Relative Intensity of a Cross-Over Resonance to Lamb Dips in the ν_3 Band of Methane

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We have extensively observed sub-Doppler resolution Stark-modulation spectra in the ν_3 band of methane (CH_4) from 87.7 to 92.8 THz (2925 to 3096 cm^{-1}) using a comb-referenced difference-frequency-generation spectrometer. In the analysis, the vibration- and rotation-induced permanent electric dipole moments have been precisely determined for the vibrational excited and ground states [1]. In the course of the study, we have found that the relative intensity of a cross-over resonance to Lamb dips depends on the transition branch.

Figure 1 depicts three saturated absorption spectra under the Stark field perpendicular to the optical electric field. The dispersion-type line profiles are caused by the Stark-modulation detection. Figure 1 (a), (b) and (c) correspond to the P-, Q- and R-branch transitions between the $|v = 0, J'' = 4, E, |M''|=0 \text{ or } 2>$ and $|v_3 = 1, J', E, |M'|=1>$ levels, respectively, where vs are the vibrational quantum numbers, Js are the total angular momentum quantum numbers, Ms are the projection of $\boldsymbol{J}$ along the applied electric field, and E is the doubly degenerate irreducible representation of the T_d point group. The double and single primes present the vibrational ground and exited states. The horizontal axis indicates the frequency deviation from each zero-field transition frequency, ν_0, reported in Refs. [2,3]. Each triplet contains a cross-over resonance at the center and two Lamb dips. Figure 2 illustrates the energy level diagram of Fig. 1 (a) with zero (a)and nonzero external fields (b). The relative intensity of the Lamb dips agrees with the prediction from the corresponding Clebsch-Gordan coefficients. However, the relative intensity of a cross-over resonance to the larger Lamb dip depends on the transition branches. In particular, the cross-over resonance is the strongest among the components of the triplet for the Q- and R-branch transitions. This characteristic behavior has also been seen for most of the observed transitions, $P(4)\,E$, …, $P(7)\,E$, $P(8)\,E^{(2)}$ and $P(9)\,E$, $Q(2)\,E$, $Q(4)\,E$, …,$Q(7)\,E$ and $Q(8)\,E^{(2)}$, and $R(2)\,E$ and $R(4)$

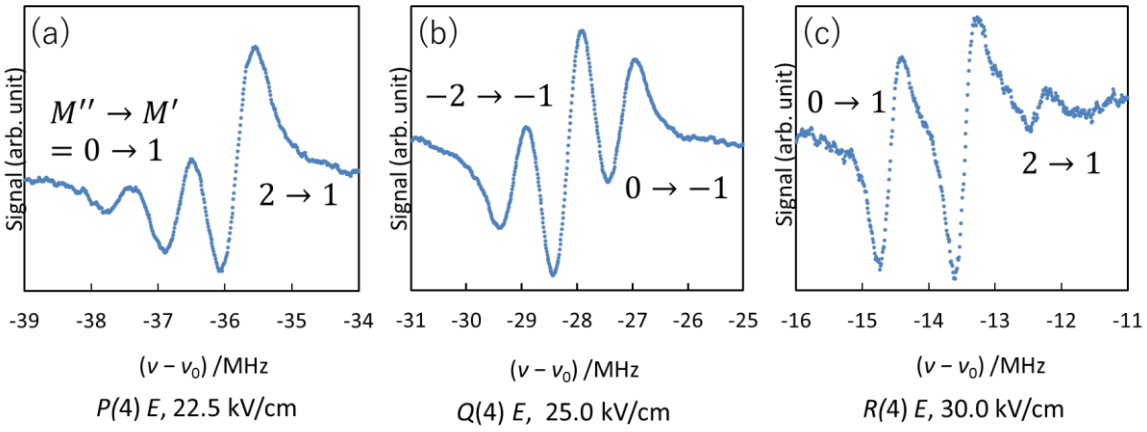

Figure 1. Observed Stark modulation spectra in the ν_3 band of methane. (a) shows the $P(4)\,E$ transition with the external field of 22.5 kV/cm, (b) and (c) are $Q(4)\,E$ with 25.0 kV/cm and $R(4)\,E$ with 30.0 kV/cm, respectively. In each figure, the center spectral component is a cross-over resonance and the others are the associated Lamb dips.

E, …, $R(7)$ E. This is often observed in atomic spectra but never in molecular spectra, as far as we know.

We have analyzed the intensity of the cross-over resonance and the Lamb dips using the rate equation, which was developed for saturated absorption spectroscopy of atoms [4], where the spontaneous emission is the dominant relaxation process. It is revealed that the intensity of the triplet agrees with the atomic theory for the Q-branch transitions, whereas that for the P- and R-branch transitions is apart from it. We attribute this to the difference in the transition dipole moments of the branches and the collisional relaxation rates.

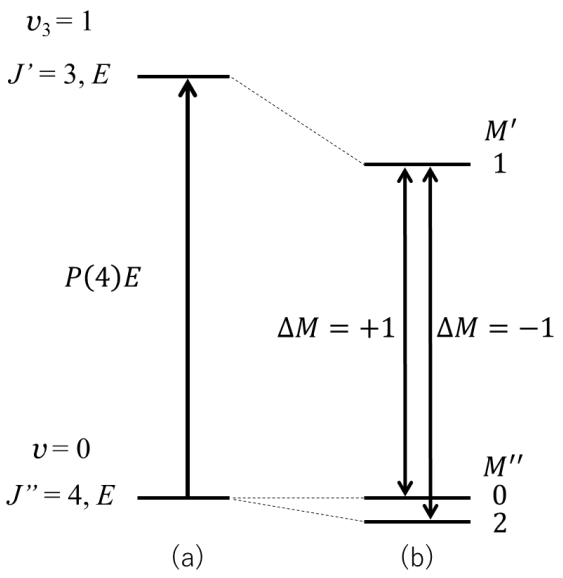

Figure 2. Energy level diagram of the $P(4)E$ transition in Fig. 1 (a) in the absence of the external electric field (a) and in the presence of it (b).

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