



Butler University Digital Commons @ Butler University

Scholarship and Professional Work - LAS

College of Liberal Arts & Sciences

1982

Travelling-Wave Sub-Doppler Excited Molecule Energy Transfer Spectroscopy


Khalid Iqbal

Shannon G. Lieb

Butler University, slieb@butler.edu

J. W. Bevan

Follow this and additional works at: http://digitalcommons.butler.edu/facsch_papers

 Part of the [Atomic, Molecular and Optical Physics Commons](#), [Biological and Chemical Physics Commons](#), and the [Chemistry Commons](#)

Recommended Citation

Iqbal, Khalid; Lieb, Shannon G.; and Bevan, J. W., "Travelling-Wave Sub-Doppler Excited Molecule Energy Transfer Spectroscopy" *The Journal of Chemical Physics* / (1982): 3461-3466.

Available at http://digitalcommons.butler.edu/facsch_papers/781

This Article is brought to you for free and open access by the College of Liberal Arts & Sciences at Digital Commons @ Butler University. It has been accepted for inclusion in Scholarship and Professional Work - LAS by an authorized administrator of Digital Commons @ Butler University. For more information, please contact fgaede@butler.edu.

Traveling-wave sub-Doppler excited molecule energy transfer spectroscopy

Khalid Iqbal, S. G. Lieb, and J. W. Bevan

Citation: *The Journal of Chemical Physics* **76**, 3461 (1982); doi: 10.1063/1.443444

View online: <http://dx.doi.org/10.1063/1.443444>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/76/7?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Sub-Doppler spectroscopy of 89Y](#)

J. Appl. Phys. **79**, 565 (1996); 10.1063/1.361420

[Sub-doppler spectroscopy of 89Y](#)

AIP Conf. Proc. **288**, 159 (1993); 10.1063/1.44898

[Purely rotational coherence effect and time-resolved sub-Doppler spectroscopy of large molecules. I. Theoretical](#)

J. Chem. Phys. **86**, 2460 (1987); 10.1063/1.452099

[Sub-Doppler Zeeman spectroscopy of the CeO molecule](#)

J. Chem. Phys. **85**, 751 (1986); 10.1063/1.451282

[Sub-Doppler laser spectroscopy of the NaK molecule](#)

J. Chem. Phys. **71**, 2005 (1979); 10.1063/1.438591

The logo for AIP APL Photonics. It features the letters 'AIP' in a large, white, sans-serif font on the left, followed by a vertical yellow bar, and then the text 'APL Photonics' in a smaller, white, sans-serif font on the right. The background is a vibrant red with a bright yellow sunburst effect emanating from the top right corner.

APL Photonics is pleased to announce
Benjamin Eggleton as its Editor-in-Chief



Traveling-wave sub-Doppler excited molecule energy transfer spectroscopy

Khalid Iqbal,^{a)} S. G. Lieb, and J. W. Bevan

Chemistry Department, Texas A&M University, College Station, Texas 77843
(Received 11 September 1981; accepted 23 October 1981)

A general formulation of traveling-wave sub-Doppler excited molecule energy transfer spectroscopy is presented. The line profile analysis is applied to that determined experimentally for the $R(22) \nu_3$ HCN transition. P_n , the noise equivalent power of the detector is demonstrated to be $\leq 10^{-12}$ W. Finally, the technique is applied to resolve the $K'R(7) \nu_1$ transition head in NH_3 .

INTRODUCTION

Excited molecule energy transfer spectroscopic techniques in which vibrationally excited molecules with a restricted velocity distribution are directly detected possess a simplicity of approach which is particularly appealing in the infrared region. In this spectral region, where fluorescence techniques are not so widely applicable, such approaches offer the opportunity of ultrahigh resolution and detection sensitivity. The advent of broadly tunable narrowband (≈ 15 MHz) cw infrared lasers¹ with output powers $\geq 100 \mu\text{W}$ have fostered the development of these spectroscopic techniques.

Gough, Miller, and Scoles^{2,3} have applied such an approach with notable success using bolometric detection of molecular beams. Both diode² and color center³ laser beams have been utilized to orthogonally excited molecules in the molecular beam producing sub-Doppler spectra. More recently Hartung, Jurgeit, and Ritze⁴ utilized cw with modulated counter-propagating⁵ laser beams and intermodulation⁶ saturation-absorption spectroscopy of SF_6 using optothermal detection with pyroelectric foils. This latter study also included a theoretical development of an alternative approach to sub-Doppler spectroscopy involving mechanical selection of molecules moving nearly perpendicular to the exciting laser beam. Recently Iqbal, Dahiya, Lieb, and Bevan⁷ successfully introduced an experimental technique similar to that proposed;⁴ traveling-wave sub-Doppler excited molecule energy transfer spectroscopy.

