

Structure and permanent electric dipole of para-fluoroaniline in gaseous phase

Invited Paper

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Abstract: By coupling a matrix assisted laser desorption source to an electric beam deflection setup, we have measured the permanent electric dipole moment of the isolated para-fluoroaniline PFAN ($\text{FC}_6\text{H}_4\text{NH}_2$) molecule in the ground state. This measurement of the electric dipole of an isolated push-pull molecule is unique. The experimental value is compared to two different calculations and the structure of the system is discussed.

Keywords: Electric dipole moment • Para-fluoroaniline • Molecular beam • Electric deflection
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1. Introduction

Experimental and theoretical interests in π conjugated molecules have been exploded with the possibility of designing and synthesizing molecules with specific electronic and optical properties and their potential applications as constituents of new electric or optical devices [1-4]. For years, doubly substituted benzene molecules have served an important model for conjugated systems, in particular for dipolar push-pull molecules [3,5]. In a push-pull molecule, donor (D) and acceptor (A) groups are connected together via a π conjugated system, here the phenyl ring. The linear and non linear optical properties of these molecules are strongly related to the internal charge transfer between the two groups and to the modification of this transfer between the ground and excited states [3,4,6,7]. Detailed experimental results are available on the electronic and optical properties of these molecules in solution but only few results are available for the molecules in gaseous state [8]. This lack

of experimental results on isolated molecules makes the comparison with theoretical predictions difficult; indeed, the solvent induces modifications in the electronic and optical properties of the molecule, in particular a shift in the optical absorption spectrum. Recently, different approaches have been developed to incorporate solvent effects into the simulation [9-14]. However, concerning the reliability and accuracy, the calculation for molecules in solvent is still less advanced than that in the gaseous phase. In parallel to the improvement of calculations in condensed phase, experimental results in the gaseous phase are needed for a better understanding of the fundamental properties of these molecules. Our experimental method concerns the study and the measurement of the permanent dipole of such type of molecules, which is a direct probe of the structure and of the internal charge transfer in the ground state. In fact, its determination is important to understand the electronic and optical properties of the molecule. In this article, we present the measurement of the permanent electric

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dipole in a gaseous state of a doubly substituted benzene molecule: the para-fluoroaniline molecule abbreviated PFAN ($\text{FC}_6\text{H}_4\text{NH}_2$). Moreover, comparison between gaseous phase and condensed phase measurements may allow a better description of the effects of a solvent on a dipolar push pull molecule. More generally, this measurement provides experimental data to asset the validity of theoretical methods to compute the structure, the geometry and the electronic properties of a π conjugated system. Two different theoretical geometries are compared to experimental results in this article.

2. Experimental procedure

The apparatus consists of a Matrix Assisted Laser Desorption source (MALD) coupled to an electric beam deflection setup and a position sensitive time of flight mass spectrometer. PFAN (or $\text{FC}_6\text{H}_4\text{NH}_2$) is purchased from SIGMA-Aldrich (purity > 99%) and mixed with cellulose in a (1:10) mass ratio. The sample is pressed under 10^4 bar in a cylindrical mould to form a solid rod. The rod is placed into the source where the molecules are desorbed from the cellulose matrix with the third harmonic of a Nd^{3+} : YAG laser (355 nm). The molecules are entrained out by a helium flush supplied by a pulsed valve that is synchronized with the desorption laser shot. At the exit of the source, the molecules were thermalized in a 5 cm long and 3 mm diameter chamber maintained at room temperature. A thermal molecular beam was produced without supersonic expansion.

The beam is collimated by two skimmers and two slits. Its velocity is selected and measured with a mechanical chopper located in front of the first slit. Then, it travels through a 15 cm long electric deflector. The deflecting field is produced using a “two-wire” field. Both the electric field F and the field gradient $\partial F/\partial z$ are perpendicular to the axis of the beam and are nearly constant over its width [15].

In the deflector, a molecule with an electric dipole moment μ is submitted to an instantaneous force along the Z axis (Z is the direction of the electric field and of its gradient), Eq. 1:

$$f = \vec{m} \partial \vec{F} / \partial Z \quad (1)$$

A deflection is produced which is proportional to the time-averaged value ($\langle \mu z \rangle$) in the deflector of the projection on the Z axis of the dipole. At 1.025 m after the deflector, the molecules are two-photon ionized with the fourth harmonic of a Nd^{3+} : YAG (266 nm) and the mass is selected with a time of flight mass spectrometer. We use a position sensitive detector coupled to the spectrometer

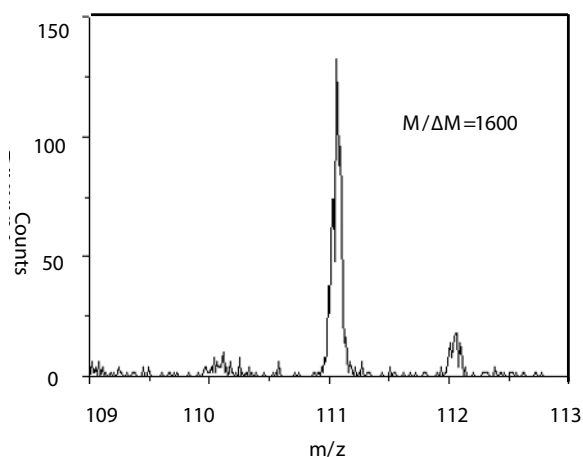


Figure 1. Mass spectrum of PFAN molecules recorded with a photoionization energy of 4.66 eV (266 nm).

for analyzing the beam profiles [16]. Those profiles are then measured as a function of the electric field.

