TRANSIENT LASER FREQUENCY MODULATION SPECTROSCOPY

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Abstract  Explicitly time-dependent implementations of optical frequency modulation spectroscopy have been recently applied to a wide range of problems in chemical physics. We provide a brief description of the methodology, with an emphasis on its intrinsic advantages for interrogating transient species. Several examples highlight the application of the technique to high-resolution absorption spectra of free radicals, rate measurements for gas-phase reactions, and Doppler spectroscopy of the gas-phase products of photoinitiated reactions.

INTRODUCTION

The early 1980s saw an intense flurry of activity as frequency modulation (FM) methods, already well known in microwave and nuclear magnetic resonance spectroscopy, were first applied to laser sources. A wide variety of spectroscopic applications of laser FM was envisioned and demonstrated at the IBM San Jose laboratories in a few highly productive years between Bjorklund’s original report (1), an early development of the theory of FM spectroscopy (2), and an early review article (3). At the same time, work by Hall and coworkers at JILA established the use of optical FM techniques for laser saturation spectroscopy, providing a precise means of frequency stabilizing lasers (4). The principles, advantages, and limitations have been described, and the methods are now widely used for stabilization of lasers and for sensitive detection of weak absorptions. One early notable example of the sensitivity of FM spectroscopy was its use in the first example of single-molecule spectroscopy (5). Optical FM techniques continue to play a central role in the advance of precision measurement, in fields as diverse...
as gravity wave detection (6, 7), frequency standards (8), and the measurement of minute magnetic fields (9).

Modulation methods are particularly well matched to diode laser spectroscopy, and extensive investigations of the relative merit of different methods have been made to optimize the sensitivity for trace-gas detection (10–13). Direct modulation of the laser diode injection current provides a convenient means of frequency modulating infrared diode lasers, although a simultaneous amplitude modulation is generally induced as well. In addition, different noise and bandwidth of infrared detectors make for some important differences in the implementation of infrared FM methods, which we do not address in this review. Werle (14) has written a recent review addressing sensitive detection methods with tunable diode lasers, with a strong emphasis on recent trends in modulation spectroscopy.

Despite its popularity in the trace detection and precision measurement field, laser FM techniques have only recently begun to find applications in transient problems: the spectroscopy of short-lived species, chemical kinetics, and Doppler spectroscopy of collisionless photofragments. This review is centered on these uses of FM laser spectroscopy as a fast transient technique. We begin with a brief review of optical FM and describe a typical experimental implementation of transient FM spectroscopy. A less formal and more visually oriented tutorial on this same material is available in the Electronic Materials section of the Annual Reviews Web site. Some examples of high-resolution spectroscopy of transient molecules are followed by recent applications to rate measurements using FM spectroscopy. The measurement of Doppler-broadened line shapes by FM spectroscopy provides a new method, complementary to LIF, REMPI TOF, and ion imaging, for measuring polarized photofragment correlations. The simplicity of analysis for one-photon absorption spectra and the high resolution and low noise of the Doppler spectra allow for the investigation of a range of detailed questions in molecular photodissociation.

GENERAL PRINCIPLES

Theory

FM consists of applying a sinusoidal variation to the frequency or phase of a narrow-band source. The electric field of the resulting light beam can be written as 

\[ E(t) = E_0 \exp[i(\omega_0 t + M \sin \omega_m t)] \]

where the field is understood to be the real part of the complex expression. An “instantaneous frequency” can be defined as the time derivative of the phase \( \omega_0 + \omega_m M \cos(\omega_m t) \). It oscillates around an average value, \( \omega_0 \), at the modulation frequency, \( \omega_m \), making a maximum excursion of \( \omega_m M \) away from \( \omega_0 \). Depending on the modulation index, \( M \), and the magnitude of \( \omega_m \) relative to the line width, \( \Gamma \), of the spectroscopic transition being probed, qualitatively different behavior is observed. Figure 1 illustrates the effect of changing the modulation index, \( M \). For graphical clarity, the modulation...
Figure 1  Frequency modulated waves for various values of the modulation index, \( M \). The modulation frequency has been chosen only 10 times lower than the carrier frequency for illustrative purposes.

frequency has been chosen here to be only 10 times less than \( \omega_0 \). For optical spectroscopic applications, \( \omega_m \) would typically be at least \( 10^6 \) times less than \( \omega_0 \).

The view of a periodically varying instantaneous frequency is most appropriate for slow modulation, when \( \omega_m \ll \Gamma \). In this case, one can crudely think of the instantaneous frequency changing slowly on the timescale of absorption. The time-dependent transmitted intensity simply follows the absorption spectrum at the instantaneous frequency, without a phase lag. For weak modulation, \( \omega_m M \ll \Gamma \), the component of the transmitted light intensity at \( \omega_m \) is proportional to the first derivative of the absorption line, and the component at \( 2\omega_m \) is proportional to the second derivative. Deeper modulation yields stronger signals, reaching a maximum for \( \omega_m M \approx \Gamma \), under which conditions the spectral line shapes are broadened and deviate from the derivative spectra in well-characterized ways (15, 16). Measurements of this type, well established in microwave (17), nuclear magnetic resonance (18, 19), and optical spectroscopy (20) in the days before lasers, provide both background reduction and noise suppression by moving the detection away from the \( 1/f \) noise at low frequencies. This slow modulation limit is often referred to as derivative spectroscopy or wavelength modulation spectroscopy.

When the modulation frequency approaches and exceeds the line width of the absorption feature, \( \omega_m \gtrsim \Gamma \), the response of the medium is better treated in terms of the fixed frequency components of the incident frequency modulated beam (17). This is the limit referred to as FM spectroscopy. Particularly useful introductory descriptions of optical FM spectroscopy and reviews of early applications can be found elsewhere (3, 21). Unified theoretical descriptions of wavelength
modulation and FM spectroscopy can also be found elsewhere (12, 22). A brief overview of the general theory follows.

Waveforms like those illustrated in Figure 1, with continuous and periodic variations in frequency, can also be written as a Fourier sum of uniformly spaced, fixed frequencies:

\[
E(t) = E_0 \exp[i(\omega_0 t + M \sin \omega_m t)]
\]

\[
= E_0 \exp(i\omega_0 t) \sum_{n=-\infty}^{\infty} J_n(M) \exp(in\omega_m t). \tag{1}
\]

In addition to the depleted amplitude at the original frequency \(\omega_0\) (referred to as the carrier frequency in the language of radio frequency communication) the modulated wave has frequency components at sidebands, displaced by integer multiples of \(\omega_m\) above and below \(\omega_0\). The amplitudes for the \(n\)th sideband are given by the \(n\)th order Bessel function of argument \(M\). In a pure frequency modulated wave, the even and odd order sidebands are, respectively, in and out of phase, as the Bessel functions of negative integer order have the symmetry property \(J_{-n}(M) = (-1)^n J_n(M)\). The effect of a sample of length \(L\) with an absorption coefficient \(\alpha(\omega)\) and index of refraction \(\eta(\omega)\) can be written in terms of a complex, frequency-dependent transmission function, \(T(\omega) = \exp(-\delta - i\varphi)\), with amplitude attenuation \(\delta\) and phase shift \(\varphi\), where \(\delta(\omega) = \alpha(\omega) L/2\) and \(\varphi(\omega) = \eta(\omega) L \omega/c\). The frequency dependence of \(\delta\) is the absorption line shape, and the frequency dependence of \(\varphi\) is the dispersion line shape. The electric field transmitted through a sample then depends on the absorption and dispersion at the carrier frequency and all the sidebands according to

\[
E_T(t) = E_0 \exp(i\omega_0 t) \sum_{n=-\infty}^{\infty} T(\omega_n) J_n(M) \exp(in\omega_m t). \tag{2}
\]