In the latter technique⁷ a mechanical selector situated orthogonal to the exciting laser beam permits only molecules with motion in the nearly perpendicular direction to be detected by a microphone. As a result sub-Doppler spectra of gas phase samples can be recorded as the narrowband laser (linewidth ≤ 7 MHz) is frequency tuned through the transition line profile under low pressure conditions. This pressure is lowered such that the mean free path of the constituent molecules is greater than the distance of the exciting laser beam from the detector. The vibrationally excited molecules transmitted through the mechanical selector can thus be collisionally quenched at the microphone diaphragm generating a signal by energy transfer from the excited molecules. As the generated signal is a function of the incident laser en-

ergy absorbed by the gaseous molecules the technique is potentially a sensitive spectroscopic detection method. It is particularly applicable in recording sub-Doppler rotational-vibrational gas phase spectra in the infrared where excited state lifetimes are in the range 10^{-5} to 10^{-2} s.

In this paper a general formulation of the traveling-wave sub-Doppler excited molecule energy transfer technique is presented. The line profile analysis developed is compared with that determined experimentally for the gas phase $R(22) \nu_3$ HCN transition and with the results predicted using a previous theoretical model.⁴ Signal to noise ratios evaluated experimentally from the $P_{1-0}(4)$ HF transition under specified conditions are combined with relevant molecular information⁸ to estimate an upper limit to the noise equivalent power of the detector. Finally, the technique is applied to resolve the transition head of the $K'R(7) \nu_1$ NH_3 transition.

THEORY

The investigated model is one which assumes that the molecules excited in the laser beam travel to the diaphragm of the microphone detector without undergoing prior collisions. At the instant of collision, the molecule is vibrationally quenched and releases its adsorbed energy to the detector. To be assured that the signal is one of direct energy transfer to the diaphragm of the detector, the molecular mean free path must be long compared to the distance from the laser beam to the detector. Otherwise an acoustic wave may be generated and changes the model system under investigation. By collimating the allowed trajectories of excited molecules orthogonal to the direction of the laser beam, the molecules interacting with the detector will have absorption energies only slightly Doppler shifted, from the resonant frequency of "stationary" absorbing molecules resulting in a much narrowed sub-Doppler line profile. With these basic assumptions, the sub-Doppler line profile will be derived.

Line profile analysis

The two dimensional model of Hartung, Jurgeit, and Ritze⁴ can be modified to provide a three-dimensional treatment of our geometrically simple experimental detector design.⁷ Extending above the diaphragm of the detector, a cylinder of height " h " and diameter " d " acts

^{a)}Robert A. Welch Postdoctoral Fellow.

as a mechanical selector allowing molecules with only a small range of velocity components perpendicular to the incident laser beam to impinge on the detector surface. The z coordinate axis is considered along the center of the laser beam and the x axis along the center of the detector cylinder. With this convention the y and z velocity components are parallel velocity components ($V_y^2 + V_z^2 = V_{\parallel}^2$) and the x velocity component is the normal component. Knowing the three-dimensional speed distribution to be

$$\frac{4}{\sqrt{\pi}} \left(\frac{m}{2kT} \right)^{3/2} V^2 \exp(-mV^2/2kT), \quad (1)$$

and the expression relating nonrelativistic speeds to the frequency shift of radiation impinging on a moving molecule⁹

$$\nu = \nu_0 \left(1 \pm \frac{V}{c} \cos \theta \right), \quad (2)$$

or

$$V \cos \theta = V_{\parallel} = \left(\frac{\nu - \nu_0}{\nu_0} \right) c, \quad (3)$$

the normal Doppler-limited line profile can be extracted from Eqs. (1) and (3) as

$$\begin{aligned} \exp(-mV^2/2kT) &= \exp \left[-\frac{mc^2}{2kT} \left(\frac{\nu - \nu_0}{\nu_0} \right)^2 \right] \\ &\quad \times \exp \left[-\frac{mV_x^2}{2kT} \right]. \end{aligned} \quad (4)$$

Since $V_{\parallel} \ll V_x$ for any given speed, $V^2 \approx V_x^2$. From simple geometric considerations, the smallest value of V_x for a given speed that can still reach the detector is related to V_{\parallel} by

$$\frac{V_x}{V_{\parallel}} = \frac{h}{d}. \quad (5)$$

The three dimensional most probable speed (V_{mp}) is $\sqrt{2kT/m}$. Redefining a reduced speed variable as $\tilde{V} = V/V_{mp}$, the three dimensional speed distribution can be reexpressed as

$$\approx \frac{4}{\sqrt{\pi} V_{mp}^3} \exp \left[-\frac{c^2}{V_{mp}^2} \left(\frac{\nu - \nu_0}{\nu_0} \right)^2 \right] \exp(-\tilde{V}_x^2 \tilde{V}_x^2). \quad (6)$$

