

# 1

## Introduction

*The construction of such models, it was hoped, would be particularly useful for the clarification of the real meaning of Planck's constant  $h$ ... Consider, says Born, an apple tree and assume that the length  $l$  of the stems of its apples, regarded as pendula, is inversely proportional to the square of their height  $H$  above ground, so that  $l \sim H^{-1/2} \sim H$ . If now the tree is shaken with a certain frequency  $\omega$ , the apples at the corresponding height  $H$  will resonate and fall to earth with energy  $E$  proportional to  $H$  and consequently also proportional to  $\omega$ .*

— Max Jammer

*The Conceptual Development of Quantum  
Mechanics*

## Electric Fields in Matter

The dominant force on the scale of atoms and molecules, which are on the order of angstroms (an angstrom is  $10^{-10}$  meters and is about the length of a chemical bond), is electronic. Gravity is so weak as to be nearly irrelevant, while the nuclear forces are so short range as to be irrelevant as well. Going farther, one can say that nearly all of chemistry, and large fractions of biology and physics, are governed by electrical interactions.

On these short distance scales, electric fields are quite large compared to the macroscopic fields we typically think about. For example, one angstrom from an isolated proton, the field is a very large  $14 \text{ V}/\text{\AA}$ . (Comparable to a car battery with the leads separated by only  $1 \text{ \AA}$ , or a high voltage transmission line  $10 \text{ m}$  away from an electrical ground). Moving closer to the proton, the electric field increases as high as  $10^{11} \text{ V}/\text{\AA}$ , a value which is limited only by the finite volume of a proton. On the other hand, scattering experiments off electrons have shown that the electric field there appears to literally increase without bound. Thus, in a microscopic view of matter, the electric potential is an extremely rough potential surface, with near singularities at every proton and opposing singularities at every electron. In order to minimize the tremendous electrical energy that would be caused by separate charges, electrons are generally located as close to protons as quantum mechanics allows, thus creating nearly neutral atoms and molecules. The atoms are not quite neutral though, leading to polar solvents, electrophiles and nucleophiles, electron transfer, microwave and infrared absorption, and many more phenomena.

One of the most direct probes of electric fields in matter is through spectroscopy of solutes in a condensed phase using variable electric fields, which can be separated into three related branches. Solvatochromism is the study of spectral shifts arising from a change in solvents, where the dominant effect is from the different electric fields intrinsic to solvents of varying polarity. Internal Stark effects are spectral shifts due to the electric field in a local organized environment, such as the field inside a protein. Stark effect spectroscopy examines spectral band shifts caused by an external field applied to the sample. Used in combination, these methods provide powerful tools for understanding

electric fields in matter. Conversely, electric fields, whether internal or external, provide unique probes into the physics of atoms and molecules.

### **The History of Stark Spectroscopy**

**Atomic transitions.** Based on Bohr's model of the hydrogen atom, Voigt predicted in 1901 that the degeneracy in atomic energy levels should be split by an electric field in a manner analogous to the Zeeman effect, an effect which was known at the time<sup>1</sup>. However, Voigt predicted that the splitting would be too small to be experimentally observable. Despite this pessimism (or perhaps because of it), Johannes Stark, who was already an accomplished experimentalist, set out to look for electric field effects on atomic spectra. In 1913, he discovered splitting of the Balmer series<sup>2</sup>. The significance of the discovery (made simultaneously by LoSurdo), was recognized quickly, leading to its quantitative explanation in 1916 by Schwarzschild and Epstein and to the award of the Nobel Prize to Stark in 1919. The excellent agreement of theory with experiment was a major achievement for quantum mechanics and formed a significant step towards its general acceptance.

**Rotational transitions.** Despite this notable early success, the study of spectra using external electric fields did not progress significantly for another thirty years. World War II was partially responsible for the next steps, through the wartime development of microwave technology and through large increases in governmental funding of basic research. Townes pioneered rotational spectroscopy of small vapor phase molecules using microwaves<sup>3</sup>, followed by his development of microwave Stark spectroscopy<sup>4</sup>. As rotational Stark effects arise from the interaction of molecular dipoles with the electric field, microwave Stark spectroscopy made it possible to measure very precise dipole moments. This was a very active area of research during the next ten to twenty years<sup>5,6</sup>, after which other methods of structural analysis largely replaced microwave Stark spectroscopy<sup>7</sup>. More recently, the method has been used occasionally to investigate the dipole moments of molecules in vibrationally excited states<sup>8-10</sup>, which could provide complementary results to those discussed in this thesis.

***Electronic transitions.*** Stark effect research on electronic states, using condensed phase samples, was started independently by Liptay<sup>11,12</sup>, Labhart<sup>13,14</sup>, and Czekalla<sup>15</sup> around 1960. Using samples in liquid solution, a dominant effect observed was that samples partially oriented themselves in the electric field<sup>16</sup>. While this was useful for determining ground state dipole moments, it partially obscured the more interesting effects, which are dipole moment and polarizability differences between the ground and excited states. Samples immobilized in either polymer films<sup>17</sup> or frozen glasses<sup>18</sup> alleviated the orientation problem, and also allowed larger electric fields without sample breakdown, thus permitting precise measurements of electro-optic properties. Boxer's research group has dominated the recent research in the Stark spectroscopy of electronic states<sup>19</sup>. Among other things, it has been used to show that functional symmetry breaking in the photosynthetic reaction center occurs directly upon photoexcitation<sup>20</sup>, to determine the charge localization of mixed valence systems<sup>21</sup>, and to analyze reaction fields of solvents<sup>22</sup>.

