Quantitative analysis of gas phase molecular constituents using frequency-modulated rotational spectroscopy

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ABSTRACT
Rotational spectroscopy has been used for decades for virtually unambiguous identification of gas phase molecular species, but it has rarely been used for the quantitative analysis of molecular concentrations. Challenges have included the nontrivial reconstruction of integrated line strengths from modulated spectra, the correlation of pressure-dependent line shape and strength with partial pressure, and the multiple standing wave interferences and modulation-induced line shape asymmetries that sensitively depend on source-chamber-detector alignment. Here, we introduce a quantitative analysis methodology that overcomes these challenges, reproducibly and accurately recovering gas molecule concentrations using a calibration procedure with a reference gas and a conversion based on calculated line strengths. The technique uses frequency-modulated rotational spectroscopy and recovers the integrated line strength from a Voigt line shape that spans the Doppler- and pressure-broadened regimes. Gas concentrations were accurately quantified to within the experimental error over more than three orders of magnitude, as confirmed by the cross calibration between CO and N$_2$O and by the accurate recovery of the natural abundances of four N$_2$O isotopologues. With this methodology, concentrations of hundreds of molecular species may be quantitatively measured down to the femtomolar regime using only a single calibration curve and the readily available libraries of calculated integrated line strengths, demonstrating the power of this technique for the quantitative gas-phase detection, identification, and quantification.

INTRODUCTION
The use of spectroscopic techniques for quantitative measurements of molecular species has a long and rich history. For gas phase chemical reactions, scientists and engineers primarily depend on three such techniques: gas chromatography (GC), mass spectrometry (MS), and electromagnetic spectroscopy. While GC and MS are most widely used for identifying species and measuring their concentrations, they have limitations. For low resolution MS, species with similar molecular mass (CO and N$_2$, H$_2$O and NH$_3$, N$_2$O and C$_2$H$_6$, etc.) are difficult to distinguish, and this ambiguity can confuse interpretation of the mass spectrum. Although high resolution MS partially solves this problem, the destructive nature of MS also limits its utility, especially for the...
analysis of molecular decomposition reactions. GC is well known for its ability to separate molecules, but specialized chromatography columns are needed to separate different gas mixtures and achieve acceptable resolution. Additionally, the time-consuming separation process in GC makes on-line or in situ detection more difficult if not impossible. Gas-phase analysis with electromagnetic spectroscopy is also widely used, where infrared absorption and Raman scattering spectra provide both qualitative and quantitative analyses. But these techniques also have limitations, including the small molecular absorption and scattering cross sections, respectively, and a degree of uncertainty and ambiguity caused by the sensitivity of vibrational mode frequencies to the host environment.

A powerful alternative technique, high resolution terahertz spectroscopy for measuring the rotational transitions of gas phase molecules, exhibits unsurpassed recognition specificity and excellent sensitivity at low pressures. However, rotational spectroscopy has not been as widely adopted because of the comparative immaturity, fragility, and expense of sources and detectors of radiation at the requisite frequencies (0.1–3.0 THz). It has nevertheless found niche applications in astrophysics and gas phase chemistry for detecting molecules or molecular fragments with permanent dipole moments. The nondestructive nature of rotational spectroscopy distinguishes it from destructive techniques like MS, especially when monitoring a decompositional reaction where hard ionization in MS could decompose the molecule yet soft ionization could leave fragments with similar molecular weight and mass ambiguity. Moreover, rotational spectroscopy can be applied in situ, making it more intuitive and interpretable than GC-based analysis where the effect of the column must be taken into consideration. Now that the technology for generating and detecting terahertz radiation is rapidly advancing, its many significant advantages, especially for applications including isotope-labeling, monitoring chemical reactions, and real time, nondestructive, in situ analysis. Let us therefore consider in detail the two most compelling features of rotational spectroscopy, its unparalleled recognition specificity, and its detection sensitivity.

Molecular recognition specificity derives from how sensitively the quantized rotational states are determined by the molecular moments of inertia. Consequently, the spectra of each molecular species is distinctively unique, especially in the low pressure (<0.1 Torr) regime where the linewidths are very narrow (<1 MHz) and the absorption features are so well resolved that overlaps are almost nonexistent. Since transition frequencies are routinely measured with very high accuracy (at least seven digits), molecular species are easily and unambiguously distinguishable by their spectroscopic fingerprint. In fact, isotopic substitutions and isomeric reconfigurations are easily resolved spectroscopically, making it trivial to distinguish structurally similar molecules, isotopologues (e.g., CH$_3$OD and CD$_2$H$_2$OH or $^{14}$N$^{15}$N$^{16}$O and $^{14}$N$^{14}$N$^{16}$O), and even enantiomers with multiple chiral centers that would be challenging for MS and GC to discriminate. Often a single, high resolution measurement of a single absorption feature is sufficient to identify a species, but molecules have dozens, hundreds, or even thousands of quantized rotational levels with energies below $kT$. Thus, by unambiguously and redundantly measuring several transitions, virtually absolute recognition specificity may be achieved. For these reasons, rotational spectroscopy is most frequently used for molecular identification.

