Microwave–microwave double resonance using a Fabry–Perot cavity spectrometer

Rabindra N. Nandi,[a] Alice M. Murray, Jong-In Choe,[b] and Marlin D. Harmony

Department of Chemistry, University of Kansas, Lawrence, Kansas 66045

(Received 9 May 1983; accepted for publication 5 June 1983)

The design and operation of a relatively simple, yet versatile spectrometer for microwave–microwave double resonance (MMDR) studies is described. The system consists of a high-Q, semiconfocal Fabry–Perot cavity resonator which is crossed at right angles by a second free-space microwave beam. We excite the cavity with a low-power unmodulated signal source, while the free-space irradiation source is square-wave frequency modulated and is of moderately high power (several hundred milliwatts). Both microwave sources are scannable; the signal source is locked to the cavity while the pumping klystron is free running. The signal (cavity) frequency has been operated in the 15–40-GHz range, and pump frequencies can be selected and easily implemented above or below the signal microwave frequency.

PACS numbers: 07.60.Ly, 07.58. + g, 33.40.Hp

INTRODUCTION

The Fabry–Perot cavity spectrometer has found appreciable, if not extensive, use over the years for a variety of microwave spectroscopic experiments.[1–3] The cavity structure is particularly useful for a variety of reasons, including its intrinsic high sensitivity[1] and relatively small volume. In addition, the open nature of the cavity, with metallic surfaces only at the ends of the resonator, makes it an ideal device for introducing additional irradiating fields in the optical or microwave frequency regions. In this work we describe a simple and convenient modification of a Fabry–Perot cavity spectrometer for use as a microwave–microwave double resonance (MMDR) spectrometer.

MMDR experiments have most often been performed in waveguide transmission sample cells with concurrent or countercurrent propagation of the two irradiating fields.[4,5] In the usual configuration, with a frequency-modulated pump radiation source, rather careful and elaborate high- or low-pass filtering must be arranged to prevent the pump radiation from falling on the crystal diode used for detecting the signal radiation. An alternative to such a system would be to utilize a Fabry–Perot cavity for the signal microwave frequency. The pump frequency can then be introduced into the cavity at right angles. Indeed, a MMDR system with two crossed Fabry–Perot cavities has been reported.[3] The use of a high-Q cavity for the signal microwave frequency is especially advantageous, since it serves as a very high-quality natural isolator for the pump radiation.

I. INSTRUMENT DESIGN

Our system utilizes *free-space* transmission of the pump radiation through the cavity at right angles to the cavity axis. A block diagram of the system is presented in Fig. 1. The cavity is of the semiconfocal variety[1] with aluminum resonator plates having diameters of 3 $\frac{3}{4}$ in. The radius of curvature of the spherical reflector is 15 cm, and the resonator plate spacing is operated near 7.5 cm. With this geometry the TEM$_{mnq}$ mode structure is well resolved, having cavity resonator frequencies given approximately by

$$\nu \cong 500(2q + m + n + 1)\text{MHz}, \tag{1}$$

and the cavity Q is in the vicinity of 10^4. Operating in the reflection mode, a single hole in the center of the flat resonator plate permits coupling of power into and out of the cavity. Substituting plates with different size irises, the cavity has been operated from 15 to 40 GHz. Tuning of the cavity is accomplished with a fine micrometer drive on the upper plate controlled by a variable speed stepper motor. Tracking of the signal (BWO) source to the cavity is accomplished by a phase-lock loop in the conventional fashion.

Pump radiation from a moderately high-power (500 mW) klystron is admitted to the resonator and collected by means of commercial horns chosen to obtain an appropriate free-space beam as shown in Fig. 2. The pump klystron has been square-wave frequency modulated at 6 kHz in our experiments, although this frequency choice is not at all critical. The cavity and horn system are fully enclosed in a high-vacuum six-arm cross (arms in $\pm x$, $\pm y$, $\pm z$ directions)

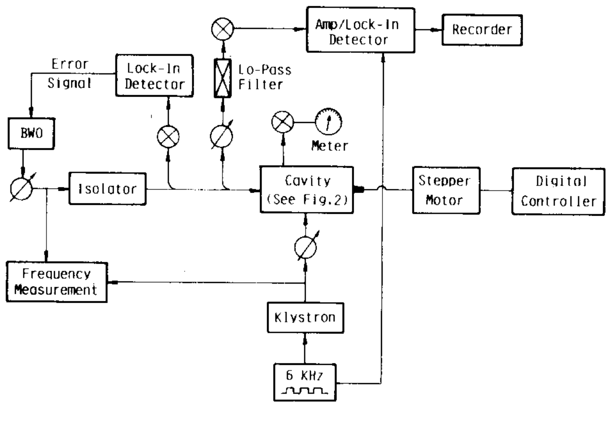

FIG. 1. Schematic diagram of Fabry–Perot cavity MMDR spectrometer.

