fields between the sorting system and resonator. In contrast to [1], in this case the effect depends on the "method of producing" the active-molecule beam before it enters the resonator, as a result of which a population difference of levels differing in the sign of M occurs. In this paper we suggest two possible mechanisms by which molecule-reorientation processes affect the asymmetry of the magnetic tuning characteristics in masers.

1. Let us consider the Stark and Zeeman effects acting simultaneously on a sorted beam of molecules in a region where reorientation occurs. Molecules belonging to the upper level (among the levels taking part in maser action) can have different values of the quantum number M determining the molecule space orientation. In a sorted beam the molecule distribution over levels with different $|M|$ differs from the equilibrium distribution [1, 4]. We are interested in the energy variation of quantum states with different M when constant electric and magnetic fields are simultaneously present (the Stark and Zeeman effects). Assuming for simplicity that the electric and magnetic fields have the same direction, the state of a molecule can again be characterized by the quantum number M; in this case the Stark and Zeeman effects can be simply added, and the transition rates remain the same [3]. In the case of ammonia the Zeeman effect is linear with respect to the magnetic field, while the Stark effect is quadratic with respect to the electric field. In this case the superposition of E and H fields leads to the situation where the transition frequencies, e.g., from the

level M = +1 to M = 0, will differ from the transition frequencies from M = −1 to M = 0. Figure 2 shows a similar shift of the levels for the simple case of a linear molecule (the level J = 1). In principle, transitions of each type can be induced by applying a variable perturbation and changing its frequency. Let us now apply a perturbation to the beam before it enters the resonator at a frequency corresponding, e.g., to transitions from M = +1 to M = 0. Owing to the different population of states with different |M|, the number of transitions from the level M = 0 to M = +1 will differ from the corresponding number of transitions from M = +1 to M = 0. Thus, after traversing the perturbing field, the number of molecules with M = +1 will differ from the number of molecules with M = −1, on which the perturbation had no effect. When there is a magnetic field in the resonator, a population difference between levels differing in the sign of M will lead to a shift of the resultant spectral-line center that will depend linearly on the magnetic field applied to the resonator.

In practical molecular oscillators in the space between the sorting system and resonator there are both electric fields scattered from the sorting system and magnetic fields (the Earth's, scattering from Zeeman coils in the resonator, etc.). It was noted in [6] that quantum transitions with a change in the number M (reorientation of molecules) can occur for nonadiabatic passage of weak fields. In principle, therefore, we have all the necessary conditions for the action of the effect described.

The probability of nonadiabatic transitions is given by the expression [5]

$$P_{12} = \frac{1}{(W_2 - W_1)^2} \left| \int_{-\infty}^{\infty} \left( \frac{\partial V}{\partial t} \right)_{21} \exp(-i\omega_1 t)\, dt \right|^2, \quad (1)$$

where $W_1 - W_2$ is the energy difference of levels between which transitions occur with frequency $\omega_{12} = (W_1 - W_2)/\hbar$, and $(\partial V/\partial t)_{21}$ is the matrix element of the derivative of the perturbation operator. As can be seen from (1), the probability of nonadiabatic transitions depends both on the energy-level difference and on the spectral content of the perturbation. In the real case the perturbation is a variable field in the space traversed by a molecule.

An experiment was set up using an $N^{15}H_3$ ammonia maser with transition J = 3, K = 3. An auxiliary magnetic field $H_0$ was applied in the region of the electric field scattered by the sorting system (before the resonator). A magnetic field either parallel to the field $H_0$ or perpendicular to it could be generated by means of coils in the resonator. Leaving the field $H_0$ off, the maser resonator was tuned to the spectral-line center by reducing to zero the quadratic dependence of the oscillation frequency on the magnetic field. In the absence of the $H_0$ field, the magnetic-tuning characteristic had an initial slope. Superimposing the $H_0$ field resulted in an increase of this slope by a factor of 5–10. When the magnetic field in the resonator was perpendicular to $H_0$, the slope increased by approximately a factor of five and the sign of the angle of slope

was independent of the sign of $H_0$. In the case of parallel fields the slope increased by one order of magnitude, and the sign of the angle of slope varied with the sign of $H_0$. When the region of action of the $H_0$ field was screened from the stray electric field by means of a brass tube with a grid for the passage of molecules, the $H_0$ field had, within the experimental accuracy, no effect. This experiment confirms the above considerations.