A square-law light detector produces a photocurrent proportional to the slowly varying part of the intensity, \(|E_T(t)|^2\), which has components at DC and at integer multiples of \(\omega_m\). Phase-sensitive detection at \(\omega_m\) with a radio frequency (rf) mixer isolates the terms arising from beating between all pairs of frequencies differing by \(\omega_m\). Expanding the square of Equation 2 under conditions where the sharp absorption and dispersion features are weak, including only the DC term and the component with a frequency of \(\omega_m\) gives (22)

\[
|E_T(t)|^2 = E_0^2 \exp(-2\delta_0) \times \left[1 + 2 \cos \omega_m t \sum_{n=0}^{\infty} J_n J_{n+1} \times (\delta_{-n-1} - \delta_{n+1} - \delta_n)
\right]

\[
+ 2 \sin \omega_m t \sum_{n=0}^{\infty} J_n J_{n+1} \times (\varphi_{-n-1} + \varphi_{n+1} - \varphi_n), \tag{3}
\]
where the implied argument $M$ of the Bessel functions has been suppressed, and the subscripts on $\delta$ and $\varphi$ label the frequency of the corresponding sideband. Phase-sensitive detection at $\omega_m$ will give a signal that depends on $\theta$, the phase difference between two paths from the rf oscillator to the mixer. At an arbitrary phase, $\theta$, the mixer output will be a sine and cosine weighted sum of absorption and dispersion contributions:

$$I_{FM}(\omega) = \cos \theta A_{FM}(\omega) + \sin \theta D_{FM}(\omega),$$

with

$$A_{FM}(\omega_0) = E_0^2 \exp(-2\delta_0) \sum_{n=0}^{\infty} J_n J_{n+1} \times (\delta_{-n-1} - \delta_{n+1} + \delta_{-n} - \delta_n)$$

and

$$D_{FM}(\omega_0) = E_0^2 \exp(-2\delta_0) \sum_{n=0}^{\infty} J_n J_{n+1} \times (\varphi_{-n-1} - \varphi_{-n} + \varphi_{n+1} - \varphi_n).$$

FM spectroscopy is frequently performed under weak modulation conditions, $M \leq 1$, when sidebands beyond the first order are negligible. For small arguments, and $n \geq 0$, $J_n(M) \approx M^n/2^n n!$, leading to the weak modulation limit $J_0 \approx 1$ and $J_{\pm 1} \approx \pm M/2$. In this limit, and for weak total absorption, Equation 4 reduces to the common working equation for FM spectroscopy (1):

$$I_{FM}(\omega_0) = E_0^2 \exp(-2\delta_0) [M(\delta_{-1} - \delta_1) \cos \theta + M(\varphi_{-1} + \varphi_1 - 2\varphi_0) \sin \theta].$$

Equation 7 shows that the FM signal detected in phase with $\omega_m$ ($\cos \theta$) depends on the imbalance between absorption of the two first-order sidebands, whereas the FM signal in quadrature ($\sin \theta$) depends on the imbalance of the average phase shift of the two first-order sidebands compared with the phase shift at the carrier frequency.

Plotting the sums of three waves, uniformly spaced in frequency, with adjustable amplitudes and phases is an exercise that is useful for strengthening one’s intuition for FM spectroscopy. In a pure frequency modulated beam, each first-order sideband beats against the carrier with a beat frequency $\omega_m$. The two beat signals are matched in amplitude and exactly out of phase, producing no amplitude modulation when the contributing frequencies are balanced according to Equation 1. If a sample absorption attenuates one sideband more than the other, as in Figure 2a (see color insert), the null is broken, and the transmitted wave has an envelope that follows in phase with the modulation frequency. Excess attenuation of the other sideband would give an amplitude modulation in the composite waveform that is out of phase with the modulation frequency.

The differential phase shifts of carrier and sidebands caused by the dispersion of the sample near the resonant absorption can also break the rf null. In order to produce a pure frequency modulated wave, the two sidebands need to come
into phase at a zero crossing of the $\omega_0$ carrier wave, and to interfere destructively at a maximum or minimum of the carrier wave. A frequency-independent phase shift corresponds to the irrelevant time at which the modulator is turned on. A constant dispersion, that is, a linear $\varphi(\omega)$, will introduce a phase shift between the modulation drive and the resultant FM, but does not spoil the rf null. Curvature in $\varphi(\omega)$ does lead to an FM signal. Figure 2b (see color insert) shows the sum of carrier and sidebands matched in amplitude, but shifted to place the constructive interference of the two sidebands 30° away from the zero crossing of the carrier wave. This phase imbalance produces an amplitude modulation in the composite wave, but now with a 90° shift relative to the modulation frequency.

**Experimental Implementation**

**FM Spectroscopy** In its most direct form, laser FM spectroscopy is performed by adding rf sidebands to a continuous wave (cw) laser with an electro-optic phase modulator, and adding information to the beam by passing it through a sample. The transmitted beam is detected with a photodiode fast enough to detect changing intensity at the rf modulation frequency. A double-balanced mixer is used for phase-sensitive detection of the photocurrent varying at the modulation frequency. A lowpass filter narrows the effective bandwidth of the detection system, and spectral lines can be scanned by recording the changing DC output of the mixer as the laser sweeps across an absorption line. Figure 3 illustrates the basic components of such an experiment.

**Sample Modulation** In its simplest implementations, FM spectroscopy often fails to achieve its maximum theoretical sensitivity owing to wavelength-dependent background signals arising from residual amplitude modulation or weak etalon effects. Understanding and circumventing these problems has been a central theme of much of the published work on FM spectroscopy. In addition to the avoidance of unwedged transmissive optics, a number of schemes have been described to overcome these problems for static samples, including chopped dual beam methods (3),

![Figure 3](image-url)

**Figure 3** Block diagram for frequency modulation spectroscopy. EOM, electro-optic modulator.
active feedback to the electro-optic modulator (23), and asynchronous dithering of optical elements (24). When applicable, one of the most direct approaches to overcoming these problems is to apply an additional modulation to the absorbing sample, independent of the probing process and its background effects. The original report by Hall et al (4) on optical heterodyne saturation spectroscopy achieved this effect by chopping a saturation laser to tag a velocity group within the Doppler width of an I$_2$ absorption line. Phase-sensitive detection at the chopping frequency isolates the FM signal due only to the Doppler-free saturation signal. The total concentration of a transient species can be rapidly modulated by driving the formation rate periodically. A sinusoidally modulated mercury lamp was used to drive a photochemical reaction producing the HCO radical (25). Phase-sensitive detection at the audio frequencies of photochemical modulation provides a simple and effective way of attaining the high theoretical sensitivity of FM spectroscopy, limited only by the shot noise of the photocurrent (21). Recent work (26) has extended this general approach, using a modulated electric discharge source to isolate the high-resolution FM spectra of the linear carbon chain ions C$_6$H$_2$C$^+$.