3. Results and discussion

A mass spectrum of PFAN ($\text{FC}_6\text{H}_4\text{NH}_2$) was recorded at room temperature (Fig. 1) which confirms the presence of the molecule in the beam. The dominant peak is observed at the parent mass near 111 and is attributed to the PFAN molecule. The small peak observed at mass near 112 is due to the isotopic distribution.

After selecting the PFAN molecule, our detector allows us to obtain a two dimension image of its beam. Fig. 2 shows the images and the profiles of the beam recorded for PFAN molecule respectively without electric field in the deflector (0 KV) and with electric field (20 KV) where $F = 8.8 \times 10^6 \text{ V m}^{-1}$ (here the 0 and the 4 KV are the potential differences across the deflector). The profile of the beam measured with the electric field is symmetrically broadened and its intensity on the beam axis decreases.

Similar profiles with a regular increase in the broadening are observed as the electric field is increased from 0 to $1.2 \times 10^7 \text{ V m}^{-1}$. To determine the experimental value of the dipole one need to simulate the rotational motion of the molecule in the electric field.

3.1. Structure Calculation

To obtain the most stable structure having the lowest energy, we have used for the parafluoroaniline molecule the MP2 method [17]. This calculation was done by considering two models (two structures): planar and non-planar. In the planar model the nitrogen atom belongs to the fluoro-benzene plane. In the non-planar model the nitrogen atom is out of fluoro-benzene plane

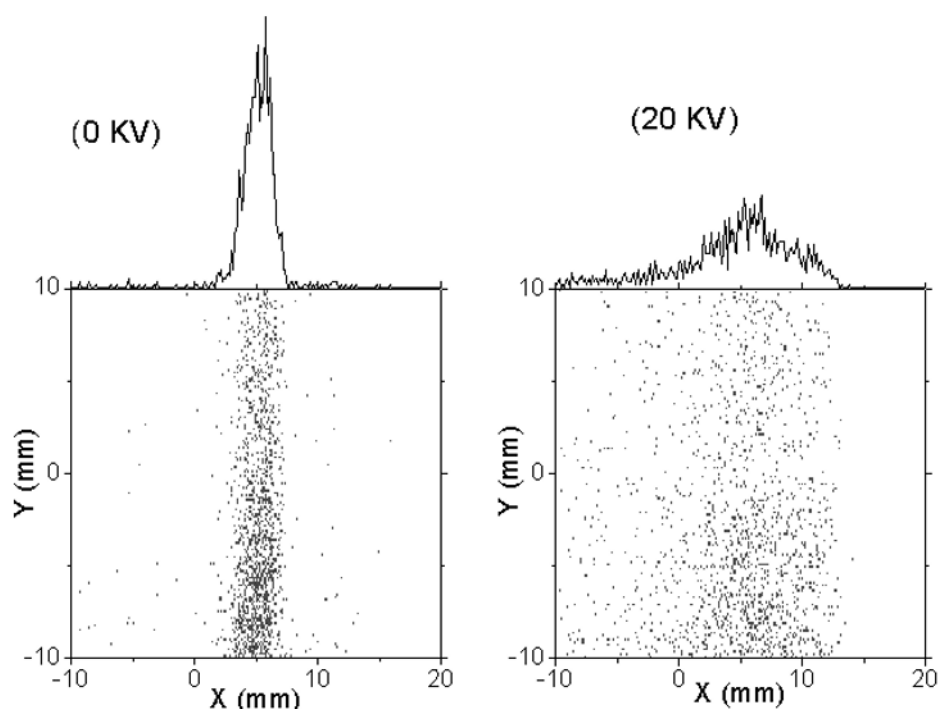


Figure 2. Experimental beam profiles and images obtained respectively for $F = 0$ (0 KV) and $F = 8.8 \times 10^6 \text{ V m}^{-1}$ (20 KV) recorded by the sensitive detector.

Table 1. Relative energies, rotational constants, and calculated electric dipole of PFAN in planar and non planar geometries obtained at MP2 level of theory, basis set 6-311++G**. The calculations were performed with Gaussian 98.

