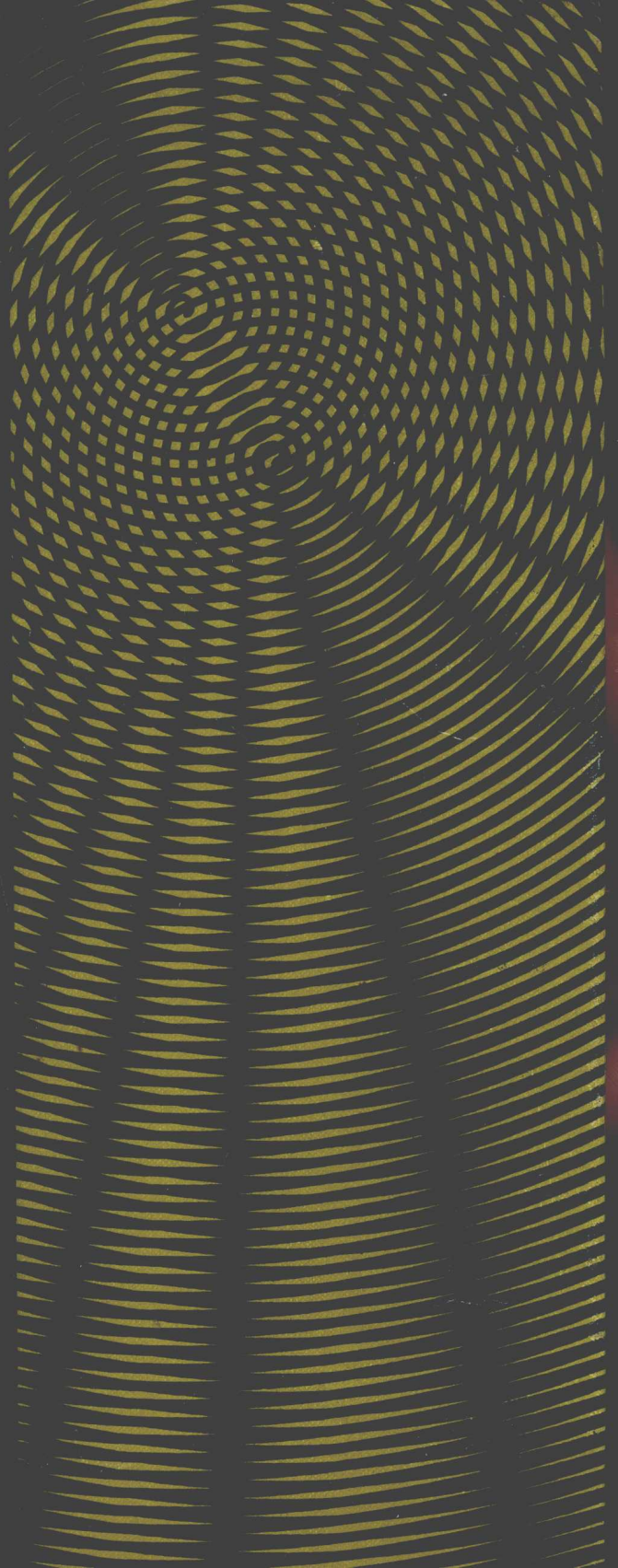


Tunneling Spectroscopy

Edited by Paul K. Hansma

Capabilities, Applications, and New Techniques



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**Capabilities, Applications,
and New Techniques**

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Paul K. Hansma

*University of California at Santa Barbara
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Preface

This book has been compiled to give specialists, in areas that could be helped by tunneling spectroscopy, a rounded and relatively painless introduction to the field. Why relatively painless? Because this book is filled with figures—A quick glance through these figures can give one a good idea of the types of systems that can be studied and the quality of results that can be obtained.

To date, it has been somewhat difficult to learn about tunneling spectroscopy, as papers in this field have appeared in a diversity of scientific journals: for example, *The Journal of Adhesion*, *Journal of Catalysis*, *Surface and Interface Analysis*, *Science*, *Journal of the American Chemical Society*, *Physical Review*—over 45 different ones in all, plus numerous conference proceedings. This diversity is, however, undoubtedly healthy. It indicates that the findings of tunneling spectroscopy are of interest and potential benefit to a wide audience. This book can help people who have seen a few papers or heard a talk on tunneling spectroscopy and want to learn more about what it can do for their field.

Tunneling spectroscopy is presently in a transitional state. Its experimental methods and theoretical basis have been reasonably well developed. Its continued vitality will depend on the success of its applications. Crucial to that success, as pointed out by Ward Plummer, is the adoption of tunneling spectroscopy by specialists in the areas of application.

At present, tunneling spectroscopy is still usually done by tunneling spectroscopists—those who specialize in this field. Will tunneling spectroscopy successfully pass from the hands of specialists in tunneling spectroscopy into the hands of specialists in applications? Will it be used by specialists in lubrication, corrosion, catalysis, adhesion, and surface science to help solve their problems?