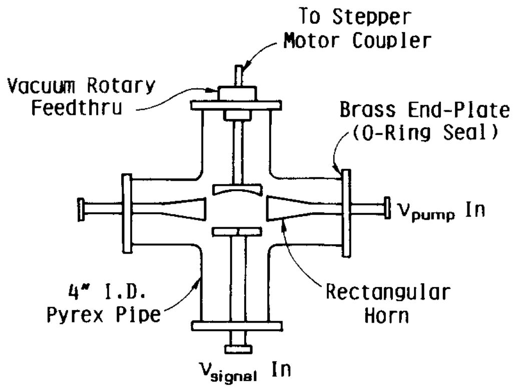

FIG. 2. Schematic of vacuum enclosure in the *xz* plane showing Fabry-Perot cavity with crossed free-space horn irradiation.

constructed from 4-in. i.d. Pyrex pipe. Removable brass or aluminum end plates facilitate changes of the cavity coupling reflector, or changes in the pumping horns. We use the remaining arms of the cross (perpendicular to those shown in Fig. 2) for high-speed pumping and gas admission.

The detection system is conventional, using narrowband amplification and lock-in detection at 6 KHz. Magnetic field modulation coils mounted inside the vacuum chamber along the edges of the resonator end plates permit the MMDR system to revert easily to a single resonance Zeeman spectrometer for free radical studies, or permit MMDR studies in the presence of a static magnetic field. Although the cavity isolates the detection system from the modulated pump radiation by at least 30 dB in general, additional isolation has been found useful when $\nu_{\text{pump}} > \nu_{\text{signal}}$. This is easily accomplished by insertion of a low-pass filter prior to the signal detector as shown in Fig. 1. Frequency measurements of either the signal or pump oscillator are performed in conventional fashion using a UHF crystal-referenced frequency standard, a communication receiver, and frequency counters.[6] Finally, the design of the cavity vacuum enclosure permits efficient introduction or generation of reactive, transient molecules immediately adjacent to the cavity. For example, we have produced the OH radical efficiently by reacting NO_2 with H atoms using a specially designed mixer which injects the reactants directly into the cavity.

II. SPECTROMETER OPERATING CHARACTERISTICS

Although MMDR spectroscopy has been utilized for two-dimensional searches,[5] the most common application involves searching for a single unknown resonance (one-dimensional search) coupled to a known microwave transition. The system described here can be operated effectively for one-dimensional searching in either of two modes. Either the signal (cavity) frequency can be set to a known transition while the pump frequency is scanned, or the pump frequency can be fixed on or near a resonance frequency while the signal frequency is scanned for the unknown transition.

Figure 3 illustrates these two scan modes for the $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ transitions of $^{16}O^{12}C^{34}S$ which occur at 23 731.3 and 35 596.9 MHz, respectively.[7] We operate the cavity frequency (ν_s) near the $2 \leftarrow 1$ transition and choose the pump frequency (ν_p) near the $3 \leftarrow 2$. The pump klystron is square-wave modulated on the reflector with 25 V p-p. In Fig. 3(a), ν_p has been set several MHz below the $J = 3 \leftarrow 2$ resonant frequency ν_p^0, while ν_s is scanned through the resonance frequency ν_s^0 of the $J = 2 \leftarrow 1$ transition. The characteristic and well-known double resonance line shape[4,5,8] is observed, with the weak "creeper" several MHz above ν_s^0. In practice the cavity can be scanned at least 50–75 MHz before it may be necessary to readjust the slide-screw tuner to maintain an adequate match of the cavity to the transmission waveguide. This mode of operation can be extended to two-dimensional searches, since the double resonance signals can be observed with the pump frequency 5–10 MHz off resonance.

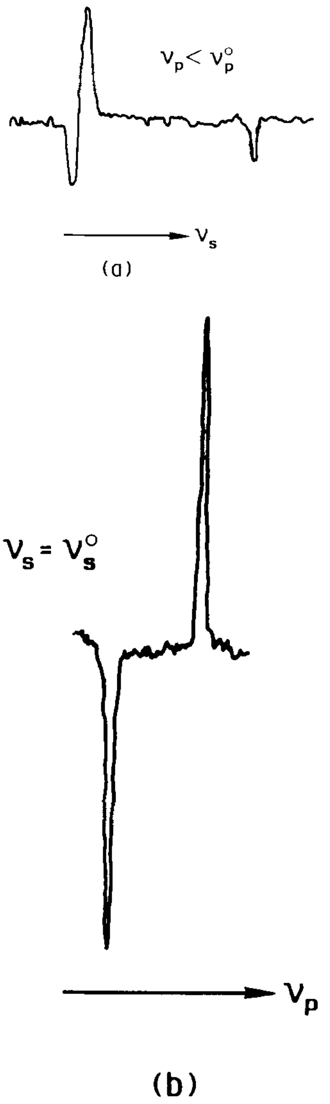

FIG. 3. $^{16}O^{12}C^{34}S$ $2 \leftarrow 1$ $(3 \leftarrow 2)$ double resonance signals. In (a), ν_p is fixed and ν_s is scanned through ν_s^0. In (b), ν_s is fixed and ν_p is scanned through ν_p^0.

