QWD43 Fig. 1 Experimental setup for detecting atoms with use of magneto-optical rotation spectroscopy. In this experiment a 795-nm diode is used to detect rubidium atoms. The polarizers surrounding the vapor cell are crossed. Only plane-polarized light that has been rotated by \( \pi/2 \) radians is detected. This rotation appears to be extremely sensitive to the number of atoms in the flame.

ogy with analytical chemistry and laser spectroscopy. The goal of this work is to use the same magneto-optical rotation (Faraday effect) in atomic vapors that has been developed as ultra-narrowband optical filters to measure and characterize atomic concentrations in flames and plasmas. To the best of our knowledge, magneto-optical rotation in flames and plasmas has never been investigated with use of a laser source for this purpose.

One traditional method of measuring atomic concentrations uses atomic absorption spectroscopy (AAS). In this technique the sample to be tested is atomized, usually by aspiration into a flame or vaporization by a graphite furnace. Light from a lamp passes through the vapor where atoms absorb part of the light. According to the Beer–Lambert's law, the measured atomic absorption varies linearly with concentration. The detection of low concentrations is limited by the ability of measuring a small signal on top of a large background. An alternative method for measuring these concentrations that involves measuring small changes in essentially no background is to use the magneto-optical effect. The mechanism behind this effect in atomic vapors is Zeeman splitting of the atomic energy levels resulting from an axially applied magnetic field. At a specific combination of optical frequency, pathlength, and atomic concentration the polarization of plane-polarized light will be rotated by \( \pi/2 \) radians. Cross polarizers placed before and after the vapor cell will block all frequencies of light except that very narrow band in the wings of the transition that has been rotated. Since the polarization rotation is very sensitive to atomic concentration, the transmission through the cross polarizers is well suited as an analytical tool for measuring unknown concentrations. A setup of the initial experiments is shown in Fig. 1.

Preliminary measurements of the signal versus concentration for both atomic absorption and magneto-optical rotation in rubidium atoms at 795 nm shows that the dynamic (linear) range of AAS is better than three orders of magnitude as compared with only two for AAS. Also, magneto-optical rotation is capable of detecting concentrations down to 50 ppb as compared with 500 ppb for atomic absorption. Furthermore, the detection limits for atomic absorption are fixed while magneto-optical rotation could be lowered with better polarizers and a more powerful laser source. Rubidium was chosen in the preliminary studies because the analysis wavelength at 795 nm was easily attainable by use of readily available laser diodes. Experiments are ongoing to prove the feasibility of this technique for more useful atoms (lead at 368 nm or nickel at 341 nm). This will be done in a similar setup as for the rubidium experiment except that the laser source will be changed. UV wavelengths of interest will be generated by use of a Nd:YAG pumped dye laser system and subsequently nonlinear optical crystals necessary to reach either 341 or 368 nm. A graphite furnace atomization technique is also being investigated.

"Naval Air Warfare Center-AD, Code 45562 MS3 Bldg 2187, 22541 Millstone Rd, Patuxent River, Maryland 20670
"Aerospace Mass Properties Analysis Inc., 2640 Amy Drive, Norristown, Pennsylvania 19403

QWD44 Velocity selection in collision-induced transitions

P. Minguzzi, S. Carocci, A. De Fenis, A. Di Lieto, D. Mazzotti, M. Tonelli, Dipartimento di Fisica dell'Università, Piazza Torricelli 2, I-56126 Pisa, Italy

A novel technique of high-resolution spectroscopy has been developed recently in our laboratory. We used a new version of the IR-mmwave double-resonance method to study CH₃ in different vibrational states and to measure the frequency of rotational and vibrational transitions at sub-Doppler resolution.

The method employs collinear propagation of pump and probe beams to select a narrow velocity class. In the experimental setup the intensity of the pump CO₂ laser is modulated by a mechanical chopper: when the laser is present, the absorption of microwaves is smaller because part of the molecules are removed from the lower state of the transition. The transmission of the mmwave radiation through the gas sample is measured with use of a synchronous amplifier referenced to the pump modulation.

Two different conditions are possible when recording the double resonance signals. In the first ("resonant") case the pump laser is tuned very close to the IR resonance, so that only the molecules with a null velocity component along the laser direction are excited and a single line is obtained with a width narrower than the Doppler limit. In the second case the laser has a large detuning from the exact center of the roto-vibrational transition, so a splitting of the rotational line is observed into two narrow components, which correspond to the velocities scattered by counter- and copropagating radiations. This line is obtained by fine tuning of the laser frequency and directly evaluated by measuring the splitting of the Doppler-induced doublet.

The sensitivity of the technique is so high that we could observe signals caused by collisional transfer from other hyperfine sublevels. When the laser is detuned far off resonance to the purpose of observing large splittings, it may happen that its frequency matches a tight resonance with a different hyperfine component of the roto-vibrational spectrum. In this case the laser effectively depletes a level not connected to the observed transition; the depletion may be transferred to one of the levels involved in the mmwave transition if the "propulsion" rules for collisions are favorable, so a third (resonant) peak appears at the center of the Doppler doublet (Fig. 1).