There has already been some progress in this direction. For example, Henry Weinberg, author of Chapter 12, is a chemical engineer who specializes in catalysis and surface science; Kerry Hipps and Ursula Mazur,

authors of Chapter 8, are chemists who specialize in the study of inorganic ions. That these groups use tunneling spectroscopy as a tool in their research areas is one of the brightest signs of hope for the future of tunneling spectroscopy.

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Introduction

Paul K. Hansma

1. Why? Why? Why?

Tunneling spectroscopy is a sensitive technique for measuring the *vibrational spectra* of molecules. It was discovered by Jaklevic and Lambe^(1, 2) in 1966.

1.1. Why Do Vibrational Spectroscopy?

Vibrational spectroscopy is a powerful way of identifying molecules and molecular fragments. Since a functional group, say —CH_3 , has roughly the same vibrational frequencies wherever it appears in a molecule, researchers can deduce the presence or absence of —CH_3 by the presence or absence of vibrations at its characteristic frequencies. Table 1 shows the characteristic frequencies of many functional groups.

From this knowledge of the presence or absence of functional groups, together with whatever other information is available, researchers can guess the structure of their unknown molecules. After they guess, they can use vibrational spectroscopy to see if they are right or wrong.

They do this by comparing the vibrational spectrum of their unknown molecule to the vibrational spectrum of what they guess it is. There are many excellent, extensive collections of vibrational spectra⁽³⁻⁷⁾ for use in this comparison. If the spectrum of the guessed molecule is not in an accessible collection, the researcher can consult the literature or, if worse comes to worst, measure it himself.

Table 1. Spectra-Structure Correlations. (Probable Positions of Characteristic Infrared Absorption Bands)^a

4000 cm^{-1}	3500	3000	2500	2000	1800	1600	1400	1200	1000	800	600	400
ALKANE GROUPS												
				CH_3-C METHYL								
				$\text{CH}_3-(\text{C}=\text{O})$								
				$\text{CH}_3-(\text{C}=\text{O}), \text{CH}_3-(\text{C}=\text{N})$								
				CH_3								
				ETHYL								
				N-PROPYL								
				ISOPROPYL								
				TERTIARY BUTYL								
				VINYL $-\text{CH}=\text{CH}_2$								
				$\text{H}_2\text{C}=\text{CH}$ (TRANS)								
				$\text{H}-\text{C}=\text{C}-\text{H}$								
				$\text{C}=\text{CH}_2$								
				$\text{C}\equiv\text{C}-\text{H}$								
				$\text{C}\equiv\text{C}$								
				MONO SUBST. BENZENE								
				ORTHO DISUBST.								
				METABENZENE								
				PARA								
				VICINAL TRISUBST.								
				SYN.								
				α NAPHTHALENES								
				β NAPHTHALENES								
ETHERS												
ALCOHOLS												
				ALIPHATIC ETHERS $-\text{C}-\text{O}-\text{C}-$								
				AROMATIC ETHERS $-\text{C}-\text{O}-\text{C}-$								
				PRIMARY ALCOHOLS $-\text{CH}_2-\text{OH}$								
				SECONDARY $-\text{CH}-\text{OH}$								
				TERTIARY $-\text{C}-\text{OH}$								
				AROMATIC								
ACIDS												
				CARBONIC ACIDS $-\text{CO}-\text{OH}$								
				IONIZED CARBONYL (SALT) $-\text{CO}-\text{O}^-$								
				FORMATES $-\text{H}-\text{CO}-\text{O}-$								
				ACETATES $-\text{CH}_3-\text{CO}-\text{O}-$								
				GLUCONATES $-\text{CH}_2-\text{CO}-\text{O}-$								
				BUTYRATES $-\text{CH}_3-\text{CH}_2-\text{CO}-\text{O}-$								
				ACRYLATES $-\text{CH}_2=\text{CH}-\text{CO}-\text{O}-$								
				FUMARATES $-\text{CH}=\text{CH}-\text{CO}-\text{O}-$								
				MALEATES $-\text{CH}=\text{CH}-\text{CO}-\text{O}-$								
				BENZATES $-\text{C}_6\text{H}_5-\text{CO}-\text{O}-$								
				ALIPH. ALDEHYDES $-\text{CH}_2-\text{CHO}$								
				AROM. ALDEHYDES $-\text{CHO}$								
				ALIPH. KETONES $-\text{CH}_2-\text{CO}-\text{CH}_2-$								
				AROM. KETONES $-\text{CO}-\text{C}-$								
				NORMAL ANHYDRIDES $-\text{CO}-\text{O}-\text{CO}-$								
				CYCLOC ANHYDRIDES $-\text{O}-\text{C}-\text{O}-$								
				AMIDE $-\text{CO}-\text{NH}_2$								
				MONO SUBST. AMIDE $-\text{CO}-\text{NH}-\text{R}$								
				DI SUBST. AMIDE $-\text{CO}-\text{N}-\text{R}_2$								