ON THE POTENTIAL APPLICATION OF RAMAN SPECTROSCOPY FOR MONITORING ACIDITY OF MINE EFFLUENTS

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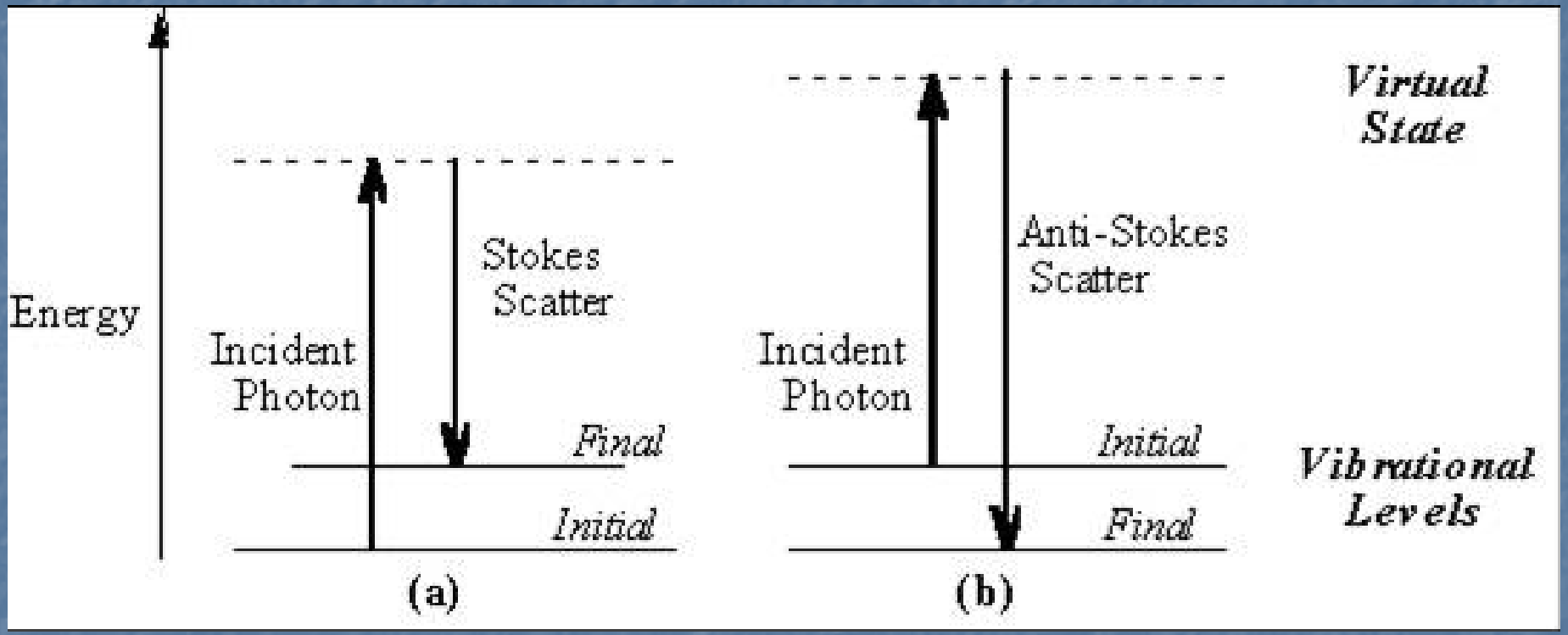
The Problem: Sulfide minerals exposed to air and water, as a result of mining activity or otherwise, will often produce acidic solutions as they oxidize. As such, the effluents from mining activities must monitored and treated so as not to allow their escape into the surrounding natural environment.

The Question: Can Raman Spectroscopy to monitor the acidity of these streams?

How does Raman Spectroscopy work?