This leads to the expression for the sub-Doppler profile at any frequency:

$$\begin{aligned} P(\nu) &= \exp \left[-\frac{c^2}{V_{mp}^2} \left(\frac{\nu - \nu_0}{\nu_0} \right)^2 \right] \frac{4}{\sqrt{\pi}} \int_{\alpha}^{\infty} \frac{V_x^2}{V_{mp}^2} \\ &\quad \times \exp(-\tilde{V}_x^2) \frac{dV_x}{V_{mp}} = D(\nu) S(\alpha), \end{aligned} \quad (7)$$

where $D(\nu)$ is the normal Doppler expression and $S(\alpha)$ is

$$S(\alpha) \equiv \frac{4}{\sqrt{\pi}} \int_{\alpha}^{\infty} \tilde{V}_x^2 \exp(-\tilde{V}_x^2) d\tilde{V}_x, \quad (8)$$

with $\alpha \equiv (h/d) | \tilde{V}_{\parallel} |$.

This model function will be used to describe the sub-Doppler line profile. Two model cases of incident laser beam characteristics are considered (i) an infinite, thin planar laser beam; diameter $> d$ with uniform beam intensity, and (ii) an infinitesimally thin pencil laser beam.

These two models are limiting approximations to the actual Gaussian-spherical intensity profile of the color center laser output.

The infinite, thin planar approximation

Equation 7 would be sufficient if the molecules passing through the laser beam with a parallel velocity component ranging from zero to $(h/d) V$ struck the detector with equal probability. But the probability of a molecule striking the detector is directly proportional to the surface area of the detector exposed to a given V_{\parallel} and V . This probability function $P(\tilde{V}_{\parallel})$ is therefore

$$P(\tilde{V}_{\parallel}) = 1 - \left(\frac{h}{d} \frac{\tilde{V}_{\parallel}}{\tilde{V}_x} \right)^2 = 1 - \frac{\alpha^2}{\tilde{V}_x^2}. \quad (9)$$

Equation 8 should thus be modified to

$$\begin{aligned} S(\alpha) &\equiv \frac{4}{\sqrt{\pi}} \int_{\alpha}^{\infty} \tilde{V}_x^2 \exp(-\tilde{V}_x^2) \left(1 - \frac{\alpha^2}{\tilde{V}_x^2} \right) d\tilde{V}_x \\ &= \frac{4}{\sqrt{\pi}} \left[\int_0^{\infty} \tilde{V}_x^2 \exp(-\tilde{V}_x^2) d\tilde{V}_x - \alpha^2 \int_0^{\infty} \exp(-\tilde{V}_x^2) d\tilde{V}_x \right. \\ &\quad \left. - \int_0^{\alpha} \tilde{V}_x^2 \exp(-\tilde{V}_x^2) d\tilde{V}_x + \alpha^2 \int_0^{\alpha} \exp(-\tilde{V}_x^2) d\tilde{V}_x \right] \\ &= 1 + 2\alpha \left[\frac{\exp(-\alpha^2)}{\sqrt{\pi}} - \alpha \right] + \operatorname{erf}(\alpha) (2\alpha^2 - 1). \end{aligned} \quad (10)$$

To obtain $P(\nu)$, α is set equal $(\nu - \nu_0)/\nu_0 (c/V_{mp})(h/d)$, so that $P(\nu)$ is

$$\begin{aligned} P(\nu) &= \exp \left[-\frac{c^2}{V_{mp}^2} \left(\frac{\nu - \nu_0}{\nu_0} \right)^2 \right] \left\{ 1 + 2\alpha \left[\frac{1}{\sqrt{\pi}} \right. \right. \\ &\quad \left. \left. \times \exp(-\alpha^2) - \alpha \right] + \operatorname{erf}(\alpha) (2\alpha^2 - 1) \right\}. \end{aligned} \quad (11)$$

This derivation is complete for a slice of the laser beam in the $y-z$ plane. To extend the treatment to include all the slices perpendicular to the x axis, the curvature at the top and bottom of the beam (in the x direction) is ignored. The resulting truncated right cone which represents the volume inside the laser beam that will allow molecules to pass onto the detector produces the same expression as given in Eq. (11).