Molecular detection sensitivity derives from the typically large permanent dipole moments (0.1–3 D), yielding strong absorption features with an intrinsically higher signal to noise ratio (SNR) than other spectroscopies like IR absorption and Raman. Perhaps more importantly, absorption line strengths are proportional to both the constituent molecular concentration and the dipolar transition matrix element. Consequently, if the transition matrix element is known and the line strength is measured for a given temperature, the concentration may be deduced. Indeed, these transition matrix elements may be accurately calculated ab initio and have been tabulated for hundreds of molecules in searchable databases, and their temperature-dependent rotational partition function may be easily estimated. So if the absorption line strengths of specific transitions can be measured at a given temperature, then rotational spectroscopy may be used for the quantitative analysis of molecular concentrations. However, accurately measuring absorption line strengths is much more challenging than accurately measuring transition frequencies, so rotational spectroscopy has been much more frequently used as an analytical technique for molecular identification than for concentration quantification.

The most common method for measuring absorption spectra is to sweep the frequency of a terahertz source, transmit it through the chamber containing the low-pressure gas, and detect the decreased transmission produced by the absorption feature. In this configuration, the principal challenge for quantitative analysis is the requirement to convert the absorption-induced decrease in the detected terahertz signal into a calibrated molecular line strength, from which the partial pressure and concentration may be deduced. Some sort of “detected power-to-pressure” conversion must be accomplished, recognizing that the source power will also vary with frequency and that the molecular absorption feature may only slightly reduce that power. This challenge is complicated by the fact that reflections and standing waves produced inside and outside the absorption chamber also produce strong frequency-dependent power variations at the detector. These variations often dwarf the tiny rotational spectral lines. Luckily, frequency modulation techniques widely applied in nuclear magnetic resonance and electron spin resonance spectroscopies are routinely used in rotational spectroscopy to flatten broad baseline variations and amplify narrow spectral absorption features. Although modulation allows the center frequency of the transitions to be measured accurately, it significantly distorts the line shape, making quantitative analysis challenging since concentrations are proportional to the strength of the undistorted line. These challenges mount as the shape of the modulated line evolves with pressure and the broadening mechanism evolves from Doppler to collisional (or “pressure”), exacerbated by several practical problems including the imperfect choice of modulation depth, the frequency dependence of the source, and the unfortunate line shape asymmetry sometimes produced by the modulation technique. Although many encouraging attempts have been made, solutions to these problems have
historically been idiosyncratic and constrained to a small library of molecules.\textsuperscript{16,18,19,23–28}

Here, we describe in detail a methodology that permits quantitative analysis of gas phase molecular concentrations of a wide range of molecular species at room temperature over a wide range of chamber pressures, using modulation spectroscopy to remove the broad power baseline variations while amplifying the molecular absorption features. This work was motivated by the growing commercial availability of terahertz technologies and a recent demonstration using rotational spectroscopy to analyze reactants and products quantitatively during plasmonic decomposition of carbonyl sulfide (OCS).\textsuperscript{7,21,23} In this report, we detail the instrumentation design and the analytical approach for performing quantitative measurements of gas-phase partial pressures over at least three orders of magnitude using frequency-modulated rotational spectroscopy. We introduce a calibration methodology that will allow this technique to be used for quantitative analysis of almost any molecular species with a permanent dipole moment, even those for which independent calibration may not be possible.

To recover the integrated absorption line strength of a selected rotational transition, we first measure the strength of the terahertz signal that is frequency stepped and modulated to produce a line shape that characteristically resembles the second derivative of the actual line shape. This modulated line shape is fitted by a line shape function described by a harmonic expansion of the modulated Voigt line shape function, used to account for both Doppler broadening and pressure broadening. An additional first-order harmonic term is introduced to account for modulation-induced line asymmetry. Using a nonlinear least-squares fitting routine that reproduces the modulated line shape, the physically meaningful amplitude, center frequency, and broadening parameters are obtained. From these parameters, the unmodulated line shape may be reconstructed, and the line strength may be calculated by a simple integral of this reconstructed line shape. Given that the integrated absorption line strengths of the measured transitions are well known and available from publicly accessible databases,\textsuperscript{18,19} a calibration curve is constructed that converts the measured integrated line strength for a given gas molecule to a deduced concentration as a function of chamber pressure. From this calibration curve, typically using a relatively inert, nonadsorbing gas like carbon monoxide, the partial pressure of any other gas in the chamber may be quantified spectroscopically through the known line strength ratio of the analyte gas to the calibration gas.

This quantitation technique, which represents the principal contribution of this paper, may be used to estimate the concentration of any other gas in the chamber for which line strengths have been or can be calculated. Prior methodologies rely instead on libraries of calibrated spectra and simply compare measured and library spectra to recover concentrations, typically in the low pressure, Doppler-broadened regime.\textsuperscript{21,22} By contrast, our technique even works for gases for which no direct calibration can be accomplished, such as for gases that exhibit strong surface adsorption, that exist transiently, or that spontaneously decompose. The operation of this technique is demonstrated through the self-calibration of two gases [carbon monoxide (CO) and nitrous oxide (N\textsubscript{2}O)] and confirmed by cross-calibration using one gas as a calibration for measuring the concentration of the other. Calibration measurements of carbonyl sulfide (OCS) spanned the Doppler- and pressure-broadened regime, confirming the applicability of this technique in both regimes. The discriminating advantage of this technique is demonstrated by accurately measuring the relative abundance of three N\textsubscript{2}O isotopologues, two of which cannot be distinguished by GC or MS but are easily resolved by rotational spectroscopy. In its current unoptimized form, our instrument is capable of detecting gas molecules with \(\mu\text{Torr}\) partial pressures or femtomolar concentrations. We conclude by discussing ways this excellent sensitivity may be further improved.

