Coherent spectroscopy of high-resolution raman scattering of methane

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A resolved spectrum of the A branch of the ν_1 branch of methane was obtained for the first time by the method of coherent anti-Stokes light scattering (CALS), and an interpretat of this branch is proposed. The possibility of observing forbidden pure rotational spectra of molecules of the spherical-top type by the CALS method is considered.

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For most molecules, the splitting of the Q branches of bands of fully symmetrical oscillations is of the order of 10^{-2}—10^{-4} cm^{-1} and cannot be resolved in the spectra of the spontaneous Raman scattering, because of certain experimental difficulties. In addition for molecules of the spherical–top type the ν_1 band is strictly forbidden in the IR spectrum, so that the observation of its structures by classical methods is practically impossible. At the same time, the new CALS method makes it possible to obtain the spectra of gases with a resolution determined by the radiation width of the employed laser. This method yielded recently the spectrum of the Q branch of band ν_2 of acetylene with a fully resolved structure, [1] and an attempt was made[2] to resolve the structure of the ν_1 (2916 cm^{-1}) band of methane, but without success. In the
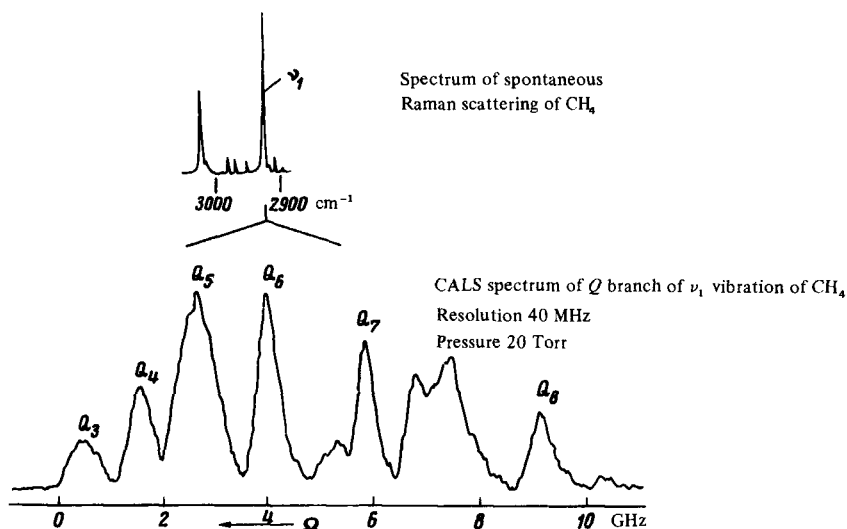

FIG. 1.

present paper we report the first resolution of the structure of this band and present its theoretical interpretation. We indicate also the possibility of observing pure rotational spectra of spherical tops by the CALS method.

1. The principal elements of the CALS spectrometer are a single-frequency argon laser and a dye laser, both operating in the transverse regime. The laser emission line widths are ≈ 40 MHz. A collinear interaction scheme is used. The anti-Stokes signal is registered with a photomultiplier in the photon counting regime. The signal to noise ratio is 10^4 at pressures above 10 atm and 5 at a pressure of 20 Torr.

The obtained spectrum is shown in Fig. 1. In contrast to the Q branch of the acetylene ν_2 band, [1] whose structure is described by the simple formula $\nu_j = \nu_0 - \alpha_2 J(J+1)$, the structure of the Q branch of the methane ν_1 band, as seen from Fig. 1, is irregular. However, the frequency differences of the sharpest lines, the intensities of which satisfy the expected regularity, are adequately described by the formula

$$\nu_J = \nu_0 - a_1 J(J+1) - b_1 J^2 (J+1)^2 , \tag{1}$$

with $J=3$ to 8 and with $a_1 = (3.6 \pm 0.6) \times 10^{-2}$ GHz and $b_1 = (9.4 \pm 0.7) \times 10^{-4}$ GHz. Inasmuch as for hydrides usually $a_1 \sim 1$ GHz and $b_1 \sim 100$ GHz $(b_1 \sim B^4/\omega^3)$, an interpretation of the methane spectrum calls for the assumption that an anomalous (resonant) effect is present. A Coriolis resonance between ν_1 and ν_3 (3020 cm^{-1}) is strictly symmetry-forbidden, so that the only possible source of the anomaly in ν_1 is a Fermi resonance between ν_1 and $2\nu_2^0$. Taking into account this resonance and the selection rules $J' = J$ and $k' = K$ (the number k distinguishes between the centrifugal components of the J level) we obtain for the frequencies of the Q branch a formula of the form (1), in which the coefficients a_1 and b_1 are given by

$$a_1 = \frac{1}{2} [(a_1 + 2a_2) + \frac{\Delta_0}{\Delta} (a_1 - 2a_2)] ; \qquad b_1 = (a_1 - 2a_2)^2 \frac{(\Delta^2 - \Delta_0^2)}{4|\Delta|^3}, \tag{2}$$