**Frequency Modulated Pulsed Lasers** The inherent potential of FM spectroscopy for fast time response absorption measurements was recognized immediately as one of the advantages of the technique (1). The first demonstration of rapid optical FM spectroscopy was done by acousto-optically chopping 1-$\mu$s pulses from a rapidly scanning, frequency modulated cw laser beam (27). Although the measurements were carried out not on a transient but on a stable sample of I$_2$ vapor, the potential for sensitive FM absorption spectroscopy on a microsecond timescale with very low total sample exposure to light was effectively demonstrated. Higher time resolution, on the 10-ns scale, has been achieved by the direct application of sidebands to pulsed dye lasers (28, 29). The advantages of working with higher modulation frequencies have been demonstrated, favoring modulation frequencies larger than the laser line width. An optimized version of this approach has been described recently (30), using transform-limited $\sim$10-ns pulses obtained from pulse-amplification of an FM cw seed laser. To escape the noise of conventional nanosecond dye lasers, the previous pulsed laser FM measurements had been performed at modulation frequencies as high as 12 GHz (29), which puts technical constraints on the choice of detectors and the amount of transmitted light that can be observed without detector saturation. The clean spectral content of an amplified cw laser pulse results in a more rapid decrease in laser noise in the 100 to 1000-MHz range, permitting the use of slower, more conventional photodetectors. Harmonic generation of frequency modulated fundamental laser beams has been shown to work surprisingly well, when sufficient care is taken in the design of the pulse amplifier to preserve the phase homogeneity across the beam cross section. Spectra of NO were recorded with 50-nJ pulses of frequency modulated light at 214.5 nm (30).

**Pulsed Transient FM** An alternative approach to the spectroscopy of pulsed transient species is to incorporate sideband generation and rf demodulation into a transient absorption or gain measurement. Zapka et al (31) demonstrated in 1982
Figure 4  Block diagram for transient frequency modulation spectroscopy. A pulsed excitation source is added to the components illustrated in Figure 3, and a transient waveform is recorded at each step of the laser. EOM, electro-optic modulator.

SPECTROSCOPY OF TRANSIENT SPECIES

The sensitivity gained by the use of FM techniques in the detection of short-lived species has been particularly useful in a number of spectroscopic studies. The first application in our group was to the near-infrared spectrum of singlet methylene,
Figure 6 Comparison of dual beam direct absorption and frequency modulation (FM) spectra for CH₂ transients measured in a 1.5-m cell with Ti:sapphire laser. [Adapted with permission from Figure 4 of Reference 33 (© 1994, American Institute of Physics).]

CH₂ (33). Figure 6 compares direct absorption (dual beam/balanced detectors) to a frequency modulated spectrum of CH₂ in the same spectral region, utilizing comparable time gates and signal averaging. Weak lines clearly discernable in the FM spectrum were obscured in the noise of the direct absorption spectrum.

Although the original experiments used an argon ion–pumped Ti:sapphire ring laser system, much of the more recent spectroscopic work at Brookhaven has made use of cavity-tuned diode lasers (34–36). These devices are simpler to use, relatively inexpensive, and operate over a wider wavelength range than does the Ti:sapphire system. Commercially available systems operate from 630–1550 nm, with some gaps, and an individual laser module typically oscillates over 30 nm at a center wavelength near 1000 nm. Laser amplitude noise is also lower, typically better than 0.5%, and peaked at low frequencies. In the absence of active frequency stabilization, the diode lasers typically have a frequency stability about 10–20 times worse than a commercial Ti:sapphire ring laser, locked to an external reference cavity, although good enough for Doppler-limited spectroscopy and kinetics. The typical diode laser output powers are 10–20 mW, more than an order of magnitude smaller than the Ti:sapphire laser, but comparable to the intensities that we actually use from the ring laser in a typical transient FM experiment.

Figure 7 shows a section of the near infrared spectrum of CH₂ recorded using a cavity-tuned diode laser-based spectrometer operating near 1 μm. The strong lines are rotational transitions in the ν₂ (bending) = 1 ← 0 band of the \( \tilde{b} \ B₁ ← \tilde{a} \ A₁ \) transition of the radical with the projection quantum number \( K_a \). This band is of interest because the upper level is located at an energy close to that where these two states become degenerate at a linear nuclear configuration and shows the effects of strong vibronic coupling caused by Renner-Teller and Coriolis effects. The upper trace was recorded using a dual-beam, balanced detector scheme combined with a Herriott-type long-path (50 m) absorption cell and represents the best sensitivity we were ever able to achieve in this mode. Approximately 3 mW of power was incident on each detector during the measurement. The kinetic lifetime of singlet CH₂ following 308-nm photodissociation of ketene is about 1–2 μs under these experimental conditions, only about 10 times longer than the...
optical transit time through the sample cell. Under these highly transient conditions, the alternative technique of cavity ring down spectroscopy (37, 38) could not be pushed to high sensitivity. The spectra shown were sampled with a 500-ns gate, following rotational and translational thermalization in a bath of He at 2 torr. The inset is the same region of spectrum recorded using FM at 191 MHz with approximately double the laser power incident on a single detector and all other experimental conditions maintained the same. The signal-to-noise ratio in the raw FM spectrum is comparable to that in the upper trace. In this case, with a relatively strong absorption and lower source noise from the external cavity diode laser, the FM methods provide little improvement over well-optimized direct absorption. In practice, however, the alignment and optical balancing of the dual detectors with a multipass sample cell was more troublesome than the single-beam FM methods, which we prefer for our routine spectroscopic-studies. More recent work on CH₂ spectroscopy (39) has resulted in the measurement and assignment of weak lines in the $\tilde{a}(0,8,0)^I \leftrightarrow \tilde{a}(0,0,0)^I$ band, located in an experimentally more challenging, longer-wavelength region, with an absorption cross section calculated (40) to be 6.5 times less than that of the band shown in Figure 7. That a transition this weak, nominally a high vibrational overtone that gains intensity via the
Renner-Teller effect, can be detected in a dilute and highly transient sample testifies to the sensitivity of the experiment.

Other recent successes include the observation of the spectra of jet-cooled free radicals (41). Very-high-resolution spectra of bromo-methylene, HCBr, have been measured following photolysis of HCBr₃ in a slit-type expansion source (42). Metal-containing radicals produced in a laser ablation/chemical reaction expansion produce ample signal levels even in a single-pass measurement through a pinhole expansion (43). With modification to a slit geometry in the jet ablation/reaction apparatus, we expect FM spectroscopy to be a productive tool for high-resolution spectroscopy of such transient species, especially when the fluorescence yield is low.

GAS-PHASE KINETICS

The response time of FM spectroscopy can approach the inverse modulation frequency and is set by the choice of low-pass filter following the mixer. Within a wide range of response times, from seconds to tens of nanoseconds, the experimenter is free to trade noise for bandwidth, remaining close to the shot-noise limit all the while. The general idea was first demonstrated by Zapka et al (31) to measure a time-dependent gain in a He-Ne plasma tube. There have been several recent applications of FM spectroscopy as a method for following rapid concentration changes in kinetics studies. North et al (44) illustrated a sensitive and low-noise monitoring of the pseudo-first order decay of CN radicals in the presence of ethylene in a repetitively pulsed photolysis experiment. The electronic time response was set by a 20-MHz low-pass filter, only 10 times below the 200-MHz modulation frequency. Monitoring a Doppler-broadened single rotational line, the early transient signals are influenced by translational and rotational relaxation from the initial nonthermal CN preparation. At a pressure of 5 torr, this thermalization is complete within a few hundred nanoseconds, and the subsequent decay represents the rate of CN + C₂H₄ reaction. Figure 8 shows the observed decay of FM signal at two different concentrations of ethylene. Based on 5 × 10¹¹ CN radicals cm⁻³ produced via photolysis, a submicrosecond detection sensitivity of <2 × 10⁸ radicals cm⁻³ per quantum state can be estimated.