**INSTRUMENTATION AND METHODS**

The experimental setup and the related electronics are depicted in Fig. 1. The spectroscopic source was composed of a microwave synthesizer that could be stepped or swept in frequency, followed by a Virginia Diodes, Inc., amplifier-multiplier chain spanning the 210–330 GHz region. Given that low pressure rotational spectra are comparatively sparse and line widths are \(\sim 1\) MHz, this spectrometer is capable of detecting gas molecules with \(\mu\text{Torr}\) partial pressures or femtomolar concentrations. We conclude by discussing ways this excellent sensitivity may be further improved.

**FIG. 1.** A diagram illustrating the instrumentation and associated electronics for this spectrometer. (a) An illustration of the experimental arrangement and (b) a block diagram of the electronics used. \textsuperscript{*}DAQ is an acronym for the "data acquisition" board.
at these frequencies, sweeping the source over 4–6 MHz allowed single rotational transitions to be monitored. It is the integrated absorption strength of these transitions that will be used to ascertain the pressure and concentration of the associated gas molecule. Probe radiation from the source horn antenna was collimated by an off-axis parabolic mirror (OAPM) and propagated through the 10 cm long, 5 cm diameter absorption cell that contained the probed molecules. The transmitted radiation was then recombined by a second OAPM and received by a horn antenna coupled to a Virginia Diodes, Inc., zero-bias Schottky diode detector. The signal, amplified by a transimpedance preamplifier and a low-noise amplifier, was band-pass filtered to reject signals other than the $\varphi = 20$ kHz modulated signal. We used a triangle wave modulation of varying modulation depth (see discussion below) whose second harmonic was detected at $2\varphi = 40$ kHz by a lock-in amplifier (10 ms time constant) with automatic phase adjustment and then read out and signal averaged (1000 times per point) by a computer. A millimeter monitored the voltage following the transimpedance amplifier as a way of measuring the power of the detected radiation. In addition to the two optical windows through which the probe radiation passed, the plus-shaped chamber also featured a third optical window on a perpendicular arm through which UV/visible light could illuminate a photocatalyst, as previously utilized in a recent report. The pressure in the chamber was monitored by an MKS Baratron capacitance manometer and kept between 0.1 and 100 mTorr for all measurements reported here.

We chose CO, N$_2$O, and OCS for this demonstration because each is a linear molecule with a strong permanent electric dipole moment, possesses simple spectra, and is not prone to adsorption on the chamber walls. We demonstrated the quantitation technique using CO and N$_2$O in the low pressure, Doppler-broadened regime, but we also measured the pressure-dependent modulated line shapes of OCS in order to demonstrate that our methodology spans both the Doppler-broadened and pressure-broadened regimes. For the isotopologues involved in the experiments, the rotational transitions we detected are summarized in Table 1.

### Table I. Rotational transitions monitored for selected probed molecules.

<table>
<thead>
<tr>
<th>Probed molecule</th>
<th>Rotational transition</th>
<th>Center frequency (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}$C$^{16}$O</td>
<td>J $\rightarrow$ J + 1</td>
<td>1–2</td>
</tr>
<tr>
<td>$^{14}$N$^{14}$N$^{16}$O</td>
<td>10–11</td>
<td>276.327 80</td>
</tr>
<tr>
<td>$^{14}$N$^{15}$N$^{16}$O</td>
<td>9–10</td>
<td>251.193 60</td>
</tr>
<tr>
<td>$^{15}$N$^{14}$N$^{16}$O</td>
<td>12–13</td>
<td>315.527 10</td>
</tr>
<tr>
<td>$^{14}$N$^{14}$N$^{18}$O</td>
<td>12–13</td>
<td>308.295 34</td>
</tr>
<tr>
<td>$^{16}$O$^{12}$C$^{32}$S</td>
<td>18–19</td>
<td>231.060 99</td>
</tr>
</tbody>
</table>

### FREQUENCY-MODULATED ROTATIONAL SPECTROSCOPY

The integrated intensity of any rotational absorption line is proportional to the molecular concentration. Specifically, for the $i \rightarrow j$ rotational transition at frequency $\nu_0$ for the usual case of $h\nu_0 \ll kT$, the dependence of the absorption coefficient on the concentration of molecules per unit volume, $n$, is

$$\alpha(\nu) = \frac{8\pi^3 n F \nu_0^2}{3ckT} \left(1 - \frac{h\nu_0}{2kT}\right) (|\langle j|\mu|i\rangle|^2 S(\nu, \nu_0),$$

(1)

where $S(\nu_0, \nu_0)$ is the area normalized line shape function at frequency $\nu_0$, $|\langle j|\mu|i\rangle|^2$ is the electric dipole transition matrix element, and $F$ is the fraction of molecules in the lower rotational state $i$ at temperature $T$ as determined by the rotational partition function. Although the analysis presented here assumes room temperature gases, adaptation to other temperatures requires a straightforward recalculation of (1) with an adjusted $F$ from the revised rotational partition function. The integrated intensity for any line shape is simply

$$\alpha_{int} = \frac{8\pi^3 n F \nu_0^2}{3ckT} \left(1 - \frac{h\nu_0}{2kT}\right) |\langle j|\mu|i\rangle|^2.$$  \hspace{1cm} (2)

After rearranging terms and taking $h\nu_0/kT \rightarrow 0$, we can separate the molecule-dependent term

$$M = F \nu_0^2 |\langle j|\mu|i\rangle|^2$$ \hspace{1cm} (3a)

from the molecule-independent term

$$U = \frac{8\pi^3}{3ckT}$$ \hspace{1cm} (3b)

so that (2) gives the simple relation between integrated intensity and molecular concentration

$$\alpha_{int} = MU n.$$ \hspace{1cm} (4)