Infinitesimally thin pencil laser beam

To produce a narrower line profile relative to the infinite, thin planar beam case, a new α' can be introduced in place of α in which $\alpha' > \alpha$. This physically can be accomplished by varying h/d (i.e., by making the diameter of the cylinder smaller or the height of the cylinder larger) or by restricting the beam size and thereby restricting the parallel velocity component magnitude. If the beam is made into a line, the minimum value of V_x depends on which parallel velocity component (V_y or V_z) is analyzed. $V_x(\min) = (h/d) V_x$ for a molecule moving in the $x-z$ plane and $V_x(\min) = 2(h/d) V_y$ for a molecule moving in the $x-y$ plane. This creates a nearly elliptical velocity distribution for the y and z components. To produce a symmetrical relationship between the two parallel components, the geometric mean of the major and minor axes of the ellipse is used as the radius of the parallel velocity component (i.e., V_{\parallel}

$= \sqrt{V_y V_z}$). This leads to the same analysis as in the infinite, thin planar laser beam approximation except $\alpha' = \sqrt{2} (h/d) |V_{11}|$ [or $\sqrt{2} (h/d) (c/V_{mp}) |(\nu - \nu_0)/\nu_0|$].

Sensitivity considerations

In the strong saturation limit at $\nu = \nu_0$ with the assumption that $\gamma_1 = \gamma_2$.¹⁰

$$S = S_0 [1 - (1 + G)^{-1/2}], \quad (12)$$

where

$$G = \left[\frac{P_{0-1} E}{\hbar \Gamma} \right]^2.$$

Therefore the S/N ratio for the traveling wave sub-Doppler excited molecule energy transfer signal is given by

$$\frac{S}{N} = \frac{\Delta P}{P_n} \leq \frac{n^* \alpha l P h \nu}{P_n} [1 - (1 + G)^{-1/2}], \quad (13)$$

where n^* is the number of incident photons per second, $\alpha = \sigma n$ (σ = absorption cross section and n is the number of molecules/cc in the given lower transition state, P is the molecular transmission coefficient through the mechanical selector, and l is the path length of effective interaction).

EXPERIMENTAL

The experimental laser arrangement is shown in Fig. 1 and is similar to that we have used previously for sub-Doppler excited molecule energy transfer spectroscopy.⁷ The color center laser system consists of a Burleigh FCL-20 laser pumped by 0.9 W of a 6471 Å single line spectra physics 171-01 Kr⁺ laser. KCl:Li and RbCl:Li crystals; tuning range 2.5 to 2.9, and 2.75 to 3.3 μm

respectively, were utilized in the laser system. Output powers of 16.5, 16.0 and 15.1 mW were available at 3788.225, 3491.2, and 3373.589 cm⁻¹ [the frequencies of the HF₁₋₀P(4),¹¹ ν₁NH₃R(7),¹² and ν₃HCN R(22)¹³ lines, respectively] with a free-running single frequency line width stability of ≤ 7 MHz.

The laser was tuned by simultaneously scanning the PZT's of the internal etalon and cavity end mirror with ramp generators, over a frequency range of 2.4 GHz. Single mode operation was monitored with 2.5 GHz and 150 MHz free spectral range external etalons. The latter was also used to produce frequency markers. A polarizer (extinction ratio 10⁴:1) and a λ/4 plate were used to avoid optical feedback into the laser cavity.

The detection cell used for HCN was similar to that we have used previously,⁷ with some modifications. It consists of a small volume cell (~0.25 cc volume, 2.0 cm long and 0.3 cm diameter) with CaF₂ windows. Two Knowles BT 1834 miniature microphones with built in FET's are mounted orthogonal to the optic axis of the cell and located in the cell wall opposite to each other. One microphone (A) is exposed to the cell with an orifice of 1 mm diameter and distance from beam is $h = 2.5$ mm. The other (B) is offset from the internal cell surface by a tube of 1 mm diameter and length $h = 15$ mm. The upper and lower sections of the cell contain the necessary electrical connecting for the microphones and are sealed with Varian high vacuum BNC electrical feed throughs from the sample areas. The purpose of the two microphone arrangements is to verify that the signal is not acoustical in nature and to enable standing-wave sub-Doppler spectroscopy to be performed. For NH₃ and HF spectra, a single microphone cell with same d and h defined for microphone A, was used. The amplified signal was detected by a PARC