Taatjes & Oh (45) have recently shown advantages to using high-frequency wavelength modulation spectroscopy for monitoring the rapid reactions of HO₂ radicals. Pulsed-laser photolysis of Cl₂ in the presence of methanol was used to produce the HO₂ radicals, and their self-reaction was followed with a InGaAsP diode laser, current modulated at 5 MHz and detecting at twice the modulation frequency. Two-tone FM spectroscopy was also performed (11, 46) on HCl using an infrared color center laser to measure the kinetics of Cl plus unsaturated hydrocarbon reactions (47). The probe beam was modulated with an external phase modulator at 498 ± 1.1 MHz and demodulated at 2.2 MHz. The authors emphasize
Figure 8  Two typical CN frequency modulation absorption traces from the reaction of CN with C\textsubscript{2}H\textsubscript{4}. The dashed and solid lines correspond to 35 mtorr and 75 mtorr of C\textsubscript{2}H\textsubscript{4} in Ar at a total pressure of 5.0 torr. The inset is the semi-log plot of decay curves showing every fourth point. [Reprinted with permission from Figure 1 of Reference 44 (© 1997, John Wiley & Sons).]

the insensitivity to the often troublesome oscillations due to thermal lensing from radial photothermal waves in their multipass Herriott cell.

Transient FM spectroscopy is well suited to monitoring time-dependent concentrations in shock tube experiments. Two groups (48–51) have recently found FM to provide more than 20-fold improvements in the detection sensitivity for NH\textsubscript{2} in shock tube studies, compared with previous direct-absorption techniques. The single-shot detection of transient signals equivalent to 0.005\% peak absorption corresponds to a 0.25-ppm detection limit for NH\textsubscript{2} radicals at high temperature. The method has been validated for the thermal decomposition of N\textsubscript{2}H\textsubscript{4} (48) and CH\textsubscript{3}NH\textsubscript{2} (50) and applied to the high-temperature reaction of NH\textsubscript{2} + NO (49, 51). The enhanced sensitivity is a particularly valuable feature in these experiments, where the consequences of side reactions can be minimized by working at ever lower radical concentrations. Particularly noteworthy is the relative insensitivity to noise associated with scattering and refractive beam steering through the shock tube because carrier and sidebands are affected equally. This is in contrast to dual-beam absorption measurements, where the reference beam cannot compensate for these effects.

For the measurement of high-temperature Doppler-broadened lines, modulation frequencies even up to 1 GHz are still in an intermediate region where \omega_0 is
smaller than, but not negligible compared with, the absorption line width, and careful calibration of line shapes and attention to the absolute detection phase is required. Calibration of the FM signals to provide absolute concentrations over a range of high temperatures with an accuracy of 10%–15% has been demonstrated with the aid of a NH₃/O₂ flame reference source and a reflective etalon (50). This calibration method, first described by Zapka et al (31), compares a direct dual-beam measurement of a small frequency-dependent attenuation in the reflection from an etalon with the magnitude of an FM measurement of the same calibration feature. Precise knowledge of the absorption line shape and line strength then provides an accurate calibration of the FM signal versus concentration, even as a function of sample temperature. Further improvements can be anticipated with the implementation of modest multipass optics, and the extension to the detection of other species with sharp absorption lines in the visible and near infrared should be straightforward.

DOPPLER FM SPECTROSCOPY

FM Line Shapes

The range of experimentally observable FM line shapes is wide, even for a simple Lorentzian line under the limiting conditions for which Equation 7 applies. Bjorklund et al (21) plotted families of FM absorption and dispersion curves at different modulation frequencies that would be obtained by scanning the carrier frequency across a Lorentzian line characterized by attenuation δ(ω) and phase shift ϕ(ω):

\[
\delta(\omega) = \delta_{\text{max}} \left( \frac{1}{R^2(\omega) + 1} \right),
\]

\[
\phi(\omega) = \delta_{\text{max}} \left( \frac{R(\omega)}{R^2(\omega) + 1} \right),
\]

where \( R(\omega) = (\omega - \Omega_0)/\Gamma \) is the detuning from resonance, normalized to \( \Gamma \), the half-width at half maximum. At modulation frequencies low compared with the resonance line width, the in-phase component approaches the derivative of \( \delta \), and the quadrature component is of negligible magnitude. Figure 9a depicts a case near this limit. Plotting the in-phase and the quadrature FM signals as functions of the scanning carrier frequency gives the line shapes shown. The zero of detection phase can be found experimentally simply by maximizing the signal intensity at small detuning of the carrier frequency from line center.

In the high-modulation frequency limit, each sideband scans across the resonance feature in isolation, giving an in-phase signal that is an offset image of the absorption, followed by an inverted image as the other sideband sweeps through the resonance. Figure 9b depicts this case. The sharp change in the quadrature signal as the carrier frequency crosses the resonance feature contrasts with the
in-phase absorption signal, which is flat as the carrier frequency scans through the resonance, again giving a distinctive operational method of adjusting to a known reference phase of 0° or 90°. For Gaussian absorption lines, the FM line shapes are qualitatively similar (52), still given by Equation 7, but using Gaussian expressions for δ(ω) and ϕ(ω) instead of the Lorentzian versions of Equations 8 and 9. The dispersion near a Gaussian absorption line is not as simple as the form of Equation 9, but it can be written (52) in terms of the Gaussian absorption using the Kramers-Kronig relations, provided the probe laser power is kept below saturating intensities (53). FM with strong fields leads to a more complex behavior, and has been treated in some detail (54, 55), using time-dependent density matrix methods.

Typical Doppler-broadened line widths for optically detected thermal and hyperthermal small molecules are in the 3- to 10-GHz range. To measure these lines in the isolated sideband limit requires modulators and detectors operating
at technically demanding frequencies of 20 GHz and higher. Alternatively, in the slow-modulation limit, signals increase linearly with both modulation frequency and modulation index. This encourages operation in a region where (a) second and higher order sidebands are not completely negligible, (b) the absorption spectrum is not simply the integral of the in-phase FM spectrum, and (c) the phase angle of detection is harder to determine than in the limiting high- or low-frequency modulation limits. For Doppler spectroscopy, one is interested in a precise determination of the absorption line shape function $\delta(\omega)$ from the measured FM spectrum, which depends also on the dispersion line shape $\varphi(\omega)$ unless the phase angle $\theta$ can be set precisely to integer multiples of 180°. Thus two potential problems need to be solved before FM measurements of arbitrarily shaped Doppler broadened lines can be used for quantitative Doppler spectroscopy. First, one must be able to measure the phase accurately enough to obtain an FM spectrum that depends only on $A_{FM}(\omega)$ as defined in Equations 4 and 5. And second, the finite difference relation between $A_{FM}(\omega)$ and $\delta(\omega)$ needs to be inverted to give $\delta(\omega)$.