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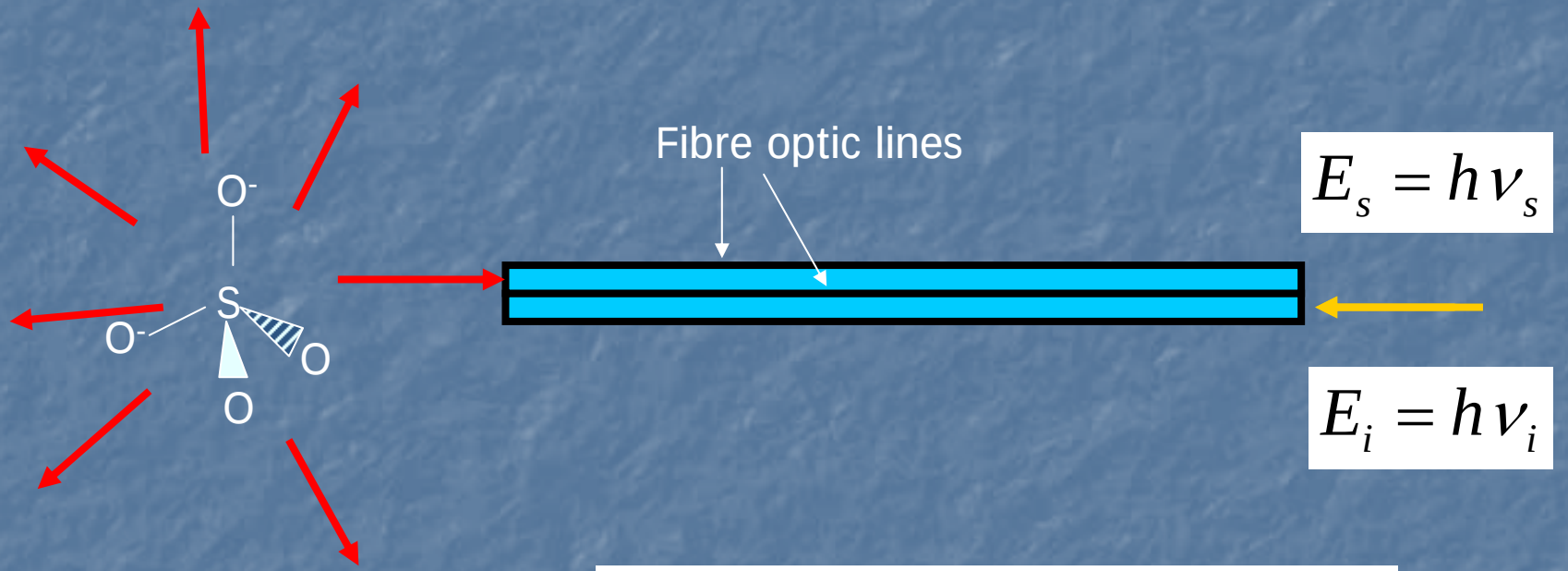

$$E_s = h\nu_s$$

$$E_i = h\nu_i$$

$$\Delta E = E_i - E_s = h(\nu_i - \nu_s) = h\Delta\nu$$

Using Raman Spectroscopy to measure acidity

Bisulfate and sulfate ion concentrations may be measured by Raman Spectroscopy

Peak Number	Position of Peak, (cm^{-1})	Assignment
1	890	S-OH fundamental vibration of HSO_4^-
2	948	S-O fundamental vibration of $H_3O^+SO_4^{2-}$
3	981	S-O fundamental vibration of SO_4^{2-}
4	1024	S-O fundamental vibration of $H_3O^+HSO_4^-$
5	1050	S-O fundamental vibration of HSO_4^-
6	1110	S-O asymmetrical vibration of SO_4^{2-}
7	1200	S-O asymmetrical vibration of HSO_4^-