While collision-induced transitions are well known in the literature, the remarkable fact here is that the collisional peak has about the same width as the lines of the nearby doublet, i.e., significantly smaller than the Doppler width.

This result can be explained by assuming that the collisional transfer between different levels takes place without appreciably affecting the velocity of the molecules. This hypothesis is supported by the observation that, if the detuning of the laser is further increased, the collisional peak splits into a doublet, with a separation corresponding to that expected for the detuning from the "parent" IR transition (Fig. 2).

These observations prove the feasibility of experiments where an arbitrary velocity of the molecules, transferred by collision to a given
hyperfine state, can be easily selected. The accuracy of selection is determined by the frequency stability of the pump laser.


QWD45
Collision-induced tunneling in methyl halides

H. Harde, R. A. Cheville,* D. Grischkowski,* Universität der Bundeswehr Hamburg, Holstenhofweg 85, 22043 Hamburg, Germany

For methyl halides two states of molecular symmetry, + and −, exist that correspond to the two configurations of the molecule with respect to the symmetry plane determined by the three H-atoms. The molecule can switch to the inverse configuration by tunneling of the carbon-halide group through the symmetry plane. The inversion corresponds to a transition between + ↔ − states of the rotational levels that are split into a close doublet. In methyl halides the tunneling potential is very high and therefore the inversion frequency extremely low. Even at moderate pressures the linewidth resulting from pressure broadening of such inversion lines is large compared with the center frequency, which can be assumed to be zero.

We have applied the powerful technique of THz time-domain spectroscopy (TDS) to measure the absorption and dispersion caused by tunneling of the vapors over a wide spectral range of more than 4 THz. The THz beam system with 100-fs temporal resolution and >5000:1 signal-to-noise ratio is shown in Fig. 1. The spectrum of the terahertz pulses, with the highest measured frequency more than 50× that of the lowest, covers the full rotational absorption band.

Thus the low and high frequency wings of the band structure can be investigated with high sensitivity to distinguish between the contributions originating from the molecular inversion and rotation.

The optoelectronic THz beam system was optimized to study the low frequency wing of the rotational spectrum, generating the pulses of Fig. 2a. Because of the propagation through 5 atm of methyl chloride a 38-cm-long gas cell the input pulses are reshaped and attenuated as shown in Fig. 2b (solid curve) while the dashed curve represents a simulated pulse with the inversion neglected. The respective Fourier transform spectra of the measured (solid curve) and simulated (dashed curve) pulses behind the vapor are shown in Fig. 2c together with the spectrum of the input pulses (dashed-dotted curve).

Standard collision theory predicts a line-shape for a pressure broadened line with zero transition frequency that is given by the Debye theory as the low frequency limit of the von Vleck–Weisskopf theory. The calculated absorption and dispersion from the Debye theory are plotted in Fig. 3 (dashed curves) showing a broad, constant absorption (Fig. 3a) and flat phase shift (Fig. 3b) at high frequencies. Their strength depends on the pressure broadening (and therefore the mean time τ between collisions) and was calculated for a broadening coefficient C = 13 MHz/hPa, identical to that of the broadening of rotational lines. This absorption resulting from the inversion of the molecule causes an unacceptable large additional contribution in the high frequency wing in disagreement with our measurements and cannot completely explain the observed spectrum in the low frequency wing.

Therefore we have developed a new line-shape theory that includes the response of polar molecules to an external electric field in the presence of collisions. It represents an unification of the basic collision theories with the molecular response time τ, as the control parameter and is applicable for both the rotational and the inversion spectrum. The calculated absorption and dispersion based on this new theory and for a response time τ = 210 fs are represented by the solid curves in Fig. 3. The absorption shows a well-restricted maximum at 150 GHz and only causes a significant attenuation in this frequency range. With this new line-shape excellent agreement between measurement and calculation is obtained over the full spectral range of our measurements.

*School of Electrical and Computer Engineering and Center for Laser and Photonics Research, Oklahoma State University, Stillwater, Oklahoma 74078


QWD46
Pulsed terahertz study and spectral analysis of a simple solution: HCl in CCl₄

B. N. Flanders, P. Moore, R. Cheville,* M. Klein, D. Grischkowski,* N. F. Scherer, University of Pennsylvania, Department of Chemistry, Philadelphia, Pennsylvania 19104-6323

Recent advances in generation of high intensity radiation in the far-infrared (FIR) spectral region¹ have suggested the possibility of performing a FIR spectral hole burning measurement to determine the homogeneous rotational dephasing time of a dipolar rotor in condensed media. Knowledge of the individual rotational line widths and shifts would be needed for such a study. This paper describes the first steps, in terms of both measured and calculated line shapes, in studying rotational line broadening phenomena in con-