**Phase Determination** For the measurement of arbitrary Doppler line shapes, with sideband spacings on the order of the Doppler widths, we have found two-channel data acquisition using an I and Q demodulator to be useful for simultaneous phase determination and phase correction (52). An I and Q demodulator is a narrow band communications device consisting of a 0° power splitter, a 90° power splitter, and a pair of double-balanced mixers. The rf signal from the photodiode is split in half and applied as input to the two mixers, which are referenced to 90° delayed (Q-channel) and undelayed (I-channel) copies of the reference oscillator signal. The Q output channel has an accurate 90° phase lag relative to the I output channel. The loss in signal level due to splitting the rf power into two channels is partially compensated by the case of performing accurate phase corrections on the data. For an arbitrary phase angle $\theta$, the $I$ and $Q$ spectral line shapes will be different linear combinations of the absorption and dispersion components:

$$I_{FM}(\omega) = \cos \theta A_{FM}(\omega) + \sin \theta D_{FM}(\omega),$$

$$Q_{FM}(\omega) = \cos(\theta - \pi/2)A_{FM}(\omega) + \sin(\theta - \pi/2)D_{FM}(\omega)$$

$$= \sin \theta A_{FM}(\omega) - \cos \theta D_{FM}(\omega).$$

When the shapes of the absorption and dispersion components are known, as for a Gaussian, Doppler-broadened line, $\theta$ can be determined with good accuracy in a one-parameter nonlinear fit to $I_{FM}(\omega)$ and $Q_{FM}(\omega)$. Phase correction is then accomplished with a numerical rotation of $I_{FM}(\omega)$ and $Q_{FM}(\omega)$ by an angle of $-\theta$ to recover pure absorption and dispersion FM line shapes (52):

$$A_{FM}(\omega) = \cos \theta I_{FM}(\omega) + \sin \theta Q_{FM}(\omega)$$

$$-D_{FM}(\omega) = -\sin \theta I_{FM}(\omega) + \cos \theta Q_{FM}(\omega).$$
Figure 10  Algorithm for phase determination with I and Q nascent data.

The phase correction method gives the most accurate results when $\theta$ has already been adjusted optically or electronically to be close to an integer multiple of $\pi/2$, and only small computed corrections are required.

We recently generalized this phase correction method to arbitrary, non-Gaussian Doppler line shapes, based on the algorithm illustrated in Figure 10. The iterative method seeks a phase angle $\theta$ that leads to a maximally consistent dispersion line shape obtained in two independent ways from the $I$ and $Q$ data. The FM dispersion spectrum generated directly from the rotated data is compared with another version using the Kramers-Kronig relation to compute the dispersion line from the trial rotated absorption spectrum. Figure 11 illustrates this approach for a very non-Gaussian line shape, observed for an anisotropic velocity distribution of monoenergetic CN photofragments from ICN (56). The starting raw spectral line shapes for $I$ and $Q$ data are shown above the numerically determined $\delta'(\omega)$ and $\varphi(\omega)$ for the best correction phase angle of 175.0°. The inversion of the trial $A_{FM}(\omega)$ to $\delta(\omega)$ is described below. The Kramers-Kronig transform is given by

$$\varphi(\omega) = -\frac{1}{\pi} P.V. \int_{-\infty}^{\infty} \frac{\delta'(\omega')}{\omega - \omega'} d\omega',$$

which can be implemented by a numerical convolution of $\delta(w)$ with the function $1/w$, where $w$ is a detuning parameter. The convergence is surprisingly good, as long as $w$ is sampled with an even number of points, symmetrically displaced around 0. Contributions from absorption more than a few line widths away from the detected feature of course determine the average value of $\varphi(\omega)$ near the resonance.
Figure 11. Sample data to illustrate the phase determination using the algorithm of Figure 10.
But because the FM dispersion spectrum depends only on a local finite difference according to Equation 6, restricting the integration limits in Equation 13 to a region near the resonance still gives a good approximation to the shape of the local dispersion, as shown in the center panel of Figure 11. A finite difference FM dispersion spectrum computed from $\varphi(\omega)$ using Equation 6 is compared with the rotated FM dispersion spectrum (see Figure 11, bottom panel). It should be emphasized that no functional form need be assumed for the line shape in this analysis, which compares two different direct transformations of the raw data. The best value of $\theta$ is typically determined in a few seconds of computer time within $\pm 0.1^\circ$ for data of the quality shown. Phase angles so determined are found to agree well with the values determined in separate measurements, from Gaussian fits to thermalized Doppler spectra acquired at higher pressures or sampled at longer times. Knowing the phase angle, one can use Equation 12 to “clean up” an experimental line shape, producing $A_{FM}(\omega)$ without contamination from the dispersion component.

**Inversion of FM Absorption Spectra to Doppler Profiles** Even with the phase calibration problem under control, one still needs to transform $A_{FM}(\omega)$ to the Doppler profile, $\delta(\omega)$, by inverting Equation 5. In the limit of closely spaced, weak sidebands, $\delta(\omega)$ can be obtained by integrating $A_{FM}(\omega)$. In the isolated sideband limit, $A_{FM}(\omega)$ is simply an offset copy of the absorption, $\delta(\omega-\omega_m)$, followed by an inverted copy at $\omega + \omega_m$. The case of intermediate modulation frequency for weak sidebands has been treated by North et al (52). A simple and exact recursive expression for $\delta(\omega_i)$ in terms of $A_{FM}(\omega_i)$ at a uniformly spaced set of $\omega_i$ commensurate with the sideband spacing can be derived. The propagation of errors from $A_{FM}(\omega_i)$ to $\delta(\omega_i)$ produces periodic variations related to the sampling interval, reflecting random walk accumulation of errors in uncorrelated subsets of the FM data. An approximate inversion, based on a Taylor expansion of $\delta(\omega)$, is independent of the sampling interval and shows better stability to noise than the exact solution. This approach is described by North & Hall (57) and consists of forming a linear combination of the integral and the first derivative of the measured FM line shape:

$$\delta(\omega_0) \approx \frac{1}{2\omega_m} \int_{-\infty}^{\infty} A_{FM}d\omega - \frac{\omega_m}{12} \left[ \frac{dA_{FM}}{d\omega} \right]_{\omega_0}. \tag{14}$$

The second term gives the leading correction to the Doppler profile as the modulation frequency increases beyond the wavelength modulation limit of small $M$ and low $\omega_m$. It is this approach that is included in the iterative evaluation of the detection phase angle, $\theta$, described above. A generalization of the inversion of in-phase and quadrature FM spectral data in the presence of amplitude modulation to give $\delta(\omega)$ and $\varphi(\omega)$ has recently been described by Wynands & Nagel (58).

For the most exacting work, if the functional form of $\delta(\omega)$ is known, determination of the line shape parameters is best accomplished by direct fitting to the
phase-corrected FM data, \( A_{FM}(\omega) \), using Equation 5 to account for the small effects of higher order sidebands. The error analysis in this approach is simplified because the errors in the FM space are independent at each step of the frequency scan. This approach has been used by Costen et al (56) in the work on ICN photodissociation, discussed below. Even if small, the errors in neighboring frequencies of the transformed Doppler spectrum, \( \delta(\omega) \), obtained using Equation 14 are strongly correlated and can produce slightly biased results and inaccurate error estimates if used as input data in a conventional least-squares parameter optimization.

**FM Doppler Spectroscopy of Photofragments**

Besides spectroscopy and kinetics, another application in chemical dynamics particularly well suited to transient FM spectroscopy is the measurement of photofragment Doppler profiles. Doppler-broadened line shapes probe the three-dimensional velocity distributions and the rotational polarization of spectroscopically selected photofragment quantum states. The early applications of Doppler spectroscopy to molecular photodissociation were based on laser-induced fluorescence (LIF) in the mid 1980s and the field has been extensively reviewed (59–62).

