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LEVEL CROSSING IN CH_4 OBSERVED BY NONLINEAR ABSORPTION

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Stark-tuned level crossing resonances in an excited vibration-rotation state of methane were detected through nonlinear optical absorption. The signal accurately follows a Lorentzian line shape with a 200-kHz minimum width. Pressure broadening studies yield the rotational relaxation in the excited vibrational state.

Nonlinear optical techniques have recently been reported which produce unusually high-resolution spectra in Doppler-broadened transitions. These nonlinear methods include level crossing, mode crossing, and Lamb-dip effects and have been restricted to atomic laser systems such as Xe,[1,2] O,[3] and Ne.[4-6] Presently, these methods are being extended to molecules where Lamb-dip resonances have been observed in CH_4,[7] I_2,[8] and NH_2D.[9] In the last case, precision Stark spectroscopy in the infrared was demonstrated.

We report here the first observation of molecular level crossing by saturated absorption. Methane in the vibrationally excited ν_3 mode is examined. This excited state possesses a small dipole moment, exhibits a weak first-order Stark effect, and allows observation of a Stark-tuned level-crossing signal about zero field. The signal is monitored by nonlinear absorption from the ground state with a magnetically tuned 3.39-μ He-Ne laser. The observed line shape reflects only the excited-state inverse lifetime of the crossing levels and accurately obeys a Lorentzian function with a half-width which is linearly dependent on pressure and which can be as narrow as 200 kHz. By comparison, the (inverted) Lamb-dip widths recently reported for CH_4[7] are nearly identical to these results. Since Lamb-dip widths reflect an average of both ground- and excited-state inverse lifetimes, we conclude that rotational relaxation in the ground and excited vibrational states is nearly the same.

A few molecular zero-field level crossings have also been observed in spontaneous emission by the conventional Hanle arrangement.[10-12] However, these signals are weak because of the competition of nonradiative relaxation processes with spontaneous emission, and studies have been limited to states with very short radiative lifetimes. In contrast, the method reported here does not suffer from this restriction; this is illustrated in the present work where the CH$_4$ radiative lifetime is as long as 0.04 sec.[13]

Level crossing in saturated absorption can be viewed as a special case of the mode-crossing resonance which has been discussed in terms of the nonlinear optical response of a Doppler-broadened transition with closely spaced level structure.[14-16] In mode crossing, two optical transitions sharing a common level are nonlinearly coupled by two traveling waves of frequency ν_1 and ν_2. A resonance condition occurs when the level splitting is tuned to the difference frequency $\nu_1-\nu_2$. This reduces to level crossing when ν_1 equals ν_2 and when one traveling wave nonlinearly couples two such transitions overlapping to within their natural widths. The nonlinear level-crossing signal can be derived from the third-order polarization expression for mode crossing and predicts a Lorentzian line shape whose half-width at half-height is the average inverse lifetime of the two crossing levels.

Methane contains two Coriolis components of the $P(7)$ transition of the ν_3 vibrational band within the tuning range of the laser (±3 GHz): the $F_1^{(2)}$ component at approximately the untuned laser frequency and the E component at nearly 3 GHz below the laser center frequency.[17,18] These are the only molecular transitions accessible to the 3.39-μ laser which have been unambiguously assigned and are furthermore the most strongly absorbing transitions known for this region. It has been shown that the E component exhibits a linear Stark effect due to the small Coriolis-induced dipole moment, in the excited state, of 0.024 D.[19] Since the ground state contains no dipole, its levels are not tuned by an electric field and no level crossing occurs. In the present case of high M degeneracy, it can also be shown that a linear Stark effect still yields a single Lorentzian. The E-component line shape therefore consists of only a single Lorentzian line corresponding to level crossing in the excited state. The $F_1^{(2)}$ component exhibits no observable Stark effect and was not studied.