As noted above, strong frequency-dependent variations of the detected probe signal in the microwave regime—arising from standing waves, multiplier cavity modes, reflections at chamber interfaces, and source spectral nonuniformity—require a technique that is able to distinguish weak signals from the obfuscating background (Fig. 2). We take advantage of the spectral narrowness of the absorption line shape compared to the broader background power variations by using the well-known spectroscopic techniques of source frequency modulation and phase sensitive detection. Specifically, the source was narrowly and rapidly frequency swept with a modulation depth $\omega_d$ and a modulation frequency $\varphi$ so that for any given frequency $\nu_i$, we have $\nu_i \rightarrow \nu_i + \omega_d \cdot f(\varphi)$. The simplest modulation would be $f(\varphi) = \cos(\varphi)$, and other modulation waveforms may be modeled as a Fourier expansion. It was expedient in our measurements to use a triangular frequency ramp, expressed as

$$f(\varphi) = \frac{8}{\pi^3} \left[ \sin(\varphi) - \frac{1}{9} \sin(3\varphi) + \frac{1}{25} \sin(5\varphi) - \frac{1}{49} \sin(7\varphi) + \cdots \right],$$

(5)

with respective rise and fall times of 25 $\mu$s for a $\varphi = 20$ kHz cycle.

This modulation technique works best when $\omega_d$ is comparable to the full width at half maximum (FWHM) of the peak, producing significant signal variation as the source rapidly sweeps over the absorption line. Since the background power variations are specifically much broader, they produce very little signal variation as the
source sweeps over regions away from the absorption line. The modulation works by setting the lock-in amplifier to detect a signal at second harmonic frequency \( \nu \), thereby measuring a modulated line shape approximating the second harmonic modulated spectrum, which can be written as \( A_2(\nu) = \frac{1}{2\pi} \int_0^{2\pi} a(\nu + \omega f(\varphi)) \cos 2\varphi d\varphi \). (6)

the second Fourier coefficient in the cosine expansion of absorption coefficient \( a(\nu + \omega f(\varphi)) \) which is modulated at \( \varphi \) and detected at \( 2\varphi \). The advantage of this approach is that the second harmonic modulated absorption feature can be subsequently amplified without amplifying the flattened baseline. To trace the entire absorption feature, the frequency \( \nu \) was discretely stepped across a 4–6 MHz window in 8–12 kHz intervals (500 frequency increments).

LINE SHAPE FUNCTIONS AND MODULATION

For rotational transitions, the two dominant line broadening mechanisms are Doppler broadening and pressure broadening. The modulated line shape depends on which broadening mechanism dominates. Three other line broadening mechanisms are negligible: the natural linewidth (very small and unchanging), saturation broadening (requires high fields at low pressures), and collisions with the walls of the chamber (small compared to pressure broadening).

Doppler broadening occurs due to the Boltzmann-distributed random velocity components of molecular motion parallel to the incident radiation. The associated frequency shifts produce spectral broadening with a half width at half maximum (HWHM) of

\[
\Delta\nu_D = \frac{\nu}{c} \sqrt{\frac{2kT}{m}} \ln 2 \quad (7a)
\]
determined by the frequency, temperature, and molecular mass \( m \). At low pressures where the rotational transition is primarily Doppler-broadened, the line shape can be characterized by the Gaussian function

\[
\alpha_D(\nu) = \alpha_D(\nu_0) e^{\left(\frac{\nu - \nu_0}{\Delta\nu_D}\right)^2}. \quad (7b)
\]

For Doppler-broadened lines, the height of a Gaussian peak \( \alpha_D(\nu_0) \) is linearly proportional to partial pressure, but the line width \( \Delta\nu_D \) is independent of partial pressure [Fig. 3(a)].

The collisional or pressure broadening mechanism yields a HWHM of

\[
\Delta\nu_L = \frac{1}{2\pi\tau} \quad (8a)
\]

where \( \tau \) is the mean time between collisions, assuming each collision is brief and randomly oriented. For molecules of interest here, distant dipole-dipole collisions and hard gas kinetic collisions dominate, especially the former for molecules with a dipole moment larger than \( \sim 0.3 \) D. Since the time between both types of collisions is inversely proportional to pressure, the linewidth in this regime is proportional to pressure. At pressures when \( \Delta\nu_L \gg \Delta\nu_D \), pressure broadening dominates and the line shape is characterized by the Lorentzian function

\[
\alpha_L(\nu) = \alpha_L(\nu_0) \frac{(\Delta\nu_L)^2}{(\nu - \nu_0)^2 + (\Delta\nu_L)^2}, \quad (8b)
\]

whose peak height \( \alpha_L(\nu_0) \) is independent of the probe gas partial pressure [Fig. 3(b)].