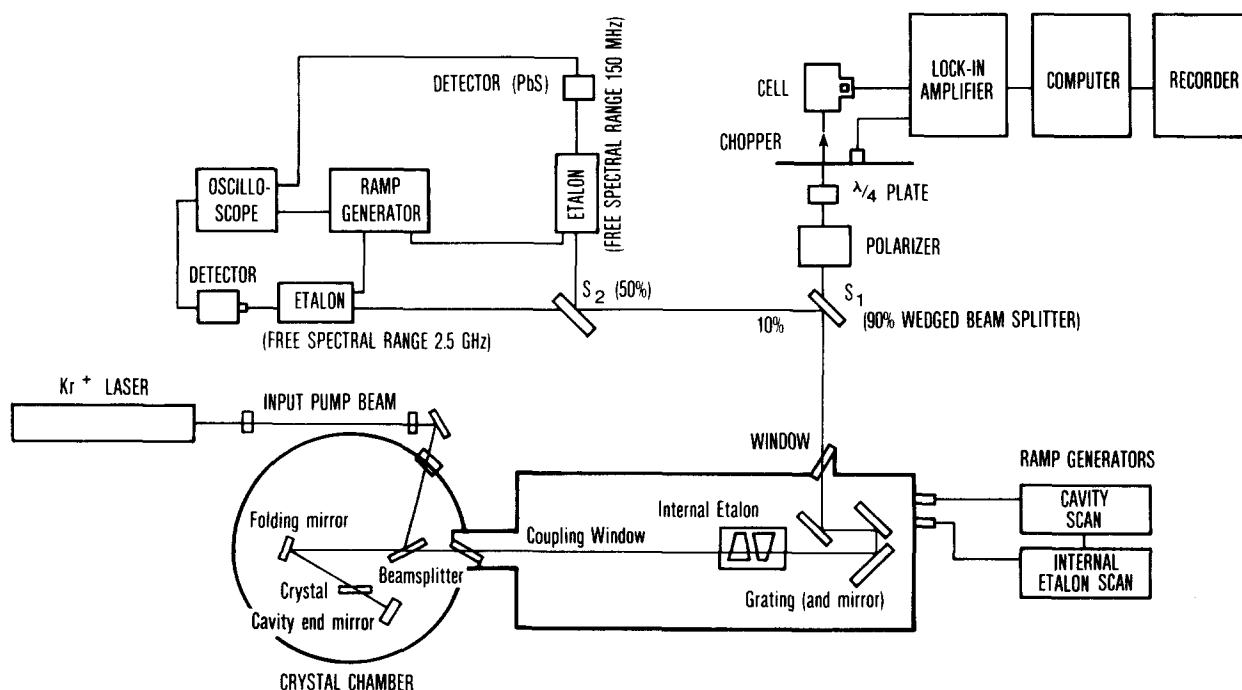


FIG. 1. Experimental arrangement for traveling-wave sub-Doppler excited molecule energy transfer spectroscopy.

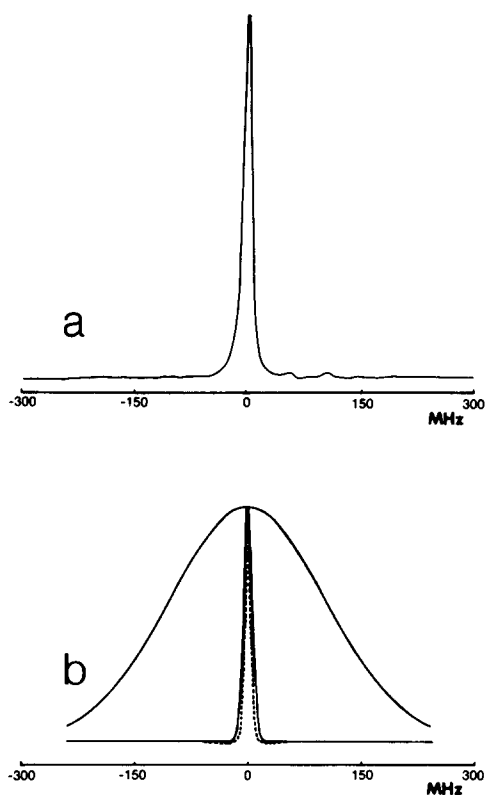


FIG. 2. (a) Sub-Doppler spectrum of $\nu_3 R(22)$ transition of HCN recorded at 30 mTorr Hg pressure with 1 s time constant of lock-in amplifier. (b) Theoretically predicted Doppler and sub-Doppler profile of $\nu_3 R(22)$ transition of HCN using narrow (\cdots) and broad beam (---) models.

HR-8 lock-in amplifier. Modulated frequencies produced by a PARC 192 variable speed chopper were monitored with a HP 5246L electronic counter. The output signal of the lock-in amplifier was either stored and processed using a Micromation Z-64 microcomputer or directly recorded on a chart recorder.

NH_3 and HF were obtained from Matheson Gas Inc. and were used without further purification. Hydrogen cyanide was prepared by the reaction of potassium cyanide with dilute sulphuric acid, dried over phosphorus pentoxide and purified by trap to trap distillation. All manipulations of the highly reactive HF gas were performed with corrosion resistant vacuum equipment.