Level-crossing signals were observed with a CH$_4$-filled Stark cell inside the laser cavity in order to take advantage of the higher power densities ($\sim\frac{1}{4}$ W/cm^2). The laser frequency was tuned by an axial magnetic field to within the CH$_4$ Doppler width of 260 MHz. However, the CH$_4$ center frequency was avoided to prevent competing standing-wave or Lamb-dip resonances. The laser polarization allowed both $\Delta M=0$ and $\Delta M=\pm1$ transitions but only the latter results in a level-crossing signal. By monitoring the laser output power as a function of the electric field across the Stark plates, the level-crossing signal was detected with Stark modulation (audio square wave) and phase-sensitive detection. The modulation depth was chosen such that the observed signal could be accurately related to a derivative of the level-crossing resonance. To further enhance sensitivity, the experiment was coupled on-line to an IBM 1800 computer for time-averaging many scans.[20]

Figure 1 shows the experimental results and a computer fit of these results for zero-field level crossing in methane at a pressure of 7 mTorr. The points are the experimentally measured line shape and represent the computer average of 32 scans of about 2 min each. The overall signal corresponds to approximately a 1% change in laser output. The nonlinear origin of the resonance was demonstrated by its being quenched at higher methane pressures or at lower laser intensities. Also, there was no observable change in line shape or width of the resonance with laser intensity, indicating that no power broadening occurred due to higher order saturation effects. The solid

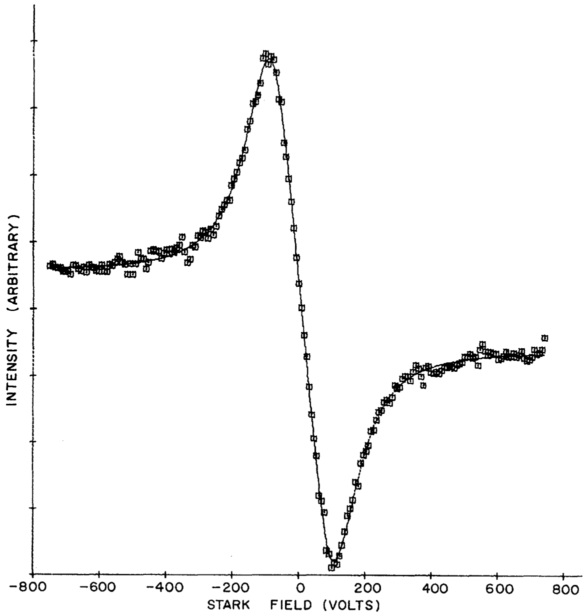

FIG. 1. Experimental and computer-fitted line shape for zero-field level crossing in CH$_4$ at a pressure of 7 mTorr. The Stark plates are separated by 0.6028 cm.

line in Fig. 1 is a least-squares computer fit of the experimental line shape by a single Lorentzian resonance. Since the center of the resonance occurs at zero Stark field, only a width and intensity were necessary to characterize its shape. In addition, a phenomenological term, a constant times the absolute value of the Stark field, was used to represent the small change in the linear Doppler-broadened absorption with Stark tuning. This term accounts for the apparent displacement of the base line in the spectrum of Fig. 1. The excellent fit of the data with a single Lorentzian indicates that any excited-state splittings due to magnetic or spin-rotation interactions are negligible, as expected.

To gain some insight into the collisional relaxation processes in the excited state, the level-crossing resonance was studied at six different methane pressures between 2 and 40 mTorr. The line shape remained Lorentzian throughout this range, and only the loss of sensitivity restricted the study to these pressures. The broadening of the resonance was approximately linear in pressure p and is given as

$$\Delta V_{1/2} = 108 \text{ V/cm} + (9.1 \pm 1.1 \text{ V/cm mTorr CH}_4)p,$$

where $\Delta V_{1/2}$ is the Lorentzian half-width at half-maximum. Using the experimental dipole moment and the Stark equations of Uehara, Sakurai, and Shimoda,[19] we converted the Stark tuning in the excited state to a frequency scale. This yields a half-width given by

$$\Delta \nu_{1/2} = \gamma' = 210 \text{ kHz} + (17.8 \pm 2.1 \text{ kHz/mTorr CH}_4)p,$$

where γ' is the average inverse lifetime of the excited state ($J=7$, $\nu_3=1$). The constant term results from the finite transit time across the beam and wall broadening, while the pressure-dependent term reflects collisional relaxation. The contribution of vibrational relaxation from fluorescence measurements implies a pressure-dependent half-width of less than 0.1 kHz/mTorr.[13] Thus, rotational relaxation in the excited state exclusively determines the pressure-dependent half-width.

