# MOLECULAR VIBRATORY BEHAVIOR UNDER HIGH ELECTRIC FIELD STRENGTH

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Keywords: Dielectric theory

## ABSTRACT

Wavemechanical calculations revealed a vibrational behavior of molecules under strong electric fields which is in general agreement with experimental observation. Also the acoustic behavior of insulating material as well as the phenomenon of electric break through seem to be understandable by these theoretical evaluations.

## 1. INTRODUCTION

Chemical catalysis has its origin in the electric interaction between catalyst and transition state of a chemical reaction (ref. 1). The accelerating activity is also attainable by means of high electric field strength ( $> 10^8$ volts/cm) which is superposed upon the transition state (ref. 2).

This field influence is not restricted to reacting molecular particles only but there is also an influence upon the dielectric behavior of insulating materials e.g. the glass walls of a field reactor. On this line it was usually observed that chemical reaction under field starts always exactly together with the production of certain noise or acoustic sound coming from the reactor wall material. These acoustic effects seem to belong to phonon emission of lattice oscillations (membrane vibration was not detectable !) being stimulated by alternating electric fields. Further increase of field strength acting upon the insulating wall material lastly will result in electric break through thus revealing the escape of electrons from their original localized positions in the lattice.

To get a better understanding of these effects it was of some interest to know whether and how far the vibrational behavior of single molecules is also altered by high electric field strength.

In the meantime F. AUSSENEGG and coworkers (reff. 3, 4 and 5) found typical effects by high electric field strength

on vibrational RAMAN bands of some simple liquids. Their experiments demonstrate especially increasing RAMAN intensities ($I_F/I_o$ ranging up to 6) with increasing field strength (up to about $10^6$ volts/cm) and after passing a maximum the intensities decrease again.

It is in the scope of the following to get a theoretical understanding of what happens if molecules are applied to relative high electric fields.

## 2.1. ELECTRONIC STATES UNDER HIGH ELECTRIC FIELD STRENGTH

A neutral particle - atom or molecule - under influence of an electric field displays a dielectric shifting of its electric charges (Fig. 1). This behavior may be demonstrated by means of the SCHRÖDINGER-equation

$$\frac{\hbar^2}{2\mu}\cdot\varphi'' + (E-V)\cdot\varphi = -e\cdot l\cdot F\cdot\varphi \qquad (1).$$

With the approximate solution

$$\varphi = A_o\cdot\sin\left[\frac{s}{r_o}\cdot(n+1)\right] \qquad (2)$$

and an average potential

$$V = \bar{V} \cong -\frac{e^2}{\sqrt{r_o^2 + l^2}} \qquad (3)$$

the eigen value spectrum is as follows

$$E_n(F) = \frac{\hbar^2}{2\mu}\cdot\frac{(n+1)^2}{r_o^2} - \frac{e^2}{\sqrt{r_o^2 + l^2}} - e\cdot l\cdot F \qquad (4).$$

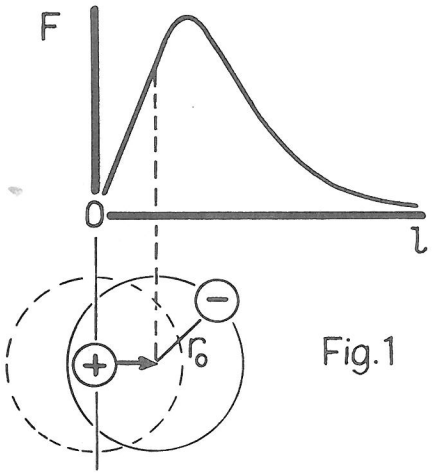


Fig.1

The extremal condition

$$\frac{d}{dl}E = 0 \qquad (5),$$

which corresponds to the principle of least action, yields

$$F = \frac{e\cdot l}{(r_o^2 + l^2)^{3/2}} \qquad (6).$$

Fig. 1 shows the functional behavior of relation (6). Exeeding of maximal field strength means beginning of ionisation and at last the initiation of electric break through.

All eigen values of (4)

show a certain variation by influence of the electric field F. The ground state especially shows the following decrease

$$\Delta E_o(F) = E_o(F) - E_o(0)$$

$$= \frac{e^2}{r_o} - \frac{e^2}{\sqrt{r_o^2 + l^2}} - e \cdot l \cdot F \qquad (7),$$

which is demonstrated in Fig. 2.

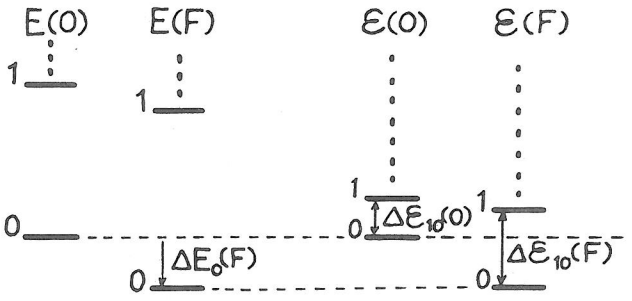


Fig. 2

## 2.2. MOLECULAR VIBRATIONAL BEHAVIOR UNDER FIELD INFLUENCE

Molecular oscillations under field action should correspond to another SCHRÖDINGER-equation