The dominant broadening mechanism evolves from Doppler broadening to pressure broadening near the critical pressure \( P_0 \) at which \( \Delta\nu_L \approx \Delta\nu_D \). The approximate \( P_0 \) values for CO, N_2O, and OCS are 96, 75, and 33 mTorr, respectively. In order to make reliable quantification at all pressures, including near \( P_0 \), it becomes necessary to use a line shape function which spans both regimes. The Voigt line shape function is a convolution of the Lorentzian and Gaussian function [Fig. 3(c)] given by

\[
\alpha_V(\nu) = \int_0^{2\pi} \alpha_L(\nu + \omega f(\varphi)) \cos 2\varphi d\varphi = \alpha_L(\nu_0) \frac{(\Delta\nu_L)^2}{(\nu - \nu_0)^2 + (\Delta\nu_L)^2} + \alpha_D(\nu_0) e^{\left(\frac{\nu - \nu_0}{\Delta\nu_D}\right)^2}, \quad (9)
\]
The effects of pressure on line shape are explored. The pressure dependence of line shape in the Doppler-broadened regime with a Gaussian function (a), the pressure-broadened regime with Lorentzian function (b), and spanning both regimes with Voigt function (c). $P_0$ denotes the critical pressure where the Doppler- and pressure-broadened line widths are equal. The second harmonic modulated line shapes for Gaussian (blue), Lorentzian (red), and Voigt (black) functions with the same line widths are compared in (d).

\[ \alpha_V(x) = \frac{\nu_0 V_0}{\pi} \int_{-\infty}^{\infty} e^{-t^2} \, dt, \]

\[ x = \frac{2\sqrt{\ln 2}(v - v_0)}{\Delta v_D}, \]

\[ y = \sqrt{\ln 2 \Delta v_D} \Delta v_L. \]

Figure 3(d) plots the second harmonic modulated spectra for all three line shape functions but with identical line widths. In the methodology presented here, we will use the modulated Voigt line shape function to quantify probe molecule concentration by fitting the measured line shape and numerically adjusting $\nu_0$, $\Delta v_L$, and the peak amplitude $\alpha_V(\nu_0)$.

FITTING FOR THE MODULATED LINE SHAPE

The strength and shape of the modulated line shape also depend sensitively on the modulation depth $\omega_d$. If the modulation depth is much narrower than the absorption line width, there is effectively no modulation at all, while if the modulation depth is much broader than the absorption line width, the line is effectively averaged away. Thus, the optimal modulation depth is comparable to the absorption line width. For our quantitative analysis methodology to be applicable over a broad pressure range spanning both the Doppler- and pressure-broadened regimes, we must therefore consider how the modulated line shape depends on $\omega_d$.

Figure 4(a) illustrates how the peak amplitude of a modulated Gaussian line shape depends on the modulation depth $\omega_d$. Representative modulated line shapes for selected ratios of $\omega_d/\Delta v_D$ are plotted in Fig. 4(b). As the ratio $\omega_d/\Delta v_D$ increases, the amplitude of the narrow, modulated line shape increases at first ($\omega_d/\Delta v_D < 2$) and then decreases as greater modulation ($\omega_d/\Delta v_D > 3$) broadens.
the line. In order to obtain the best signal to noise ratio (SNR), we applied \( \omega_d/\Delta v_0 = 2.7 \) for all the transitions measured. It is this line shape that is fit to each measured modulated absorption line so that the peak amplitude, center frequency, and line width may be extracted.

In an ideal case, retrieving the unmodulated peak intensity from the modulated line shape simply involves fitting the measured line by the modulated Voigt profile

\[
I_v(v) = -SA_2(v),
\]

where \( S \) is the unknown scaling parameter obtained from the fit to ascertain the amplitude of the line shape, and \( A_2(v) \) is the second order Fourier component \((i = 2)\) from Eq. (10). Like the line itself, Eq. (11a) is symmetrical, but due to the frequency-dependent imperfections in the experimental alignment of the source, chamber, and detector, the modulated line shape may exhibit asymmetry. Following an established methodology, we introduce a first harmonic term \( A_1(v) \) to account for this asymmetry, so

\[
I_v(v) = -S\left[A_2(v) - \frac{c_{as}}{2}A_1(v)\omega_d\right],
\]

where \( c_{as} \) is an asymmetry parameter obtained from the fit.

Since the center frequency and Doppler linewidth of a given transition are known, our methodology requires that only four parameters be adjusted to obtain a fit of the modulated line shape in Eq. (11b): amplitude parameter \( S \), modulation depth \( \omega_d \), pressure broadening parameter (defined as \( \omega_p = \Delta v_f/\Delta v_D \)), and line asymmetry \( c_{as} \). The nonlinear least squares Marquardt fitting method was used to obtain these parameters. We fit for the modulation depth because we found the experimentally programmed modulation produced an imperfect triangle wave whose modulation depth slightly differed from the expected value. But this imperfection remained constant throughout our measurements, so we first fit low pressure (<0.5 mTorr) lines with \( \omega_p \) set to 0 to obtain the modulation depth \( \omega_d \) and fixed this value for all subsequent fits. We then fit for \( \omega_p \) in the pressure-broadened regime (\( >P_0 \)), so \( \omega_p \) and \( \omega_d \) could be fixed for a given transition. The remaining pressure-dependent parameters, \( S \) and \( c_{as} \), were then obtained from the fit for each measured line. For all fits, especially for mixed gas samples such as when monitoring the reactants, intermediates, and products of a catalytic reaction, effort must be made to ensure the fits are insensitive to initial guesses. To examine the quality of the fitting, we monitor the fitting residual (measured – fitted line shape) when changing parameters. Examples of line shape fittings can be found in Fig. 8 in the Appendix.

FROM FITTING PARAMETERS TO CORRECTED INTEGRATED LINE STRENGTH

After obtaining a good fit for the modulated Voigt line shape as assessed by the flatness of the fitting residual plot, the obtained \( S, \omega_p, \) and \( \omega_d \) parameters were used in Eq. (9) to reconstruct the symmetric unmodulated Voigt line shape for each measurement. Examples of the fitting parameters and the reconstructed unmodulated Voigt line shapes are, respectively, provided in Table II and Fig. 9 of the Appendix. This unmodulated line shape was then integrated to give the integrated line strength \( I_{uncorrected} \), and this is the value needed in Eq. (4) for subsequent calibration or quantitative concentration measurements.