It is interesting to compare the broadening here with that obtained by Barger and Hall in their Lamb-dip study of the $F_1^{(2)}$ component.[7] They obtained

$$\Delta \nu_{1/2} = \tfrac{1}{2}(\gamma + \gamma') = 150 \text{ kHz} + (16.3 \pm 0.6 \text{ kHz/mTorr CH}_4)p,$$

where γ is the inverse lifetime in the ground state ($J=6$, $\nu_3=0$) and γ' is again the inverse lifetime in the excited state ($J=7$, $\nu_3=1$).[21] The two results are identical within experimental error and indicate nearly identical collisional cross sections for rotational relaxation in the ($J=6$, $\nu_3=0$) and ($J=7$, $\nu_3=1$) states. The implication of this result toward a theoretical understanding of the relaxation processes is under further investigation.

Zero-field level crossings have also been observed in several of the methyl-fluoride transitions within the tuning range of the 3.39-μ laser. No investigations of the line shape have been undertaken since the assignments of these transitions are as yet unknown. However, each transition is expected to consist of two superimposed Lorentzians since both the ground and the excited states are Stark tunable and exhibit level crossings.

The experiments reported here represent another approach in our program to utilize saturation techniques in high-resolution spectroscopic studies of molecules. These results clearly show that nonlinear molecular resonances of this type, with linewidths of less than 0.5 MHz, are readily attainable and can be extended to a host of molecules which exhibit the C-H vibrational stretch in the 3.39-μ region.

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LOCAL THERMODYNAMIC EQUILIBRIUM CONDITIONS IN SUPERHIGH-PRESSURE HELIUM PLASMAS PRODUCED BY LASER ACTION

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This paper presents an analysis of gas breakdown by laser action, assuming that the final state of the laser-beam–gas interaction is described by a plasma in local thermodynamic equilibrium. A simple formula is obtained which correlates the threshold electric field with the initial gas pressure and the temperature, in agreement with experiments.

Breakdown experiments in superhigh-pressure gases[1] irradiated by a focused Q-switched laser show a dependence of threshold electric field versus initial gas pressure in the rather large interval of 20 to 2000 atm. These curves present electric-field minima, which approximately agree with the values predicted by the well-known theory of electron-impact ionization. In other kinds of experiments performed on laser-produced plasmas,[2] it has been shown that local thermodynamic equilibrium (LTE) conditions may be approximately attained in time intervals as short as the laser-pulse duration ($\simeq$65-nsec half-width), working at energy density levels of 1000 J/cm^2 (power density $\simeq 1.5\times10^{10}$ W/cm^2). Measurements made at that laser energy density show that the plasma electron temperature, the gas temperature, and the blackbody radiation temperature converge to the same limit.

This Letter presents a theoretical analysis, attempting to define a unique local temperature T for electrons, ions, neutrals, and radiation, and to deduce a relation between threshold breakdown power, temperature, and pressure that may account for the experimental curves.[1]

Different mechanisms have been proposed to explain the gas heating: the radiation-supported shock-wave process[3,4]; the traveling ionization-breakdown–wave process[5]; or a possible luminous mechanism,[4] due to the short-wavelength radiation emerging from the initial heated focal region ionizing the adjacent layers and so allowing the absorption of laser radiation. Recently, Evans and Grey Morgan[6] presented the theory that the breakdown wave may be due to aberration effects in short–focal-length lenses. It is rather difficult to make a decision about the different interpretations: It might be that one or more of the proposed mechanisms predominate with different experimental parameters. Then we assume that, independent of the possible heating and plasma-formation process, the final state of the laser-beam–gas interaction, after the peak intensity passage of the laser pulse, is described by a model consisting of a plasma in LTE conditions. We adopt a spherically symmetric distribution of the plasma properties, surrounding the initially heated focal region, which is considered as a radiation source. The observed asymmetries in the plasma formation[3-5] are evidently due to the asymmetrical laser radiation propagation relative to the focus. In a thought experiment, with a symmetric distribution of the coherent radiation, it would be possible to obtain a plasma with spherical symmetry.

Fundamental equations. –In such a plasma, it