2. Population inequality of states having different signs of M can also arise if molecule-reorientation processes in the sorted beam are induced by a rotating field. In contrast to the previous mechanism, this effect can also be observed in the absence of a magnetic field. Let us consider in greater detail the transition processes between two quantum levels, such as, e.g., sublevels with different M value, split by the Stark effect. The state of a two-level quantum-mechanical system subjected to a small perturbation V is described by the superposition of stationary wave functions

$$\psi = C_1 \psi_1^0 \exp\left(-i\frac{W_1}{\hbar}t\right) + C_2 \psi_2^0 \exp\left(-i\frac{W_2}{\hbar}t\right).$$

Here, $C_1$ and $C_2$ satisfy the equations [5]

$$i\hbar \dot{C}_1 = V_{12} C_2 \exp(i\omega_{12}t),$$
$$i\hbar \dot{C}_2 = V_{21} C_1 \exp(-i\omega_{12}t), \quad (2)$$

where $W_1$ and $W_2$ are the system energy levels, $\omega_{12} = (W_1 - W_2)/\hbar$, $V_{ij} = \int \psi_i^{0*} V \psi_j\, dv$ are the perturbation matrix elements; usually $V_{11} = V_{22} = 0$. Under the action of the electric field $\mathcal{E}$, a quantum-mechanical system with dipole moment $\mu$ undergoes a perturbation

$$V = -\mu \mathcal{E} = -(\mu_x \mathcal{E}_x + \mu_y \mathcal{E}_y + \mu_z \mathcal{E}_z),$$

which can be represented in the form

$$V = -\frac{1}{2}(\mu^+ \mathcal{E}^- + \mu^- \mathcal{E}^+ + 2\mu_z \mathcal{E}_z),$$

where

$$\mathcal{E}^\pm = \mathcal{E}_x \pm i\mathcal{E}_y, \quad \mu^\pm = \mu_x \pm i\mu_y.$$

Denoting the projection of the angular momentum J upon the z-axis by M, we shall use known properties of the matrix elements of the operators $\mu^\pm$ and $\mu_z$. The matrix elements of the operators $\mu_z$, $\mu^+$, and $\mu^-$ can be nonzero, respectively for the allowed transitions M → M, M → M −1, and M → M +1 [5]. Let us consider the transitions with $\Delta M = \pm 1$ in the case of circular polarization of the perturbation field, i.e., for

$$\mathcal{E}_x = \mathcal{E} \cos(\omega t), \quad \mathcal{E}_y = \mathcal{E} \sin(\omega t).$$

Then, $\mathcal{E}^\pm = \mathcal{E} \exp(\pm i\omega t)$, and the matrix elements of the perturbation V are equal to

$$V_{12} = -\frac{1}{2}\mu_{12}^+ \mathcal{E} \exp(-i\omega t)$$

for the transition $1 \to 2$ with $\Delta M = -1$,

$$V_{12} = -\frac{1}{2}\mu_{12}^- \mathcal{E} \exp(i\omega t)$$

for the transition $1 \to 2$ with $\Delta M = 1$.    (3)

Note that $V_{21} = V_{12}^*$ and $(\mu_{12}^+)^* = \mu_{21}^-$. By substituting (3) in Eq. (2), it can be seen that for the rotating-field polarization selected by us (counterclockwise), the resonance terms determining the secular variations of $C_i$ are only apparent for the transition $1 \to 2$ with $\Delta M = -1$ (and, correspondingly, for $2 \to 1$ with $\Delta M = +1$), while such a perturbation will not cause transitions $1 \to 2$ with $\Delta M = +1$. For the opposite direction of rotation of the electric-field vector, the resonant terms correspond to the transition $1 \to 2$ with $\Delta M = +1$. Note that such transitions can also be induced by a rotating magnetic field.

Transitions with a variation of M can occur in the space between the resonator and the sorting system [6]. The space-inhomogenous static field traversed by a molecule plays the role of a perturbation. A rotating field is obtained in the case in which the field direction varies along the molecule path. For example, the stray field of a sorting system varies its direction as it penetrates the limit waveguide aperture at the resonator input.

In the simplest case when the lower rotational transition of a linear molecule is used, reorientation will correspond to transitions between levels $J = 1, M = 0$ and $J = 1, M \pm 1$*. The presence of a rotating field leads to the situation where, depending on the direction of rotation of the field, either only molecules with $M = +1$ or only molecules with $M = -1$ will take part in transitions from a level $M = \pm 1$. Under conditions of nonequilibrium population of levels with $M = 0$ and with $M = \pm 1$ in the sorted beam of molecules, this leads to a difference in the number of molecules with $M = +1$ and $M = -1$ entering the resonator, which in its turn leads to unequal intensity of the Zeeman line components.