However, this value must first be normalized to account for the frequency-dependent power variations in the spectrometer caused by the frequency dependence of the source and detector as well as standing waves in the chamber. This normalization is essential so that the integrated line strength obtained gives the same concentration regardless of which rotational transition is measured for a given molecule. Given the power absorbed by the gas \( \Delta W \) is proportional to the power in the chamber \( W (a \sim \Delta W/W) \), this frequency dependent correction is performed by measuring the signal strength at the frequency of the line but with the chamber evacuated. The power of the radiation received by the detector was measured by a Schottky diode detector whose output voltage was read by the multimeter in Fig. 1(b). Since the gas molecule only responds to the power in the chamber, the frequency dependence of the detector must be normalized away as well. The flat spectral response of our detector obviated this requirement for the measurements presented here, but by omitting this step, we have slightly misestimated the power correction. More importantly, during the experiments, we ensured the source power was kept low enough that our measurements remained in the linear state.
response regime of the detector. Thus, the output voltage remained proportional to the power of the detected radiation. The power-normalized integrated line strength $I_{\text{corrected}}$ of any measured transitions can then be calculated from the unnormalized Voigt integral $I_{\text{uncorrected}}$ as

$$I_{\text{corrected}} = \frac{I_{\text{uncorrected}}}{W_{\text{measured}}},$$

where $W_{\text{measured}}$ is the detected power at the frequency of the measured transition.

MEASURING THE CALIBRATION CURVE

The final step is the conversion of the power-normalized line strength to the partial pressure of a specific molecule. To accomplish this, we developed a calibration methodology in which a gas molecule of chosen pressure and known line strength is introduced into an empty chamber. By making a series of measurements of power-corrected line strengths as a function of measured gas pressure, a calibration curve may be constructed to convert integrated line strengths to pressure.

The ideal “calibration gas,” which need not be a gas used in subsequent experiments, is one with simple rotational spectra, preferably a linear molecule with a modest dipole moment and a low probability of adsorption to the chamber walls. Our calibration experiments were performed by introducing a calibration gas in increments of $\sim 1$ mTorr into the chamber and measuring a single rotational spectrum three times at each pressure. Calibration curves using CO, N$_2$O, and OCS were made by plotting their power-normalized integrated line strength vs the known gas pressure as measured by a capacitance manometer calibrated for N$_2$. The calibration curves for CO and N$_2$O in the low pressure, Doppler-broadened regime are shown in Figs. 5(a) and 5(b), respectively, showing the expected linear dependence of integrated line strength on pressure. The minimal scatter in the measured line strengths, even at the lowest pressures, indicates the quantitative reproducibility of the technique. The standard deviation of only 0.5% could be improved with better agreement between the actual and simulated modulations.

An important attribute of our technique is that it spans the Doppler and pressure broadening regimes, whereas spectroscopic analyses based on free induction decay are constrained to operate below $P_0$ to minimize collisional dephasing.$^{21,34}$ As confirmation, we performed calibration experiments for OCS over the range 0.5–85 mTorr, below and above the critical pressure $P_0 \approx 33$ mTorr [Fig. 6(a)]. The results, summarized in Fig. 6(b) and Fig. 10 in the Appendix, indicate acceptable linearity was achieved. The slight nonlinearity observed is also a consequence of experimental imperfections in the frequency modulation not adequately accounted by the modulation function used in Eqs. (5) and (6).

FIG. 5. The self-calibration and the cross-calibration curves for CO and N$_2$O are compared. The self-calibration curves of CO (a) and N$_2$O (b) showed an expected linear relationship between the power-normalized Voigt integral and gas pressure. Both cross-calibration curves, CO pressure calibrated by N$_2$O (c) and N$_2$O pressure calibrated with CO (d), showed consistency with the measured pressure and reveal the level of accuracy achievable by the proposed quantitative analysis procedure. Both cross-calibration curves used the integrated absorption line strengths available from the HITRAN database. 19
The essential utility of this quantitation technique is its ability to recover the pressures and concentrations of other molecular species in the chamber using the prior calibration curve obtained from a reference gas like CO, N₂O, or OCS. To do this, a calibration curve for the uncalibrated gas is synthesized from the calibration curve for the reference gas using two simple multiplicative factors. The first factor is the ratio of the known integrated line strengths from the relevant transitions of the desired probe gas. Room temperature line strengths of the relevant transitions for the reference gas and probe gas, respectively, are widely available in several databases including the HITRAN database. Their room temperature line strengths have been calculated and are available in several databases including the HITRAN database.

The second factor is the ratio of the detected power in the empty chamber at the transition frequencies for the probe and reference gases. By this simple conversion, the calibration curve of any probe gas can be calculated from the calibration curve of the reference gas as

\[ I_{\text{probe}} = \frac{\alpha_{\text{probe}}}{\alpha_{\text{ref}}} \left( \frac{p_{\text{probe}}}{p_{\text{ref}}} \right) I_{\text{ref}} \]

(13)

where \( \alpha_{\text{ref}} \) and \( \alpha_{\text{probe}} \) denote the theoretical integrated absorption line strengths of the relevant transitions for the reference gas and probe gas, \( I_{\text{ref}} \) and \( I_{\text{probe}} \) denote the power-normalized integrated line strengths introduced in Eq. (12) of the reference and probe gas, and \( p_{\text{ref}} \) and \( p_{\text{probe}} \) are the partial pressures of the reference gas and probe gas, respectively. \( s_{\text{ref}} \) is the slope of the calibration curve of the reference gas.