RESULTS

The sub-Doppler spectrum of the $R(22) \nu_3$ HCN transition (frequency¹³ 3373.589 cm^{-1}) is shown in Fig. 2(a) at a sample pressure of 30 mTorr Hg using the experimental arrangements shown in Fig. 1 and microphone B. A modulation frequency of 260 Hz was used to optimize the signal with the PARC 192 variable speed chopper. Frequency markers are recorded at 150 MHz intervals showing 12 ± 3 MHz full width at half-maximum. This compares with the natural full Doppler with ($\Delta\nu_D$) at half-maximum absorption of 242 MHz for this transition predicted using the relationship $\Delta\nu_D = \nu_0 7.1623$

$\times 10^{-7} \sqrt{(T/M)} (\text{cm}^{-1})$. To estimate the extent of sub-Doppler narrowing expected for the considered transition, expression (11) is used. Computer drawn Doppler and sub-Doppler profiles are shown for the $\nu_3 R(22)$ HCN transition in Fig. 2(b). The predicted spectral full widths at half-maximum are 8.6 ± 2 and 12.7 ± 2 MHz, respectively, using pertinent experimental cell dimensions for the theoretical models, the infinitely thin pencil and infinite, thin planar laser beam ($d=1$ mm, $h=15$ mm). This result compares favorably with corresponding experimentally determined value of 12 ± 3 MHz.

The extensive information currently available for the $P_{1-0}(4)$ HF transition⁸ provides us with the opportunity of calibrating P_n for the detector. Using our best S/N ratio for the $P_{1-0}(4)$ HF transition, $10^5:1$, at 30 mTorr pressure in a cell with $h=2.5$ and $d=0.5$ mm (expression 12) enables P_n to be experimentally determined $\leq 10^{-12}$ W ($E=9$ mW). It is pertinent to note that this particular detector had to be dismantled to make it resistant to the highly corrosive HF. This resulted in a loss in sensitivity of a factor of 10 during the latter process. The sub-Doppler spectrum of the $P_{1-0}(4)$ HF transition is shown in Fig. 3 at a sample pressure of 40 mTorr with the previously mentioned cell dimensions and a modulation frequency of 245 Hz used to optimize signal magnitude. The sub-Doppler FWHM is 32 ± 3 MHz which compares with the corresponding expected Doppler-limited value of 315 MHz.

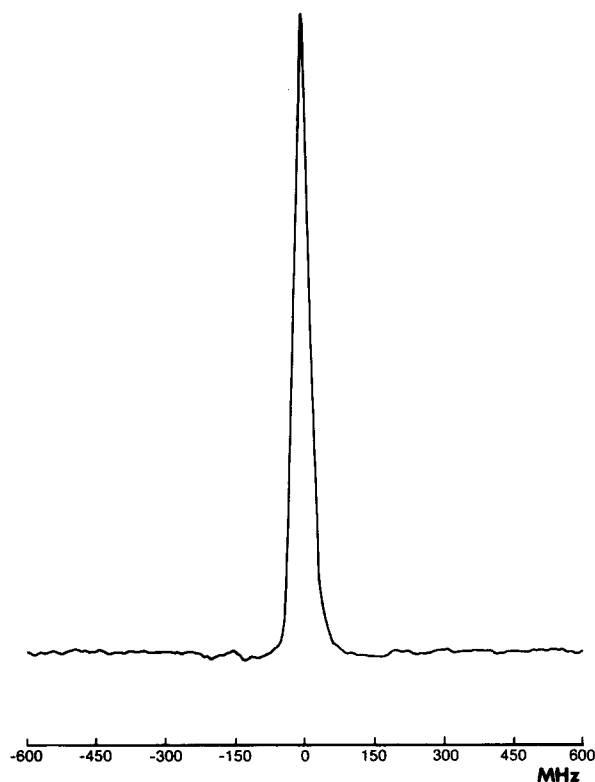


FIG. 3. Sub-Doppler spectrum of $P_{1-0}(4)$ transition of HF recorded at 40 mTorr Hg pressure with 1 s time constant on lock-in amplifier.