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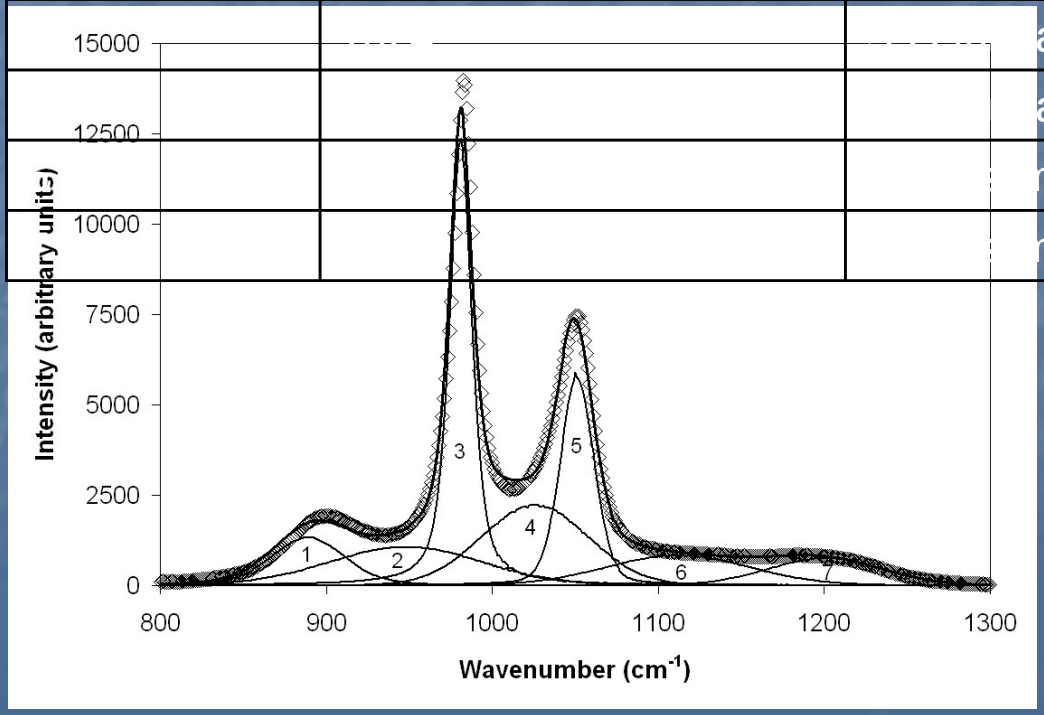

$$I_{\bar{\nu}} = \sum_{n=1}^{7} I_{\bar{\nu}_n} \left[\frac{1-G_n}{1+4\left(\frac{\bar{\nu}_n-\bar{\nu}}{w_n}\right)^2} + G_n \exp\left\{ -4\ln\left[2\left(\frac{\bar{\nu}_n-\bar{\nu}}{w_n}\right)^2 \right] \right\} \right]$$

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Using Raman Spectroscopy to measure acidity