As a demonstration of the accuracy and reproducibility of using the calibration curve for one gas to predict the pressure measured for another gas, we performed cross-calibrations from CO to N₂O and vice versa, respectively. In both cross-calibrations, consistency between the measured pressure and the calibrated pressure was observed. The self-calibration curves [Figs. 5(c) and 5(d)] have \( R^2 \) values of 0.998 and 0.997, respectively. The cross-calibration curves [Figs. 5(c) and 5(d)] have virtually identical \( R^2 \) values, but their slopes differ slightly from unity (1.062 \( \pm \) 0.006 and 0.909 \( \pm \) 0.004, respectively) primarily because of the \( \pm 5\% \) uncertainty in measured power. These cross-calibration analyses, limited only by correctable experimental imperfections and uncertainties, confirm the potential of frequency-modulated rotational spectroscopy as an accurate technique for quantitative analysis of any gas phase molecular species. Indeed, this technique makes it possible to measure the gas phase concentrations of molecules with large dipole moments like H₂O, NH₃, and H₂S for which calibration curves would be difficult to obtain due to their propensity for strong surface adsorption in the reaction chamber often known as the memory effect.

We conclude by reconsidering a clear advantage of rotational spectroscopy: its ability to distinguish isotopologues and measure their abundances over many orders of magnitude in concentration. To illustrate these advantages, we performed an isotopologue abundance analysis by introducing N₂O (99.5% purity) into the chamber and measuring the modulated rotational transitions of its four most abundant isotopologues: \( ^{14}\text{N}^{14}\text{N}^{16}\text{O} \), \( ^{13}\text{N}^{15}\text{N}^{16}\text{O} \), \( ^{14}\text{N}^{14}\text{N}^{16}\text{O} \), and \( ^{14}\text{N}^{14}\text{N}^{18}\text{O} \) (see Table I for details). The partial pressures of each were calculated from the \( ^{14}\text{N}^{14}\text{N}^{16}\text{O} \) calibration curve and the integrated absorption line strengths in the HITRAN database using Eq. (13). These partial pressures were then converted to relative abundances with respect to the most common isotopologue, \( ^{14}\text{N}^{14}\text{N}^{16}\text{O} \), and the deduced abundances were summarized in Fig. 7. The technique recovered the expected natural abundance to within the experimental uncertainty of the technique: 2.4% (\( ^{15}\text{N}^{14}\text{N}^{16}\text{O} \)), -4.1% (\( ^{14}\text{N}^{15}\text{N}^{16}\text{O} \)), and 15.4% (\( ^{14}\text{N}^{14}\text{N}^{18}\text{O} \)), respectively. The accuracy for \( ^{14}\text{N}^{14}\text{N}^{18}\text{O} \) was worse because the spectra were near the detection limit, so they exhibited a noisy line shape and a residual baseline curvature not included in the fit of the modulated line shape. Not only do the results clearly demonstrate the ability of rotational spectroscopy to pinpoint the position of a single isotope atom (like \( ^{14}\text{N} \)) in a multiatom molecule (N₂O) with tremendous spectral resolution (~8500 linewidths of separation for the J = 9–10 transition, as demonstrated in Fig. 11 of the Appendix), they also confirm its ability to recover concentrations accurately, to within experimental uncertainties.
Note that these abundances are three orders of magnitude lower than the pressures used for the calibration gas, yet the abundance predictions are accurate to within experimental uncertainties. In order to estimate the limit of detection (LOD) of this method, we measured the noise level \( \sigma_n \) of the modulated spectra in the blank chamber at different frequencies and adopted the universally accepted line strength criteria of 3\( \sigma_n \) above the noise level as the minimum detectable signal. Given the linear relationship between the amplitude of the modulated line shape and the pressure of the probed gas in the Doppler broadened regime, the LOD for CO, \( \text{N}_2\text{O} \), and OCS is calculated to be 80 \( \mu \text{Torr} \) (4300 fmol/l), 32 \( \mu \text{Torr} \) (1710 fmol/l), and 10 \( \mu \text{Torr} \) (600 fmol/l), respectively, values consistent with previously published values using a similar technique. There are several factors that affect the LOD. For example, the factor of 2.5 difference in LOD between CO and \( \text{N}_2\text{O} \) is caused by differences in the integrated absorption line strengths (with a ratio of 2.84) and the frequency-dependent differences in the noise level at different source powers (a factor of \( \sim 0.88 \)). The latter is partially a consequence of townes noise in the detector for which the noise increases with increasing received power. It must therefore be recognized that the sensitivity of this technique depends on the molecular species of interest and can be predicted \textit{ab initio} for a given spectrometer using a calibration curve, a table of rotational transition line strengths, and a plot of the measured power spectrum in the spectrometer.