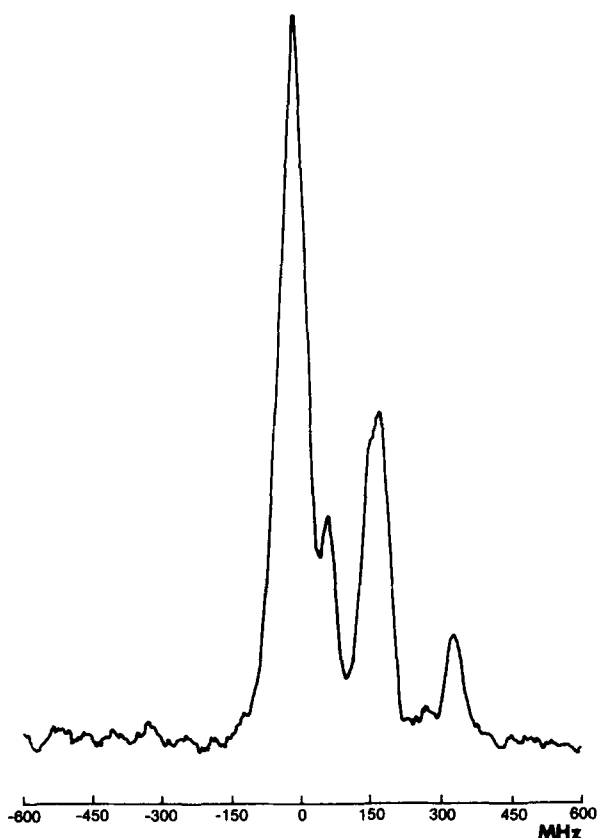


FIG. 4. Sub-Doppler spectrum of part $K^s \nu_1 R(7)$ transition of NH_3 recorded at 35 mTorr Hg pressure with 1 s time constant on lock-in amplifier.

Figure 4 shows a scan through part of the $K^s R(7) \nu_1$ NH_3 transition head (3491.2 cm^{-1}) demonstrating resolution of the K structure which could not be resolved in a previous high resolution study.¹² The sample pressure in this case was 35 mTorr with the same cell dimensions as used previously for the $P_{1-0}(4)$ HF transition.

DISCUSSION

A more general three dimensional formulation of traveling-wave sub-Doppler excited molecule energy transfer spectroscopy has been analyzed in terms of two models (a) an infinite, thin planar and (b) infinitely thin pencil laser beam. The line profile predicted for the $R(22) \nu_3$ HCN transition according to the previously proposed two dimensional model of Hartung, Jurgeit, and Ritze⁴ is shown in Fig. 5 ($d = 1.0 \text{ mm}$, $h = 15.0 \text{ mm}$). Corresponding predictions according to the three dimensional approaches are included in Fig. 2(b). One fundamental difference concerns the shape of the peak maximum. The former approach results in a cusp at peak maximum, whereas the corresponding three-dimensional models predict parabolic behavior. The linewidth, full width at half-maximum (FWHM) for the two dimensional model (6 MHz) is approximately one half the FWHM based on the infinite, thin planar laser beam model predicted to be 13 MHz. The experimental observed value of $12 \pm 3 \text{ MHz}$ falls inside the two limiting cases (13 and 9 MHz) for the two three-dimensional models. As the laser beam of the FCL-20 is expected to possess a Gaus-

sian-spherical intensity profile with a beam waste of about 1.5 mm the correlation of experimental and predicted full width at half-maximum is considered satisfactory.

Optimization of detector design to minimize FWHM and maximization of signal to noise ratio for given molecular systems is spectroscopically important. This can be accomplished by (a) optimizing detector design and (b) utilizing alternate modulation techniques. If h is the same as the molecular mean free path (L), the effect of increasing h will be detrimental to the S/N ratio. This can be seen through the effect of the parameter α in the same Eq. (13). However, $P \sim d^2$ in the same equation means an increase of S/N for a constant h/d ratio and increasing h . In principle, one could move the detector up to 50 cm away from the exciting beam, which would result in a time-of-flight of 1 ms for light molecules. At this distance, fluorescence becomes a competing mechanism. This extreme h value would require a maximum pressure of 0.3 mTorr for HCN.

Another consideration in the analysis of the narrowing of the sub-Doppler profile versus loss in sensitivity involves the question of how narrow can the linewidth be made. To attain a FWHM of 3 MHz using HF for example a h/d ratio of 60:1 is necessary. If the exposed diameter of the microphone is 1 mm, the pressure in the cell would have to be reduced to 2 mTorr so the molecular mean free path would be about 60 mm. This means that with the current detector NEP, $P_n \alpha$ loss in sensitivity of 15 with respect to the best S/N ratios presently available for the $P_{1-0}(4)$ HF transition would be expected. We are currently attempting to improve the sensitivity of the technique by (i) decreasing the P_n value, (ii) increasing P by factors of 30 to 100 by utilizing an annulus detector, and (iii) using alternative more sensitive modulation techniques including (a) Stark, (b) frequency, and (c) polarization methods. By these means the resolution and sensitivity of the technique can be better optimized.

