Possibility of observing the rotational spectra of nonpolar molecules

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It is noted that rotational transitions in nonpolar molecules due to the dipole moment induced by an external electric field can be observed by means of a submillimeter microwave gas spectroscope having an acoustic detector used in conjunction with powerful sources of coherent submillimeter radiation.

1. The existence in nonpolar molecules of rotational transitions associated with the dipole moment induced by an external electric field has been pointed out by Townes and Schawlow[1], for example. Their estimates, however, indicate that it is practically impossible to observe the resulting spectra with microwave spectroscopes of the usual type. In this note we wish to point out that such transitions can be observed by using the recently devised submillimeter microwave spectroscope with an acoustic detector (MSAD)[2] in conjunction with powerful sources of coherent radiation[3]. The improvement of the situation stems from the possibility of passing powerful beams of radiation at the frequency of the observed spectrum line through the investigated gas in the MSAD without increasing the receiver noise, which allows one, on the one hand, to increase the degree of polarization of the molecules, i.e., the intensity of the spectrum lines, and on the other hand, to increase sensitivity of the MSAD to the absorption coefficient of the line as compared with the microwave spectroscopes usually employed[2,4].

2. The maximum sensitivity of microwave spectroscopes to the absorption coefficient of the gas and the permissible radiation power level depend on the manner in which the signal is formed from the spectrum lines. In this respect the spectroscopes can be classified into two types: by instruments of the first type the line is signalled by a change in the intensity of the radiation passing through the specimen, while by those of the second type it is signalled by a change in the characteristics of the specimen itself under the action of the radiation[4]. In considering the optimal parameters of a spectroscope we may assume that the power P_S absorbed by the specimen is small compared with the power P_0 of the radiation source: $P_S \ll P_0$. With instruments of the first type, therefore, the useful signal P_S must be observed against the strong background P_0 (which bears no information), and this gives rise to a number of phenomena that reduce the sensitivity[1]. Ordinary microwave spectroscopes are instruments of the first type, and the disadvantage noted above limits their absorption-coefficient sensitivity to a value of the order of 10^{-10} cm^{-1}, and the permissible power level, to a quantity of the order of 10^{-3} W[1]. Inherent in instruments of the second type is a "null-type" detector which records only the useful signal P_S, the detector noise being in principle independent of the power of the radiation traversing the specimen. Hence the absorption-coefficient sensitivity increases linearly with the radiation power until the power becomes so high that the transition becomes saturated or the gas breaks down[4]. A microwave spectroscope with an acoustic detector that records the change in the gas pressure incident to

absorption of radiation by the gas is an instrument of the second type[1]. The condition that the signal be detectable is determined by the spectral density of the energy fluctuations of the gas at the optimal radiation intensity modulation frequency[4] and can be written in the form

$$P_c \approx \gamma l P_0 \sim kT (N \Delta f^c \Delta f^{\,r})^{1/2}. \qquad (1)$$

where γ is the absorption coefficient at the line, T and N are the temperature and the total number of particles of the gas, l and τ^c are the length and thermal relaxation time of the cell containing the gas ($\Delta f^c \sim 1/\tau_c$), and $\Delta f^{\,r}$ is the receiver bandwidth at the modulation frequency.

3. To estimate the absorption coefficient due to rotational transitions in nonpolar molecules associated with the dipole moment induced by an external field it is sufficient to use the well known expression

$$\gamma \approx \frac{8\pi^2 N f \nu_{rot}{}^2 |d_{eff}|^2}{3ckTV\Delta\nu}, \qquad (2)$$

for the absorption coefficient for electric dipole rotational transitions for the case $h\nu_{rot} \ll kT$ after making the order-of-magnitude substitution

$$|d_{eff}|^2 \sim \frac{|\mu_{vib}|^4 E^2}{h^2 \nu_{vib}^2}. \qquad (3)$$

for the square of the modulus of the dipole-moment matrix element. Here ν_{vib} is the frequency of the vibrational transition between the ground and excited vibrational states, $|\mu_{vib}|$ is the modulus of the dipole-moment matrix element for that transition, E is the strength of the electric field, f is the fraction of the molecules in the lower rotational state, ν_{rot} and $\Delta\nu$ are the frequency and width of the rotational transition (the selection rules are different from those for ordinary electric dipole transitions[1]), and V is the volume of the cell.

Using (1)—(3), we obtain the following approximate formulas for the power flux required for observing the spectrum line at a signal-to-noise ratio of unity:

a) For molecules polarized by the alternating field that induces the transitions,

$$\frac{P_0}{S} \sim \frac{1}{8\pi} kT \left[\frac{(\Delta\nu)^2 \Delta f^c \Delta f^{\,r}}{N} \right]^{1/2} \frac{\nu_{vib}}{\nu_{rot}} \frac{hc}{|\mu_{vib}|^2} \frac{1}{f^{1/2}}, \qquad (4)$$

b) For molecules polarized by a constant field of strength E_{dc}

$$\frac{P_0}{S} \sim \frac{1}{8\pi} (kT)^2 \Delta\nu \left[\frac{\Delta f^c \Delta f^{\,r}}{N} \right]^{1/2} \frac{1}{E_{dc}^2} \frac{\nu_{vib}^2}{\nu_{rot}^2} \frac{h^2 c}{|\mu_{vib}|^4} \frac{1}{f}. \qquad (5)$$

4. Now let us put in some numbers. Using the values $N \sim 10^{17}$, $T \sim 300°$K, $|\mu_{vib}| \sim 1$ debye, $\Delta f^c \sim 10^3$ sec^{-1}, $\Delta f^{\,r} \sim 1$ sec^{-1}, $f \sim 10^{-2}$, $E_{dc} \sim 1$ kV/cm, and ν_{vib}/ν_{rot}

$\sim 10^2$, which are close to realistic values, we find

$$(P_0/S)_a \sim 10 \text{ W/cm}^2, \quad (P_0/S)_b \sim 0.1 \text{ W/cm}^2. \tag{6}$$

At present the actual sensitivity of the MSAD to the line absorption coefficient is about 30 times lower than the optimal sensitivity given by (1). The estimates given above for the necessary radiation power flux must therefore be increased by factors of $\sqrt{30}$ for case a) and 30 for case b). The cross section area of the absorption cell is of the order of 1 cm^2, so the required power is $\sim 3-60$ W. It is entirely possible to obtain coherent radiation with considerably higher powers, even in the millimeter range[3].

The results obtained above show that it is quite possible to observe the rotational spectra of nonpolar molecules; this is of theoretical interest, makes it possible to study the effects of the polarization of molecules, and considerably broadens the range of molecules accessible to study by the most accurate microwave methods.

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1)It is a secondary effect—the change in a macroscopic characteristic of the specimen—that is registered by the MSAD. Registering a primary effect—the change in the populations of the resonance levels—would result in greater sensitivity, but the necessary "quantum-counter" technique has not yet been developed for microwave spectroscopy.

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