Figure 3(b) illustrates the second operation mode in which the signal (cavity) frequency is fixed at $\nu_s = \nu_s^0$, while the pump frequency ν_p is scanned across ν_p^0. Now we observe the resonance as each of the two modulation sidebands pass over ν_p^0. The phase-sensitive detector inverts the two signals since they are out of phase by 180°. In this mode of operation the signal intensitities deteriorate rapidly as ν_s is tuned off ν_s^0

by more than 1 MHz. Nevertheless, assuming that ν_s^0 is known as in common cases, this method provides the most efficient and rapid method for broadband searching for an unknown transition, since the free-running pump oscillator can be scanned easily and rapidly, and oscilloscope presentation of the signals can be utilized by superimposing a low-frequency sawtooth on the square-wave modulation. With ν_s precisely on resonance ν_s^0, the optimum signal intensity is obtained.

III. DISCUSSION

The Fabry–Perot cavity/free-space MMDR spectrometer described here provides a useful alternative to the common waveguide systems. Under optimum conditions its sensitivity should be in the range of $\gamma = 10^{-10}$ cm^{-1}, which is comparable to waveguide transmission systems. While the spectrometer is not as frequency agile as one having two free-running oscillators,[5] it does provide complete scan capability for both the signal (cavity) frequency and the pump (free-space) frequency. Although some spurious, easily distinguished resonances may occasionally be coupled into the signal channel from the high-power pump, the cavity generally serves as an excellent filter.

Overall, the microwave system is quite simple once the cavity is constructed. It consists of fewer components than the usual waveguide MMDR system and permits especially easy changing of the pump frequency band. Thus, for example, the OCS $1 \leftarrow 0$ and $2 \leftarrow 1$ double resonance pair can be investigated merely by changing the microwave horns and pumping source for operation at ≈ 12.4 GHz. No other essential component changes are required, in contrast to the situation for a waveguide system, which would typically require major changes of ferrite isolators, directional couplers, cutoff filters, etc.

Another distinct advantage is that the Fabry–Perot cavity system is ideally suited for MMDR studies of transient molecules. With its open geometry and low surface-to-volume ratio, and when coupled to a high-speed pumping system, it provides an almost perfect environment for reactive species.

Finally, the system brings to a practical realization in a very simple way the earlier attempts to perform MMDR experiments using the Fabry–Perot cavity.[3] Although the dual Fabry–Perot MMDR system represented a perfectly valid concept, and was especially appealing because it required only low-power microwave oscillators, in practice the added complication of operating two synchronized oscillator/cavity systems lessened its versatility and convenience.

ACKNOWLEDGMENTS

Acknowledgments are made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grant CHE 81-16131), for support of this research.

[a] Present address: Saha Institute of Nuclear Physics, Calcutta, India 700009.

[b] Present address: Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48104.

[1] L. W. Hrubesh, R. E. Anderson, and E. A. Rinehart, Rev. Sci. Instrum. **42**, 789 (1971).

[2] M. Lichtenstein, J. J. Gallagher, and R. E. Cupp, Rev. Sci. Instrum. **34**, 843 (1963); L. W. Hrubesh, R. E. Anderson, and E. A. Rinehart, Rev. Sci. Instrum. **41**, 595 (1970); T. J. Balle and W. H. Flygare, Rev. Sci. Instrum. **52**, 33 (1981); J. K. Myler, J. R. Sambles, and J. E. Cousins, J. Phys. E **13**, 289 (1980); I. P. French and T. E. Arnold, Rev. Sci. Instrum. **38**, 1604 (1967).

[3] M. C. Lee and W. F. White, Rev. Sci. Instrum. **43**, 638 (1972).

[4] A. P. Cox, G. W. Flynn, and E. B. Wilson, Jr., J. Chem. Phys. **42**, 3094 (1965); R. C. Woods, A. M. Ronn, and E. B. Wilson, Jr., Rev. Sci. Instrum. **37**, 927 (1966).

[5] O. L. Stiefvater, Z. Naturforsch. **30A**, 1742 (1975); 1756 (1975).

[6] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).

[7] F. J. Lovas, J. Phys. Chem. Ref. Data **7**, 1445 (1978).

[8] A. Javan, Phys. Rev. **107**, 1579 (1959).