Quartz-enhanced photoacoustic spectroscopy of HCN from 6433 to 6613 cm$^{-1}$

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Abstract: The HCN absorption spectrum from 6433 to 6613 cm$^{-1}$ was acquired at room temperature by means of a tunable external cavity diode laser based quartz-enhanced photoacoustic spectroscopy (QEPAS) technique.

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1. Introduction
The detection, quantification and monitoring of hydrogen cyanide (HCN) is of interest because it is a highly toxic chemical species and it is also a warfare chemical agent. Therefore, the development of a HCN sensor capable of detecting sub-ppmv concentration levels and operating in harsh environments is an important issue [1]. A novel approach to photoacoustic spectroscopy (PAS) called quartz-enhanced photoacoustic spectroscopy (QEPAS) was introduced in 2002 by the Rice group, which utilized a quartz tuning fork (TF) as a resonant acoustic transducer [2]. Compared to conventional resonant PAS, QEPAS has several practical advantages: the sensor is immune to environmental acoustic noise, inexpensive, compact and has the capability to analyze extremely small gas samples [3]. In this work, we primarily report QEPAS based spectroscopy of HCN from 6433 to 6613 cm$^{-1}$ using a commercial tunable external cavity diode laser.

2. QEPAS experimental set-up
A tunable fiber-coupled telecom-grade external cavity diode laser was employed as a QEPAS excitation source. The laser source (Tunics Plus), emitting single mode and single frequency radiation with a maximum optical power of 5 mW, is continuously tunable in the near infrared from 1500 to 1640 nm (C and L bands) with a wavelength resolution of 0.001 nm (~ $4 \times 10^{-3}$ cm$^{-1}$) and a laser emission linewidth of $< 1$ MHz. The laser beam was first collimated by a fiber optic collimator, and then focused between the prongs of the tuning fork by a lens with focal length of 30-mm. Alignment of the diode laser beam to the accurate positioning of the TF was achieved by using a He-Ne laser. A quartz tuning fork with a high Q factor (Q ~ 8700 at normal atmospheric pressure) and a resonant frequency $f_0$ of ~ 32,768 kHz was used as a photoacoustic transducer.

The laser current was sinusoidally modulated at half the TF resonant frequency $f_0/2$. The TF generated current was converted to voltage by a transimpedance preamplifier and then demodulated at $f_0$ by the lock-in amplifier (Stanford Research Systems, Model SR 830 DSP). The lock-in amplifier and laser were controlled by a GPIB card. The 2$^{nd}$ harmonic signal was acquired by an AD card and sent to a personal computer for further analysis. All of
these functions were performed using a customized program in C.

3. HCN spectrum

In the present work, the absorption spectrum of HCN from 6433 to 6613 cm\(^{-1}\) was acquired by the tunable diode laser based QEPAS technique. The cell was filled with 74.3 mbar HCN and the integration time was 3 s. The upper panel of Fig. 1(a) shows the complete spectrum at this spectral range. The absorption at 6463.656 cm\(^{-1}\) is shown in Fig. 1 (b). In this work we focus on the analysis of the P branch of (20^0\(^0\)) – (00\(^0\)) band (middle panel of Fig. 1(a)). The line positions agree well with the calculated results according to the ro-vibrational constants from Ref 4 and the experimental and calculated results in Refs 5 and 6, with a standard deviation of ~ 0.056 cm\(^{-1}\). The observed difference of the relative absorption intensities of the experimental data with the line intensities of GEISA 03 database [7] was caused by the laser power variations and pressure broadening effects. The absorption spectrum from 6501 to 6596 cm\(^{-1}\) was more complex. A portion of this range, from 6524 to 6537 cm\(^{-1}\) is shown in the lower panel of Fig. 1(a). The absorption in this spectral range belongs to the R branch of (20\(^0\)) - (00\(^0\)) band and the absorption of its isotopologue H\(^{13}\)CN. Furthermore, the \(l\)-type resonance may also redistribute the intensity of the high-\(J\) rotational transitions and affect the \(e\) and \(f\) levels differently.

4. Conclusion

Details of the HCN absorption spectroscopy from 6433 to 6613 cm\(^{-1}\)obtained by means of near infrared cw tunable external cavity diode laser based QEPAS will be reported.

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6. References