The speed distribution of a state-selected photofragment, derived from Doppler spectroscopy, mirrors the internal energy of the undetected coincident fragment through energy and linear momentum conservation. The recoil velocity angular distributions provide information about the excited state symmetry, dissociation timescale, and geometry changes during dissociation. The rotational polarization, and its correlation with the recoil velocity, can provide a rich signature of the stereodynamics of dissociation, coherent and incoherent contributions, and diabatic and adiabatic fragmentation paths on multiple potential energy surfaces. The access to this type of highly correlated information accounts for much of the power and popularity of Doppler spectroscopy and the related techniques of ion imaging, Rydberg tagging, and REMPI-time-of-flight spectroscopy. These techniques have been reviewed recently in the context of contemporary progress in photofragmentation dynamics (63–65). We here wish to highlight some of the features of FM Doppler spectroscopy that distinguish it from these related methods.

As a linear absorption spectroscopy, the method is independent of the fluorescence quantum yield and can take advantage of long-path or multipass geometries for signal enhancement. This can partially compensate for the intrinsically lower sensitivity of absorption-based techniques, compared with fluorescence or ionization-based methods. The single-photon nature of the probe process limits the complexity of the vector analysis for polarization studies while retaining high sensitivity to a dynamically useful set of low-order moments of the correlated velocity-angular momentum distribution. The use of stable, high-resolution cw lasers means that the instrumental resolution is typically a negligible source of broadening in the Doppler profiles, avoiding the troublesome procedure of correcting for imprecisely known and possibly unstable laser line widths in some
pulsed LIF Doppler experiments. Background luminescence, an unpredictable, and occasionally unavoidable, problem in pump-probe Doppler LIF experiments, does not produce a background signal in FM spectroscopy. Consequently, even though the theoretical shot-noise sensitivity limit for FM absorption spectroscopy does not closely approach the theoretical photon-counting sensitivity for LIF, in our experience, much higher quality Doppler spectra are often attainable by transient FM methods, even for a good LIF molecule, like CN.

Even for similar signal-to-noise ratios in raw LIF and transient FM Doppler profiles, the useful information in the FM spectrum can be larger because of the derivative nature of the FM spectrum. With noiseless data, the integral \( \delta \) and differential \( A_{\text{FM}} \) forms of the Doppler line shape are interconvertible and carry the same information. But in the inevitable presence of noise, the transformation from \( A_{\text{FM}}(\omega) \) to \( \delta(\omega) \) is a smoothing operation similar to integration; the inverse process reduces the signal-to-noise ratio.

For multicomponent, polarized distributions with nonseparable speed and angular distributions, less-averaged techniques will have advantages over Doppler spectroscopy. Core-sampled TOF and Rydberg tagging restrict the detection to molecules moving in one direction, enhancing the velocity resolution by reducing the detected solid angle. Ion imaging methods maintain the Fellgett advantage of Doppler spectroscopy, but record planar rather than linear projections. The calibration, frame transformation, and image analysis can be substantially more complex for ion imaging than for Doppler spectroscopy, but the reconstruction of highly structured velocity distributions should generally be more stable from image or core-sampled data than from Doppler measurements.

Unimolecular Dissociation Dynamics

Unimolecular reactions that proceed without a reverse activation barrier constitute an important class of reactions the understanding of which continues to present a special challenge to modern rate theory. The usual concept of a transition state becomes ambiguous when no saddle point can be identified from an inspection of the potential energy surface. Testing and refining the theoretical treatment of such reactions remains a topic of active interest (66–68). Direct rate measurements for energy-selected molecules are the primary experimental data. More detailed experimental probes of the energy-dependent mode couplings and tests of the statistical approximations come from measurements of photofragment excitation spectra, correlated state distributions, and photofragment rotational polarization. We highlight recent work on NCCN and CH$_2$CO, prototype molecules for this class of reactions, to illustrate the kinds of questions that can be addressed with high-resolution FM Doppler spectroscopy.

**NCCN: K-Scrambling and Exit Barriers** The photodissociation of NCCN at 193 nm was the first photoinitiated unimolecular reaction studied by FM Doppler spectroscopy (57). Optical excitation to the $^1\Sigma_u^-$ and $^1\Delta_u$ states leads to a pair
Figure 12  Nascent Doppler profiles for CN photofragments from the unimolecular dissociation of NCCN. For each rotational state, \( N \), the difference between broader Q-branch lines and narrower R-branch lines is fit with a single parameter to give the average \( v \cdot j \) correlation. [Adapted with permission from Figure 5 of Reference 57 (c⃝ 1997, American Institute of Physics).]

of ground state CN radicals following nonradiative coupling to the continuum. Previous experiments had shown that the product state distributions could be well modeled using phase space theory (PST), which suggests fragment separation through a loose transition state on the barrierless ground state surface (69, 70). Nascent CN fragment FM Doppler profiles, however, reveal significant differences from statistical predictions and surprisingly rich dissociation dynamics.

Figure 12 shows Q- and R-branch Doppler profiles for three CN \((v = 0)\) states, following phase correction and transformation of the FM data to absorption line shapes. The profiles become narrower for higher rotational states (labeled by \( N \), the integer rotational quantum number excluding electron spin), in accordance with energy conservation and PST. The concave Q-branches and convex R-branches are the signature of a perpendicular correlation between the fragment rotational angular momentum vector, \( j \), and its recoil velocity, \( v \) (59, 60, 71). The solid lines are fits to the data that involve a single adjustable parameter corresponding to the ensemble average of \( P_2 (\hat{v} \cdot \hat{j}) \), the \( v \cdot j \) correlation. Although it is now understood (72, 73)
that such a correlation can arise in a purely statistical dissociation as a simple consequence of angular momentum conservation, the strength of the correlations in NCCN exceed PST predictions by a factor of about two, indicating additional dynamical constraints. Figure 13 shows the $N$-dependent $v$-$j$ correlations for CN fragments in both $v = 0$ and $v = 1$. The lines in Figure 13a show the PST predictions, where the combined projection of the two fragment angular momenta along the recoil direction (the total helicity, $\Lambda$) is bounded only by the total angular momentum of the parent molecule. At room temperature, this assumption of full mixing of the helicity states seriously underestimates the observed fragment vector correlations. The lines in Figure 13b were computed with the restriction of the total helicity to $\Lambda \leq 1$. In the axial recoil limit, $\Lambda$ correlates to the $K$ projection number of a symmetric top, or the vibrational angular momentum of a linear molecule dissociating along its principal axis. The constraint on $\Lambda$, therefore, gives the predicted consequences of an approximate conservation of the $K$-quantum number in the dissociation, following its initial optical selection to be $K = 1$. Up until the last few accessible quantum states of CN, these predictions match the data exactly. Since publication of the work by North & Hall (57), new FM results have probed the highest accessible rotational states for both $v = 0$ and $v = 1$ states of CN. These measurements, included in Figure 13, show a reduction in the $v$-$j$ correlation in the last few quantum states, which can be modeled as a breakdown of the axial recoil approximation for small radial velocities, spoiling the correlation between...
Accurate speed distributions measured for state-selected CN fragments revealed that the bond dissociation energy that gave reasonable PST fits to the state distributions and the right appearance threshold for CN fragments (75) could not consistently describe the total energy balance. No energy adjustment within a PST model could fit the observed speed distributions. Instead, flat-topped Doppler spectra indicate a failure to generate the highest energy coincident fragments, or in other words, a minimum kinetic energy for each fragment state. This is consistent with a small exit barrier, whose energy is preferentially partitioned into product translation. The explanation for this pattern in the correlated state distribution is unclear at this time. We suggested the strong electrostatic anisotropy in the exit channel as a possible explanation within the context of ground-state dissociation (57). The photophysics and nonradiative coupling of the bright state to the dissociative continuum is complex, however, and a role for triplet surfaces cannot be ruled out (76, 77). It is almost certainly an oversimplification to consider the optical and nonradiative processes as merely a convenient way to prepare ground state NCCN molecules with a specific energy at time zero.