where α_1 and α_2 are the α constants, not affected by the resonance, for the oscillations ν_1 and ν_2, while Δ_0 and Δ are the values of the difference $2\nu_2^0 - \nu_1$ without and with allowance for the resonance, respectively. At sufficiently reasonable values $\alpha_2 \approx 0.08$, [3] $\alpha_1 \approx -0.03$, $\Delta_0 \approx 100$ and $\Delta \approx 150$ cm^{-1}, we obtain $a_1 \approx 0.04$ and $b_1 = \approx 8 \times 10^{-4}$ GHz, which agree in order of magnitude with the values obtained from the spectrum in Fig. 1. Thus, the irregularity of the structure of ν_1 of CH$_4$ can be attributed to a Fermi resonance. Favoring the presence of such a resonance are also the appearance of a $2\nu_2^0$ band in the low-resolution CALS spectrum and in the spontaneous Raman scattering[4] with sufficiently high intensity (see Fig. 1). We are inclined to ascribe the broad spectrum between the lines $Q(7)$ and $Q(8)$ and other weak lines (see Fig. 1) to "tetrahedral" components of the lines $P^+(10)$ and $P^-(9)$ of the ν_3 band of CH$_4$, which agree in accord with the estimates[4] with ν_1 and can be enhanced by interference between ν_1 and ν_3.

2. The polarizability tensor of a rigid spherical top is isotropic, so that a pure rotational spectrum of spontaneous Raman scattering (RS) is forbidden. The centrifugal distortion of the molecule produces a small anisotropy, but the intensity of the RS spectrum resolved in this case is smaller by 4—6 orders

of magnitude than the intensity of the allowed spectra of the spontaneous RS. [5,6] At the same time, the CALS intensity is determined by the tensor of the cubic susceptibility $\chi^{(3)} = \chi_R^{(3)} + \chi_{NR}^{(3)}$ which, generally speaking, is not isotropic. However, the anisotropy of $\chi^{(3)}$ for a gas of rigid spherical tops is due only to the anisotropy $\chi_{NR}^{(3)}$ (the nonresonant part of $\chi^{(3)}$), which in most cases is smaller by several orders of magnitude than $\chi_R^{(3)}$ (the resonant part of $\chi^{(3)}$). Of practical importance is therefore the anisotropy of $\chi_R^{(3)}$ due to the centrifugal distortion. For $\chi_R^{(3)}$ of a spherical top, corresponding to the rotational and vibrational-rotational spectra of CALS, we can write, when account is taken of first-order centrifugal distortion

$$\chi_{R,abcd}^{(3)} = N\frac{6}{\hbar} \sum_{\alpha\beta\gamma\delta} \lambda_{a\alpha}\lambda_{b\beta}\lambda_{c\gamma}\lambda_{d\delta} \{ \sum_{\epsilon\eta} \sum_t (-B_t^{\epsilon\eta}/\omega_t)$$

$$\times J_\epsilon J_\eta [a_{\alpha\beta}(\partial a_{\gamma\delta}/\partial q_t) + a_{\gamma\delta}(\partial a_{\alpha\beta}/\partial q_t)][\omega_r - (\omega_1 - \omega_2) - i\Gamma_r]^{-1}$$

$$+ \sum_s (\partial a_{\alpha\beta}/\partial q_s)(\partial a_{\gamma\delta}/\partial q_s)[\omega_s - (\omega_1 - \omega_3) - i\Gamma_s]^{-1} \}, \tag{3}$$

where $a,b,c,d = X,Y,Z$ are the immobile and $\alpha,\beta,\ldots,\eta$ mobile coordinate axes, $\lambda_{a\alpha}$ are the direction cosines, $\alpha_{\gamma\delta}$ is the polarizability tensor, $\partial\alpha_{\gamma\delta}/\partial q_t$ is the derivative of $\alpha_{\gamma\delta}$ with respect to the dimensionless normal coordinate q_t, $B_t^{\epsilon\eta}$ are "rotational derivates,"[6], J_η are the components of the angular momentum, ω_t and ω_s are the oscillation frequencies, ω_r are the frequencies of the rotational transitions, Γ_r and Γ_s are the line widths, ω_1, ω_2, and ω_3 are the frequencies of the lasers, and N is the density of the number of molecules. If there is no ω_3, then we obtain a purely rotational CALS, whose intensity is 4—6 orders of magnitude smaller than the intensity of the allowed CALS, and if all three frequencies $\omega_1, \omega_2, \omega_3$ are used, with ω_1 and ω_3 constrained by the condition $\omega_1 - \omega_3 = \omega_s$, then by scanning ω_2 we obtain a pure rotational interference CALS, whose intensity is determined by the product of both terms in (3) and which is only two or three orders of magnitude lower in intensity than the allowed CALS. In view of the high efficiency of the CALS method, observation of such spectra entails no difficulty. Thus, a fundamental difference exists between the centrifugal mechanism of the appearance of spontaneous RS and CALS, making the CALS method highly promising for the investigation of forbidden rotational transitions.

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