Solu
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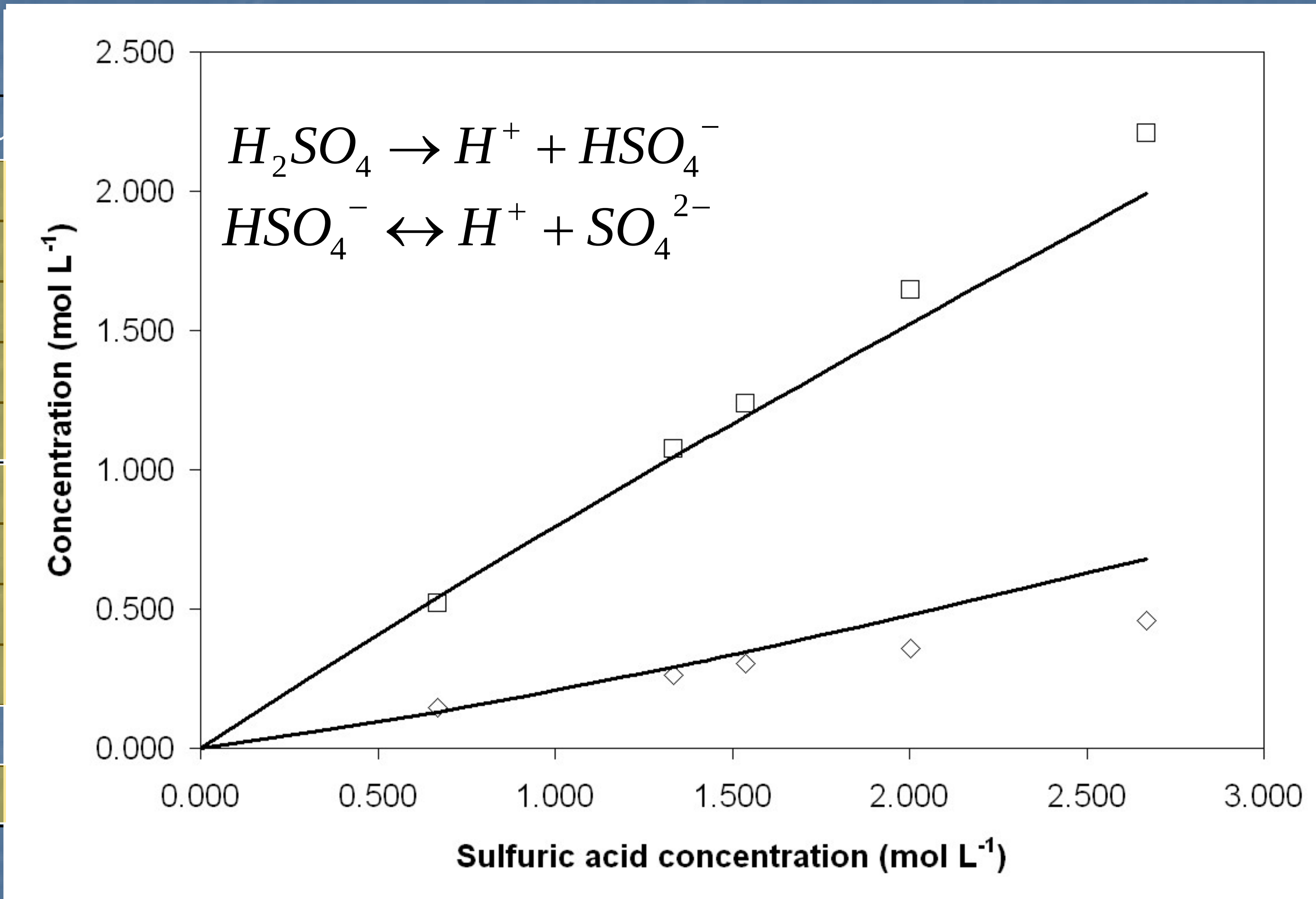


Using Raman Spectroscopy to measure acidity

Mine effluent will contain cations such as Fe^{2+}, Zn^{2+}, Mg^{2+}, Ca^{2+}, Cu^{2+}, etc. that will affect the bisulfate equilibrium. Without a way of measuring their concentrations, how can the acidity be calculated?

$$HSO_4^- \leftrightarrow H^+ + SO_4^{2-}$$

$$K_2 = \frac{a_{H^+} a_{SO_4^{2-}}}{a_{HSO_4^-}} = \frac{f_{H^+}[H^+] f_{SO_4^{2-}}[SO_4^{2-}]}{f_{HSO_4^-}[HSO_4^-]}$$