$$\frac{\hbar^2}{2m} \cdot \varphi_x'' + \left(\mathcal{E} - \frac{m}{2} \cdot \omega^2 \cdot x^2\right) \cdot \varphi_x = - e \cdot \bar{l}_x \cdot F \cdot \varphi_x \qquad (8);$$

m meaning the reduced mass and $\bar{l}_x$ (x is the oscillation coordinate) is the spatial average of the dielectric vector l

$$\bar{l}_x = \frac{4}{\pi^2} \cdot l \qquad (9).$$

Solving (8) by colocation with the approximation

$$\varphi_x = B \cdot (A - x) \cdot (A + x) \qquad (10)$$

yields an amplitude

$$A = 2 \cdot \sqrt[4]{\frac{2}{3}} \cdot \sqrt{\frac{\hbar}{m \cdot \omega}} \qquad (11)$$

and the first state of excitation

$$\mathcal{E}_1(F) = 0.816 \cdot \hbar \cdot \omega - \frac{4}{\pi^2} \cdot e \cdot l(F) \cdot F \qquad (12).$$

As easily can be seen from Fig. 2 the transitional energy which corresponds to molecular oscillation under field action is given by

$$\Delta\mathcal{E}_{10}(F) = \mathcal{E}_1(F) - \Delta E_o(F)$$

$$= 0.816 \cdot \hbar \cdot \omega - \frac{4}{\pi^2} \cdot e \cdot l \cdot F - \frac{e^2}{r_o} + \frac{e^2}{\sqrt{r_o^2 + l^2}} + e \cdot l \cdot F \qquad (13),$$

and without field, respectively

$$\Delta\mathcal{E}_{10}(0) = 0.816 \cdot \hbar \cdot \omega \qquad (14).$$

## 2.3. TRANSITION INTENSITIES WHICH BELONG TO MOLECULAR OSCILLATION

Intensities are proportional to transition probabilities ($P_{10}$)

$$I \sim P_{10} \sim \Delta\mathcal{E}_{10}^3 \cdot |\mathcal{H}_{10}|^2 \qquad (15).$$

The matrix element may be approximated as (ref. 6)

$$\mathcal{H}_{mn} = A_m - A_n \qquad (16).$$

With neglect of zero point oscillation (i.e. $A_o(F) = A_o(o) = o$) and since the amplitude is independent from the field strength F - see relation (11) - it follows simply

$$|\mathcal{H}_{10}(F)| = |\mathcal{H}_{10}(0)| \qquad (17).$$

The final result for the interesting intensity ratio is as follows

$$\frac{I_F}{I_o} = \left\{ \frac{\Delta\mathcal{E}_{10}(F)}{\Delta\mathcal{E}_{10}(0)} \right\}^3$$

$$= \left\{ 1 + \frac{1}{0.816 \cdot \hbar \cdot \omega} \cdot \left[ \left(1 - \frac{4}{\pi^2}\right) \cdot e \cdot l \cdot F + \left( \frac{1}{\sqrt{r_o^2 + l^2}} - \frac{1}{r_o} \right) \cdot e^2 \right] \right\}^3 \qquad (18).$$

Fig. 3 shows the functional behavior - the intensity ratio is always passing a certain maximum - for different molecular sizes $r_o$ and for a RAMAN frequency of $\omega$ = 1 ooo $cm^{-1}$.

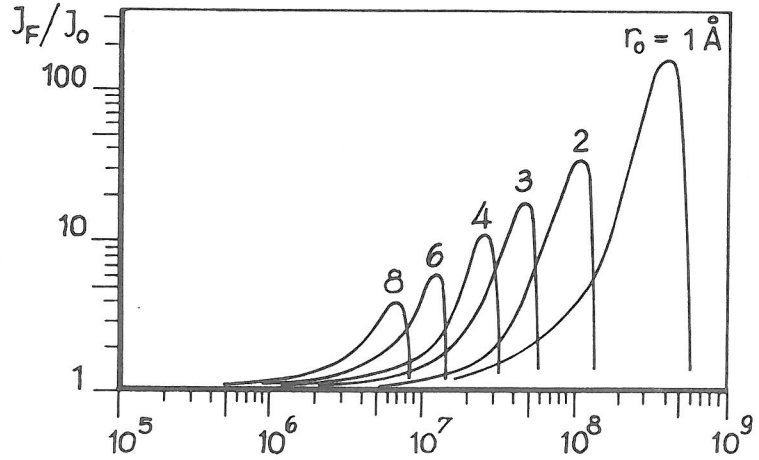


Fig. 3

Since certain temporal after-effects were observed experimentally (ref. 5) the above derived solution was also used for calculating the average life times of excited states. The calculation was based upon the transition probability

$$P_{10}(F) = \frac{64 \cdot \pi^4 \cdot e^2}{3 \cdot h^4 \cdot c^3} \cdot \Delta\mathcal{E}_{10}^3(F) \cdot \left| \mathcal{X}_{10}(F) \right|^2 \qquad (19),$$

and finally and approximately it should be

$$\bar{\tau}_{10}(F) = 1/P_{10}(F) \qquad (20).$$

The results are shown in the following table which agree

| $r_o$ Å | $\bar{\tau}_{10}(F_{max})$ msec |
|---|---|
| 1 | 0.394 |
| 2 | 1.75 |
| 3 | 3.94 |
| 4 | 6.30 |
| 6 | 11.23 |
| 8 | 15.75 |

in the order of magnitude alsowith experimental observation.

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