The sensitivity of this technique may easily be improved through several methods. First, a longer absorption cell will increase the absorption line strength. For most transitions, the line strength depends linearly on cell length, and the measurements performed here used an absorption chamber on 10 cm long instead of the more typical 1 m. Second, a simple Schottky diode detector was used, but sensitivity and the signal-to-noise ratio may be increased by several orders of magnitude if the detector is replaced by a heterodyne receiver. Finally, and perhaps most importantly, the sensitivity of rotational spectroscopy depends sensitively on the line strength of the rotational transition selected. For example, using a similar technique, Medvedev et al. report an LOD for \( \text{CH}_3\text{CN} \) 83 times lower (0.12 \( \mu \text{Torr} \)) than our LOD for OCS in a chamber 12 times longer and a transition 4.7 times stronger. Moreover, for a given concentration, line strengths can vary by many orders of magnitude depending on the transition matrix element, which in turn depends on the state-dependent quantum mechanical selection rules. In other words, sensitivity may be improved dramatically simply by choosing a strong absorption line. For the gases and spectral range used here, the principal isotope of CO had only one line, \( \text{N}_2\text{O} \) had only five, and OCS had ten, but most gases of interest will have dozens, perhaps hundreds of transitions to choose within the tuning range of the spectrometer. Propitious selection of the strongest line will improve detection sensitivity.

**CONCLUSION**

A new quantitative analysis procedure is introduced for measuring the partial pressures of gaseous species with frequency-modulated rotational spectroscopy. A Voigt line shape was used so that quantitative analysis spanned the Doppler- and pressure-broadening regimes. The versatility and accuracy of this technique was demonstrated with two calibration molecules, CO and \( \text{N}_2\text{O} \), whose molecular concentrations were quantified and verified with one another through cross-calibration. This calibration procedure allows the accurate estimate of the partial pressures of almost any gas molecule, including those for which calibration curves are not feasible experimentally, such as gas molecules that may be formed during chemical reactions or molecules like \( \text{H}_2\text{O} \) with a propensity for adsorption. We have used the calibration of \( ^{14}\text{N}^{14}\text{N}^{16}\text{O} \) to estimate the relative abundance of its three most common isotopologues, \( ^{14}\text{N}^{13}\text{N}^{18}\text{O} \), \( ^{15}\text{N}^{14}\text{N}^{16}\text{O} \), and \( ^{14}\text{N}^{14}\text{N}^{18}\text{O} \), thereby demonstrating the ability to pinpoint the atomic position of a \( ^{15}\text{N} \) isotope in the \( \text{N}_2\text{O} \) molecule, a nearly impossible task for alternative gas phase analytic techniques. The detection limit for the method presented here is on the order of femtomolar, reinforcing the utility of this tremendously powerful technique for determining quantitative abundances of dilute gas-phase species. Coupled with the growing availability of terahertz technologies, the technique introduced here realizes long-standing expectations of rotational spectroscopy as a practical tool for quantitative analysis. Although frequency-modulated rotational spectroscopy is powerful as a stand-alone technique, it could also be used to complement standard GC and MS gas-detection methodologies. The combination of rotational spectroscopy with GC or MS would remove its inherent drawback of being confined only to molecules with permanent electric dipoles.

**ACKNOWLEDGMENTS**

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APPENDIX: LINESHAPE FITS AND ANALYSES

FIG. 8. Selected fitting curves for CO at 1 mTorr (a), CO at 44 mTorr (b), N\textsubscript{2}O at 2 mTorr (c), and N\textsubscript{2}O at 35 mTorr (d) associated with the calibration curves in Fig. 5. The green line shows the residual difference between the fitting curve and the measured line shape. Although the broadening mechanism is different at low pressure and high pressure, the fitting procedure gives flat residuals in both regimes.

TABLE II. Fitting parameters extracted from the fitting curves in Fig. 8.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Pressure (mTorr)</th>
<th>Amplitude (mV/MHz$^2$)</th>
<th>Doppler HWHM (MHz)</th>
<th>Modulation depth (MHz)</th>
<th>Pressure broadening parameter</th>
<th>Line asymmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}$C$^{16}$O</td>
<td>1.00</td>
<td>0.45</td>
<td>0.268</td>
<td>0.899</td>
<td>0.003</td>
<td>−33</td>
</tr>
<tr>
<td>$^{12}$C$^{16}$O</td>
<td>44.27</td>
<td>18.04</td>
<td>0.268</td>
<td>0.899</td>
<td>0.458</td>
<td>−23</td>
</tr>
<tr>
<td>$^{14}$N$^{14}$N$^{16}$O</td>
<td>2.01</td>
<td>4.73</td>
<td>0.260</td>
<td>0.893</td>
<td>0</td>
<td>−85</td>
</tr>
<tr>
<td>$^{14}$N$^{14}$N$^{16}$O</td>
<td>35.78</td>
<td>67.38</td>
<td>0.260</td>
<td>0.893</td>
<td>0.397</td>
<td>−91</td>
</tr>
</tbody>
</table>

FIG. 9. Reconstructed unmodulated Voigt line shapes associated with the modulated lines measured in Fig. 8 using the extracted parameters provided in Table II. (a) 1 mTorr CO, (b) 40 mTorr CO, (c) 2 mTorr N\textsubscript{2}O, and (d) 35 mTorr N\textsubscript{2}O.
FIG. 10. Modulated line shape (red), fit (black), and residual (green) curves associated with the OCS transition monitored in Fig. 6 at selected pressures. (a) 4 mTorr in the Doppler-broadened regime, (b) 33 mTorr at the critical pressure $P_0$, and (c) 82 mTorr in the pressure-broadened regime. The modulated line shape broadens and the amplitude decreases in the pressure-broadened regime.

FIG. 11. Spectral separation of the J = 9–10 transitions for isotopologues $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ (red) and $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ (blue) is about 8500 times the linewidth of the measured modulated spectrum of $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ shown in the inset.

REFERENCES