It is perhaps pertinent to note that moving the laser beam with respect to the mechanical selector should have little effect on the line profile so long as the mean free path of the molecules does not become significantly short relative to the distance from the beam to the detector surface.

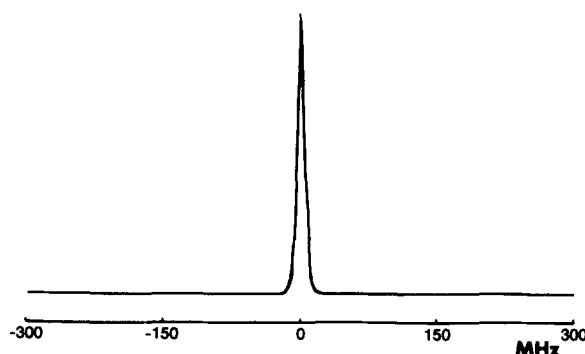


FIG. 5. Theoretically predicted line shape (Ref. 4) of sub-Doppler profile of $\nu_3 R(22)$ transition in HCN.

CONCLUSION

A more general formulation of the novel spectroscopic technique traveling-wave sub-Doppler excited molecule energy transfer spectroscopy has been completed. This three dimensional approach provides a better correlation with experimentally determined line profiles than the previously derived two dimensional approximation. Spectroscopically the technique has been successfully applied to the $R(22) \nu_3$ HCN, $K^2R(7) \nu_1$ NH₃ and $P_{1-0}(4)$ HF transitions. An upper limit to $P_n (\leq 10^{-12} \text{ W})$ was experimentally determined for this mode of detection. These experiments indicate that the technique is both sensitive and capable of producing spectra with FWHM of $\frac{1}{10}$ to $\frac{1}{100} \Delta \nu_D$ for a wide range of rotational-vibrational molecular transitions accessible to this laser system. This relatively simple optical arrangement has the advantage of minimizing reflections which can destabilize the laser and often prove a problem in saturation-absorption techniques involving counter-propagating beams.^{5,6} In addition the technique also has the advantage of minimizing the effect of laser output amplitude fluctuations which can be significant in amplitude unstabilized laser systems such as color center lasers (0.5%–1%). Such effects would otherwise result in severe limitations in the detection of weakly absorbing molecular species but are minimized in this particular technique as the signal is proportional to the laser energy absorbed by participating molecules.

ACKNOWLEDGMENTS

We would like to express our appreciation to the National Science Foundation (Grant CHE-79-23237), The

Robert A. Welch Foundation (Grant A-747), The Petroleum Research Fund administered by the American Chemical Society and CEMR, TAMU for supporting this research. We would also like to thank David Danzeiser for technical assistance and Dr. Bill Perry and Dr. H. A. Schüssler for suggestions and discussion.

- ¹R. S. McDowell, in *Advances in Infrared and Raman Spectroscopy*, edited by R. H. Clark, and R. E. Hester (Heyden, Philadelphia, 1978), Chap. 1, p. 1.
- ²T. E. Gough, R. E. Miller, and G. Scoles, *Appl. Phys. Lett.* **30**, 338 (1977).
- ³T. E. Gough, High Resolution Infrared Applications and Developments, Natl. Bur. Stand. Conference, June 23–25, 1980.
- ⁴C. Hartung, R. Jurgeit, and M. H. Ritze, *Appl. Phys.* **23**, 403 (1980).
- ⁵T. W. Hansch, I. S. Shahin, and A. L. Schawlow, *Phys. Rev. Lett.* **27**, 707 (1971).
- ⁶(a) A. Di. Lieto, R. Minguzzi, and M. Tonelli, *Opt. Commun.* **31**, 25 (1979); (b) E. E. Marinero and M. Stuke, *ibid.* **30**, 349 (1979).
- ⁷Khalid Iqbal, J. N. Dahiya, S. G. Lieb, and J. W. Bevan *Appl. Phys.* (to be published).
- ⁸K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure; Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979), p. 304.
- ⁹V. S. Letokhov and V. P. Chebotayev, in *Nonlinear Laser Spectroscopy* (Springer, Berlin, 1977), p. 4.
- ¹⁰Reference 9, p. 39.
- ¹¹D. U. Webb and K. N. Rao, *J. Mol. Spectrosc.* **28**, 121 (1968).
- ¹²W. S. Benedict, E. K. Plyer, and E. D. Tidwell, Jr., *Chem. Phys.* **32**, 32 (1960).
- ¹³D. H. Rank, D. P. Eastman, B. S. Rao, and T. A. Wiggins, *J. Opt. Soc. Am.* **51**, 929 (1961).