For experiments we again used an $N^{15}H_3$ ammonia maser operating on the transition $J = 3, K = 3$. After a ring-type sorting system, the beam of molecules was admitted through a plane condenser, similar to that used for molecule reorientation in [6]. The sorting-system stray field, somewhat attenuated by a diaphragm having an aperture 6 mm in diameter, penetrated the condenser. The total field along the molecule path was the resultant of the mutually perpendicular stray fields from the sorting system and the field in the condenser. The variation of the resultant-field direction along the molecule path was determined by the rotating field component. It is easily seen that a sign change of one of the fields reverses the direction of rotation of the resultant field. A simultaneous sign

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*Such transitions are forbidden in the absence of a field; by perturbing the wave functions an electric field can give rise to a nonzero matrix element of the dipole moment. The matrix elements of similar transitions can be calculated by methods of perturbation theory [3, 8]. The case shown applies to a molecular generator operating on the transition $1_{01} - 0_{00}$ of the formaldehyde molecule [7].

change of both fields leaves the direction of rotation unchanged. The occurence of population inequality of states differing in the sign of M with respect to the magnetic-field direction in the resonator (assumed to be the z-axis) must be expected as a result of transitions with change of the quantum number M by unity, which are induced by a field rotating in the xy-plane.
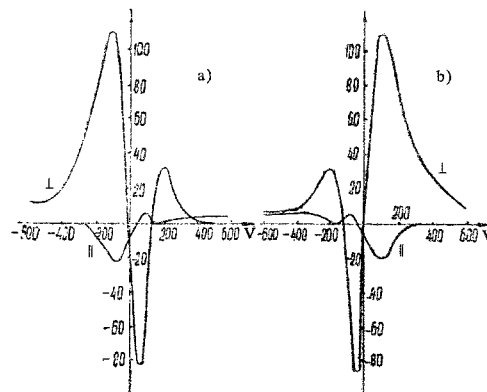


Fig. 3. Slope of the magnetic-tuning characteristics as a function of the condenser voltage. The ordinate scale gives the oscillation-frequency deviation in cps for a magnetic field increment in the resonator of about 2 Oe.

A change in the direction of rotation must change the sign of the asymmetry. A field rotating in the xz- or yz-planes should not cause asymmetry.

As in the previous experiment, a transverse magnetic field of the order of 2 Oe, either parallel to the electric field in the condenser or perpendicular to it, could be generated by means of coils in the resonator. By leaving the condenser voltage equal to zero, the generator was tuned to the spectral-line center by the above method. We measured the slope of the magnetic tuning characteristics in relative units as a function of the condenser voltage for various orientations of the magnetic field in the resonator, as well as for various signs of the condenser voltage and sorting-system voltage (Fig. 3). Curves $a$ and b were measured for different signs of the voltage of the sorting-system ring nearest to the condenser, i.e., for opposite directions of the stray field. An electric-field component rotating in the xy-plane was obtained in the case in which the electric field in the condenser was perpendicular to the magnetic field in the resonator; the corresponding experimental curves are labeled with the symbol $\perp$. It can be seen that the slope is strongly dependent on the condenser field, the maximum slope being attained for condenser fields that maximize the reorientation effect [6].

A sign change of the condenser field causes a sign change of the asymmetry, while a simultaneous sign change of the condenser field and stray field restores the previous situation. This demonstrates that the direction of rotation of the field is the governing factor. (It is easily seen that in the first experiment a sign variation of $H_0$ did not result in changing the direction of rotation of $H_0$, and that the electric fields were not

reversed.) A field rotating in the xz- (or yz-) plane was obtained when the electric field in the condenser was parallel to the magnetic field in the resonator (the curves labeled with the symbol ‖). In this case the asymmetry is much less dependent upon the condenser voltage, and its presence is attributable to inaccurate parallel alignment of the fields. Thus, the experimental results agree with the above considerations. Note that when the condenser was screened from the sorting-system stray field by a diaphragm with a grid for letting molecules through, a voltage applied to the condenser did not give rise to asymmetry of the magnetic-tuning characteristics.

Summing up, we have given a qualitative interpretation of the effect of molecule-reorientation processes on the form of the magnetic tuning characteristics of molecular generators. This interpretation was confirmed by experiment. The relative importance of the mechanisms here suggested as giving rise to asymmetry of the characteristics depends in each case on the specific design of the generator.

The authors are indebted to M. Ya. Ovcharov for kindly providing unpublished data on a formaldehyde generator, which proved useful in assessing our results, as well as to A. A. Ul'yanov, Yu. V. Timofeev, and L. A. Sinegubko who took part in evaluating them.

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