$$\log f_i = -\frac{Az_i^2\sqrt{I}}{1+Ba\sqrt{I}} + bI$$

$A = 0.5116$, $Ba = 0.39$, and $b = 0.13$

$$I = \frac{1}{2}\sum z_i^2 c_i = [H^+] + 4[M^{2+}] + [HSO_4^-] + 4[SO_4^{2-}]$$

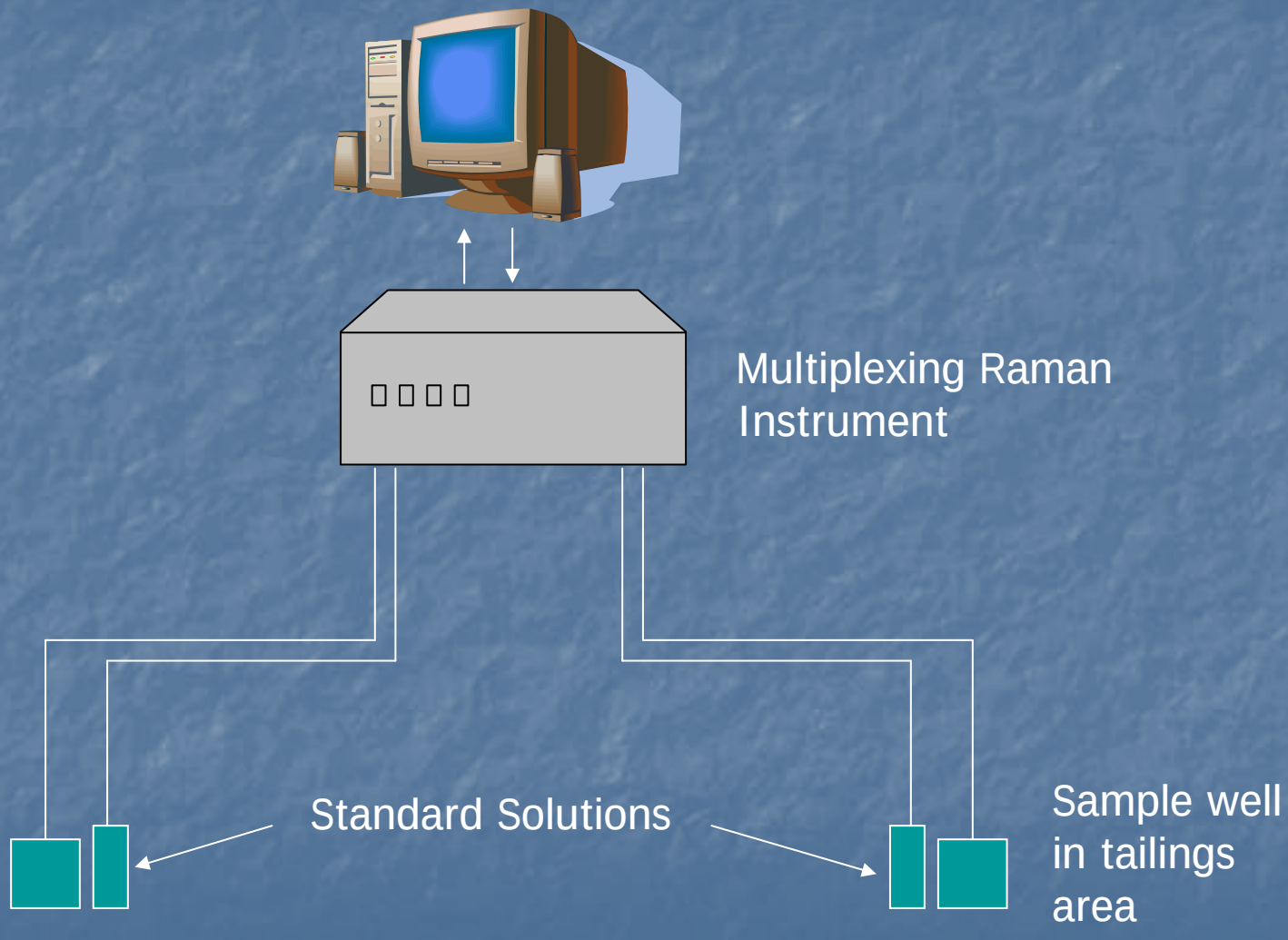
$$\sum z_i[i] = [H^+] + 2[M^{2+}] - [HSO_4^-] - 2[SO_4^{2-}] = 0$$

Using Raman Spectroscopy to measure acidity

Solution	H_2SO_4 (mol L^{-1})	$ZnSO_4$ (mol L^{-1})	$(NH_4)_2SO_4$ (mol L^{-1})
1	0.668		
2	1.335		
3	1.538		
4	2.003		
5	2.670		
7		0.459	
8		0.918	
9		2.300	
10		2.300	
11	1.531	0.917	
12			0.917

Calculated to be 1.47 *M* H_2SO_4 and 0.82 *M* MSO_4

How might an acid monitoring system look like?



Limits:

1. Precipitation on probe tips?
2. Use of Raman for weakly acidic solutions?

Conclusions:

1. Raman spectroscopy is a proven method for measuring sulfate and bisulfate concentrations in solutions (which can be correlated to acid concentration)
2. Because Raman probes are made of fibre optic lines, they can be used for remote sampling and do not require power at probe tips
3. Raman instruments are cheaper than ever due to advancements in LEDs as light sources
4. Multiplexing Raman instruments allow a single machine to be used to measure multiple sample locations

Acknowledgements

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