	Energy (Hartree)	Rotational constants (cm^{-1})			Dipole components (Debye)			
		A	B	C	μ_a	μ_b	μ_c	μ_{total}
PFAN PLANAR MP2	-385.888509	0.1862	0.04800	0.03817	3.34	0.00	0.00	3.34
PFAN NON PLANAR MP2	-385.8925274	0.1858	0.04802	0.03820	2.60	0.00	1.14	2.83

(Fig. 3, Table 1). Both structures have a plane of symmetry perpendicular to the ring containing the two substituted carbon atoms, the fluorine, and the nitrogen. They have also quite the same rotational constants but the main difference between them is in the electric dipole components. The dipole moment of the planar structure have only one component ($\mu_a \neq 0$) due to the symmetry. Concerning the non-planar one the charge transfer between the amine group and the fluorine leads to a non zero dipole moment along c-axis due to the out of plane position of the polar nitrogen atom, therefore μ_c is found to be now different that zero.

3.2. Calculation for deflection profiles

It is known that a molecule having J_a , J_b , and J_c as components of the angular momentum and A , B , and C as rotational constants, has in the presence of an electric field, an Hamiltonian H :

$$H = H_{\text{rot}} + H_{\text{Stark}} = AJ_a^2 + BJ_b^2 + CJ_c^2 - F_z \sum_{g=a,b,c} \mu_g \theta_{zg} \quad (2)$$

This is valid after neglecting the small effect of the polarizability. The direction of the applied electric field is considered to be Z, μ_g represents the dipole moment components along the principal axes. the direction cosine θ_{zg} is considered between the various molecular axes and Z.

The deflection profiles are obtained by numerical calculation as following. First of all the Hamiltonian matrix in a convenient eigenvectors basis needs to be diagonalized, for that the rotational constants and dipole components obtained from MP2 structure calculation are used [17].

The energies obtained (eigenvalues) from diagonalization are used in order to determine the average force acting on molecules. In fact the force can be considered as the derivative of the energy with respect

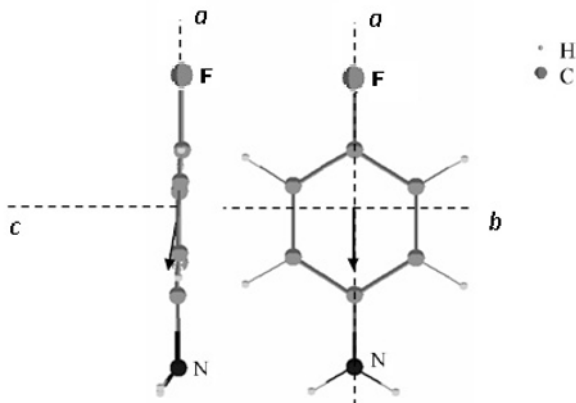


Figure 3. Geometry diagram for the PFAN non-planar model, showing the three principal axes (*a*, *b* and *c*).

to the electric field (force derived from a potential). Supposing that the beam is thermal and molecules enter the electric zone in an adiabatic process, the calculated-simulated profiles show a symmetric broadening of the molecular beam.

Quantitatively the broadening can be measured and considered as the relative beam intensity, which decreases when the electric field increases. The simulated broadening or relative intensities for the each of the above structures (planar and non-planar) are compared to the ones obtained from the experiment (detected profiles) (Fig. 4).

Fig. 4 shows clearly a divergence between planar and non-planar behavior. This divergence increases with the electric field. For high electric field, this divergence becomes more significant. Such result is expected since the two structures have two different dipole components mainly in the *c* direction. It is also quite normal that the non-planar molecular beam presents a stronger broadening than the planar one since it has the highest dipole moment. In the other hand the experimental broadening is very close to the simulated planar one.

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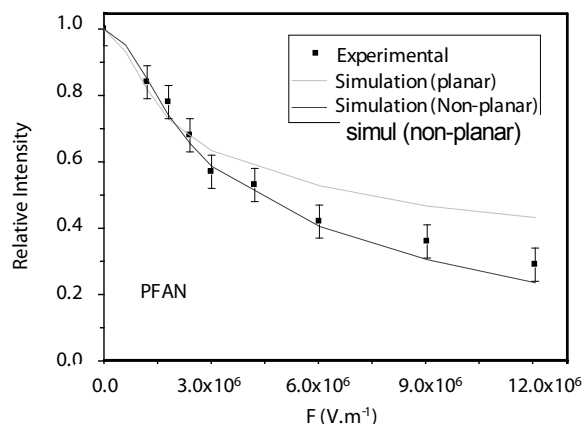


Figure 4. Relative intensity of the beam profile on the beam axis as a function of the electric field *F* for PFAN molecules. Squares correspond to experimental data and the lines to the rigid rotors quantum simulations performed using dipole values and rotational constants for planar and non-planar structures (see Table 1).

Therefore our experiment can ensure a discrimination between the possible molecular structures and allow us to determine the right one, even that the precision of our experimental beam broadening measurement (therefore the precision of the measured dipole) is about 15% [16].

4. Conclusions

In conclusion, we have measured the value of the permanent electric dipole of the PFAN molecule on its principal axis. This value leads to the correct structure of the molecule in its fundamental state and gives a reference to test the accuracy of theoretical methods to predict the structure of simple π conjugated systems. Otherwise stated, the method of electric deflection used in this work allows the probe of molecular structure in gaseous phase.

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