***Vibrational transitions.*** This thesis concerns a fourth chapter in the development in Stark spectroscopy, the influence of electric fields on molecular vibrations. The previous experimental research in this sub-field, summarized in Table 1, is sparse by comparison to the others. As with electronic Stark effects, the first vibrational Stark spectra were measured with liquid phase samples<sup>23,24</sup> resulting in, primarily, measurements of molecular dipole moments, but also yielding some Stark tuning rates. Similarly, vapor phase samples were used to measure static dipole moments and, sometimes, excited state dipole moments<sup>25,26</sup>. Vibrational Stark effects were also used to quantify the fixed anisotropy of thin polymer films<sup>27</sup>, again, along with Stark tuning rates.

Several researchers have observed that vibrational frequencies of diatomics adsorbed to metal surfaces, at the electrode-solution interface, shift upon changing the surface potential<sup>28-32</sup>, presumably due to Stark effects. However, knowledge of just the surface voltage is insufficient to calculate the local electric field, so these data were not used to quantify them. Also using molecules adsorbed to an electrode, David Lambert was the first person to seriously study vibrational Stark effects caused by known electric fields and shifts in energy levels, rather than molecular orientation effects. His work

started with Stark effects of CO bound to nickel surfaces in ultra-high vacuum<sup>33,34</sup>, and later expanded to other diatomics and other electrode surfaces in both ultra-high vacuum

**Table 1. Previous measurements of vibrational Stark effect tuning rates**

Year	Authors	Sample	State or Solvent	Field MV/cm	Tuning rate cm <sup>-1</sup> /(MV/cm)	Method
1967	Handler and Aspnes <sup>a</sup>	2,6 di-isopropyl phenol	CCl <sub>4</sub> liquid	0.08	0.3 for fundamental 1.0 for overtone	dispersive IR
1971	Rumyantzev and Blinov <sup>b</sup>	dioxydinaphthyl	neat film	0.1 to 1	1.7 for 2.94 $\mu$ m band -0.2 for 2.87 $\mu$ m	dispersive IR
1981	Gough, Miller and Scoles <sup>c</sup>	HF	vapor	0.046	0.772	mol. beam and laser
1981	Gough, Miller and Scoles <sup>c</sup>	HCN	vapor	0.046	0.460 for CH mode	mol. beam and laser
1983	Lambert <sup>d</sup>	CO	Ni (110) in UHV	0.06	1.1	reflection- absorption
1988	Lambert <sup>e</sup>	CO	Ni (100) in UHV		0.53	reflection- absorption
1992	Spitzer, Sievers, and Silsbee <sup>f</sup>	NaCN	KBr matrix	0.0051	0.37 KCNNa 0.10 KNCNa	hole- burning
1995	Chattopadhyay and Boxer <sup>g</sup>	4-methoxy- benzonitrile	2-MeTHF frozen glass	0.96	0.8±0.3 /f	dispersive IR

(a) Ref. 23. (b) Ref. 27. (c) Ref. 25. See also ref. 10 for difference dipoles of several other vapor phase inorganic compounds (d) Refs. 33,34. See also Table 4 in ref. 36 for CO Stark tuning rates on other electrodes. (e) Ref. 35. (f) Ref. 46. (g) Ref. 40.

and at an electrode-aqueous interface<sup>35-37</sup>. For the former experiments, a second electrode near the sample provided the electric field, whereas the latter ones used a theoretical model of the interface<sup>38</sup> to estimate local electric fields. Using perturbation models similar to those described later in this work, Lambert showed that the dominant cause of the Stark effects observed were from bond anharmonicity<sup>39</sup>.

Vibrational Stark measurements using isotropic bulk samples were started by Arun Chattopadhyay, who measured the linear and quadratic Stark tuning rates of 4-methoxybenzonitrile<sup>40</sup> and, in unpublished work, acetonitrile. Much of the work in this thesis represents a continuation of his preliminary studies.

The history of vibrational Stark effects, does not stop with this work, of course, but is continuing with active research on a variety of interesting problems<sup>41-45</sup>.

***Definition of a Stark effect.*** Throughout the history of Stark effect measurements, the definition of what constitutes a Stark effect has changed. Initially it meant just a splitting of degenerate energy levels, while later it included shifts of non-degenerate energy levels and sometimes spectral intensity changes as well. Here, a broad and empirical definition is used, which is that a Stark effect is simply the reversible change observed in a spectrum upon application of an electric field. While the definition is not intended to include sample re-orientation effects, these effects may contribute in certain situations because they can be undetectable and, moreover, because re-orientation cannot be adequately defined for non-rigid molecules.

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