**CH\textsubscript{2}CO: Dynamical Constraints and Correlated State Distributions** The unimolecular dissociation of ketene, CH\textsubscript{2}CO, has been extensively studied (66) as an important benchmark system for testing statistical models of dissociation. The general features of the dissociation are well known; product state distributions and microcanonical reaction rates as a function of excitation energy have been reviewed by Green et al (66). At wavelengths near the singlet dissociation threshold, the product state distributions and reaction rates are well described by PST. As the excitation energy is increased, the transition state tightens and a quantitative description of the experimental data requires more sophisticated theoretical treatments. The reaction rate does not increase with energy as quickly as the PST prediction, and the product state distributions deviate from PST, consistent with an underpopulation of some asymptotically allowed product channels. Several prescriptions for representing these deviations have been developed. Wade et al (78) found that rescaling the PST-correlated CO rotational distributions by the experimental population of the CH\textsubscript{2} rovibrational states describes the leading deviation from PST in the global CO rotational distributions. This behavior could be expected if the more widely spaced CH\textsubscript{2} rotational levels were adiabatically frozen out before the CO rotational degrees of freedom uncouple from the transitional modes. Correlated state distributions of CH\textsubscript{2} for selected CO states have been directly measured by a metastable tagging technique (79). The data could be modeled by restricting a PST-correlated state distribution with adjustable upper and lower bounds on allowed impact parameters for each detected CO state, in an attempt to represent plausible transition state geometries. Neither empirical modification of PST can completely describe all the available data, the latter treatment failing to reproduce measured photofragment excitation spectra at lower energies.
Clearly additional work is necessary to distinguish between models whose choices of constraints suggest very different physical origins.

At excitation energies above the threshold for the formation of CO ($v = 1$), the CO vibrational distribution is not well predicted by PST. The separate statistical ensembles (SSE) model (80), which assumes that the product vibrations become adiabatic before rotations, provides excellent agreement with the experimental vibrational distributions. Modification of the PST correlated product state distribution within the SSE model is straightforward, applying a single scaling factor to each coincident vibrational channel while leaving the correlated rotational distribution unaffected within each vibrational channel. Earlier Doppler spectroscopy of CH$_2$ (33) following ketene photolysis at 308 nm has suggested that the low rotational states of CH$_2$ in its vibrational ground states are formed in coincidence with two to three times as much CO ($v = 1$) as the SSE prediction. Because the global population of CO in $v = 1$ agrees with SSE, this indicates that the rotational state correlations within each vibrational channel are not PST-like.

Shown in Figure 14 are two new sets of FM Doppler line shapes for three CH$_2$ rotational states above and below the energetic threshold for formation of CO ($v = 1$). The spectra on the left are from ketene photodissociation obtained in a room-temperature, low-pressure cell. The contribution from the slower CO ($v = 1$) coincident channel is clearly observed for the $J_{K_a K_c} = 1_{10}$ state, a result of the sensitivity of the “derivative-like” nature of FM spectra to features of the correlated distribution, which appeared as less convincing inflection points in the

![Figure 14](image-url)
direct absorption line shapes (33). This feature is absent in the $6_{52}$ state, a CH$_2$ level with an energy high enough to close the coincident CO ($v = 1$) channel. Despite the improved signal-to-noise over previous measurements, detailed analysis of the data is highly dependent on the treatment of the threshold dissociation from hot bands in the thermal sample. The data to the right are Doppler spectra taken in a single-pass slit-jet that removes the contributions of the parent internal energy and greatly reduces the effect of the initial parent velocity on the spectra. Significant contributions from the CO ($v = 1$) channel are easily resolved in the $1_{10}$ and $3_{12}$ spectra, the latter only 67 cm$^{-1}$ below threshold for closing the CO ($v = 1$) coincident channel. The two CH$_2$ lines previously illustrated in Figure 5 probe $4_{14}$ and $5_{15}$ states, respectively 29 cm$^{-1}$ below and 58 cm$^{-1}$ above the threshold for closing the CO ($v = 1$) coincident channel. The prompt spectra of these states confirm the formation of coincident CO ($v = 1$) only with the $4_{14}$ state.

The shapes of the derived CO rotational distributions in $v = 0$ coincident with these CH$_2$ states are qualitatively different from the common functional form predicted by PST, SSE, and the constrained PST model of Wade et al (78). The potential of FM Doppler spectroscopy in the study of the photodissociation of jet-cooled molecules is enticing, permitting in this case a view of the coincident state distribution from an orthogonal vantage point to the CO metastable studies (79). In ketene, this should provide new tests for increasingly sophisticated unimolecular theory. A full report of the jet-cooled FM Doppler line shapes is in press (80a).

**Direct Dissociation on Multiple Excited States: ICN Photodissociation** The ultraviolet photodissociation of ICN has become a prototype system for multiple surface dynamics. Good summaries of the extensive past experimental (81) and theoretical (82) work have been recently published. The continuum near 260 nm contains five bright states. A bent $^3\Pi_{0^+}$ ($A'$) state correlates diabatically to the $^3\Sigma^{-}$ excited state of iodine (I') and is reached by a parallel transition from the linear $^1\Sigma^{+}$ ground state. Bent $A'$ and $A''$ components of $^1\Pi_1$ and $^3\Pi_1$ states correlate diabatically to ground state iodine and are populated by weaker perpendicular transitions centered to the blue and the red, respectively, of the $^3\Pi_{0^+}$ transition. An avoided crossing between the $A'$ component of the $^1\Pi_1$ state and the ($A'$) $^3\Pi_{0^+}$ state accounts for the interesting nonadiabatic dynamics in this system. Direct dissociation on multiple excited states typically produces substantial recoil velocities and highly polarized photofragments, whose characterization by Doppler spectroscopy is highly revealing.

FM Doppler profiles of CN fragments arising from photodissociation at 222 nm, 248 nm, 266 nm, and 308 nm (56, 83) represent an extensive set of high-quality data for comparison to current theory. The extra rotational branches of the $A-X$ probe transition (compared with the more commonly used violet $B-X$ system), the higher spectral resolution of the cw probe laser, and high signal-to-noise permit a full polarization analysis of the nascent Doppler line shapes,
even for those CN rotational states produced in coincidence with both I and I'.
The results provide insight into (a) the relative transition strengths to the excited
states, (b) curve-crossing probabilities and their relation to bending angle and the
asymptotic fragment angular momentum, and (c) the role of vibrational hot-bands.
Although there is agreement with the broad conclusions of recent multi-surface
dynamics calculations, refinements are also necessary, including a reassessment
of theoretical transition moments. In this review, we highlight the resolution of
adiabatic and diabatic paths to the same product states through the polarization
analysis of the FM Doppler spectra (56).

Figure 15 shows nascent FM absorption phase line shapes for CN (N = 30,
v = 0) arising from the ICN photodissociation at 248 nm. The six panels show R₁

![Figure 15](image_url)
branch (a–c) and Q₁ branch (d–f) transitions probing the same state with linearly polarized pump and probe light in three different geometries. Fast and slow contributions from the I and I’ channels are clearly resolved and reveal differences in their angular distributions and their rotational polarization. The FM Doppler profiles were analyzed using incoherent linear combinations of the five orthogonal limiting cases of the relative directions of v and j with respect to the parent molecule’s transition moment, µ, described by Dixon (71) as cases A–E. Coherent alignment effects, arising from interference between multiple paths of different symmetry, were shown to vanish in the limit of high-j fragments (84), justifying the incoherent analysis. The simultaneous fitting of six Doppler profiles for each CN state (R- and Q-branches measured in three different geometries) allows a stable determination of the relative A–E contributions in each channel and an I/I’ branching ratio. The solid lines shown in Figure 15 represent the best global fit to the full data set. The reader is referred to Costen et al (56) for a more thorough description of the polarization analysis.

Representation of the photofragment distributions as linear combinations of cases A–E for fully resolved coincident states of I and CN permits a clear physical interpretation of the data through a polarization label that identifies the optical parentage of each final state. Dixon’s case B can be associated with the parallel transition to the 3Π₁ state, and cases C and E can be associated with the A’ and A” components of a perpendicular transition, respectively. In each of these three cases, v and j are perpendicular, the limiting behavior for the rapid dissociation of a slowly rotating triatomic molecule. Cases A and D, respectively, correspond to parallel and perpendicular transitions leading to v || j, which can occur in a triatomic dissociation through a depolarization associated with deviations from the axial recoil limit. Figure 16 summarizes the results of the A–E analysis of CN FM Doppler profiles from dissociation at 248 nm.

In ICN dissociation at 248 nm, only cases B and E contribute significantly to the I’ channel, corresponding to a (dominant) diabatic and a (minor) adiabatic A’ path. In contrast, there is an additional path to formation of CN in the I channel: the uncoupled path from the A” component of the 1Π₁ state. The involvement of this path is confirmed by observation of significant case C(A”) contribution in the resulting fits, but only in the I channel. This is consistent with the previous conjecture of Black (85), based on the rotational state-dependent alignment of CN. The theoretical prediction that the 5A’ (1Π₁) state is linear beyond the conical intersection (82) has interesting consequences in the dissociation dynamics. Trajectories that originate on the 4A’ (3Π₁) surface (case B) and reach the conical intersection at small bending angles are more likely to make a nonadiabatic transition to form I’ and result in low N CN fragments due to the restoring force on the 5A’ surface. Trajectories that originate on the 4A’ (3Π₁) surface and reach the intersection highly bent follow an adiabatic path to form I, but the CN fragments continue to accumulate angular momentum beyond the avoided crossing. This behavior is clearly observed: The contribution of case B dominates the low rotational states in the I’ channel and becomes increasingly significant at higher rotational states in the I channel.
Figure 16  Fitted parameters for ICN photodissociation at 248 nm. (a) Rotational state-dependent I' branching ratio; (b) CN rotational distributions for the I(•) and I'(•) channels. Total populations from (81); branching ratio from FM Doppler measurements. (c) Stacked bar graph showing the contributions cases A–E to the fits for the I' channel, from bottom A (black), B (dark grey), C (white), D (black), and E (light grey). (d) Stacked bar graph showing the contributions of cases A–E to the fits for the I channel, sequence identical to c. [Adapted with permission from Figure 9 of Reference 56 (© 1999, American Institute of Physics).]
The rotationally averaged contributions can also provide substantial insight into the wavelength dependence of the dynamics. The partitioning of the total case E contribution between the I and I* channels reflects the fate of trajectories starting on the 5A’ (1Σ1) surface. The fits reveal that these primarily follow an adiabatic path to I* at 266 nm and become more diabatic at shorter wavelengths, consistent with an increase in the kinetic coupling between adiabatic surfaces with excitation energy. It is interesting to note that the opposite trend is observed from the rotationally averaged case B contribution to I and I* channels, which suggests that the radial dependence of the bending coordinate is very different for the 4A’ and 5A’ states. In addition, the dominant case B contribution to all wavelengths is contrary to theory and suggests that the relative intensity of the absorption to the 3Π0+ state in the red and blue wings of the absorption spectrum have been significantly underestimated.

Finally, FM Doppler spectra have recently been obtained using circularly polarized photolysis and probe beams to resolve the angular distribution of oriented CN photofragments. Unlike the linearly polarized Doppler spectra, these measurements do depend on the phase difference between multiple excitation paths to the same final state. Their interpretation can extend the understanding of both the dissociation dynamics of ICN and the more general questions of coherent effects in multiple surface reactions.

SUMMARY

We have reviewed the basic practice of FM spectroscopy, as originally developed nearly 20 years ago, and provided several exciting and compelling new demonstrations from the recent literature of its use in the study of transient spectroscopy, kinetics, and chemical dynamics. The incremental expense and difficulty of applying FM techniques to an existing cw laser spectroscopy apparatus are minimal. With the expanding commercialization and spectral range of external cavity diode lasers, such experiments are becoming easier, cheaper, and smaller. The extension to shorter wavelengths of electro-optic phase modulators will expand the range of detectable molecules.

One promising future application is to the Doppler spectroscopy of bimolecular reactions (86, 87), where differential cross sections and rotational polarization of reaction products may be deduced from a set of Doppler profiles of nascent reaction products. The sensitivity should be adequate for such measurements under bulb conditions with photogenerated reactants.

The combination of FM techniques with high-Q cavities offers some advantages of both cavity ring down and conventional FM spectroscopy. An astounding noise-equivalent absorption sensitivity of 10^{-14} per cm in 1 s has recently been demonstrated for weak molecular overtone transitions near 1000 nm (8). With lower reflectivity cavity optics, sensitivity can be traded for improved time resolution, merging toward conventional FM spectroscopy in a multipass cell. We hope
this review will encourage more chemical physicists to consider the possibilities of FM in their next transient spectroscopic problem.

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Figure 2  Superposition of three uniformly spaced sine waves. The black, red and blue waves at the bottom of each panel represent $\omega_0$, $\omega_0-\omega_m$ and $\omega_0+\omega_m$, while the low frequency wave in the middle of each panel is $\omega_m$. The composite waveform at the top of each panel is the sum of carrier and sidebands, showing the amplitude modulation arising from (a) unbalanced amplitudes of the two sidebands and (b) unbalanced phases of the sidebands. Notice the 90° phase shift between absorption (a) and dispersion (b). Animated versions of these figures are available in the Supplemental Materials Section of Annual Reviews world wide website.

Figure 5  Illustration of the two-dimensional transient FM Doppler spectra. The rows of the data are time-dependent spectra; the columns are wavelength-dependent transient waveforms. The spectra probe two rotational states of singlet CH$_2$ produced in the unimolecular dissociation of ketene in a supersonic jet. An animated version of this figure, illustrating multiple time and wavelength cuts through the data is available on the Annual Reviews website.
Figure 16  Fitted parameters for ICN Photodissociation at 248 nm. (a) rotational state-dependent I* branching ratio (b) CN rotational distributions for the I (○) and I* (●) channels. Total populations from reference 81, branching ratio from FM Doppler measurements (c) stacked bar graph showing the contributions cases A-E to the fits for the I* channel, from bottom A(black), B(blue), C(white), D(black), and E(green) (d) stacked bar graph showing the contributions of cases A-E to the fits for the I channel, sequence identical to (c). (Adapted with permission from Figure 9 of reference 56, © 1999, American Institute of Physics.)