3036 *J. Phys. Chem. A* **2003,** *107,* 3036−3039

Permanent Electric Dipole of Gas-Phase *p*-Amino Benzoic Acid

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Received: October 17, 2002; In Final Form: February 13, 2003

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 *p*-amino benzoic acid (PABA) molecule in the ground state along its principal axis. This is the first measurement of the electric dipole of an isolated push−pull molecule. The experimental value is compared to different calculations, and the accuracy of Hartree−Fock and density functional approaches to predict the electronic properties of π-conjugated systems is discussed.

Introduction

Experimental and theoretical interests in π-conjugated molecules have 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 as an important model for conjugated systems, in particular for dipolar push−pull molecules.[3,5] In a push−pull molecule, a donor (D) and an 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 very few results are available on gas-phase molecules. This lack of experimental results for isolated molecules makes difficult the comparison with theoretical predictions. 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 (see, for example, references 8−13). However, the calculation for molecules in a solvent is still less advanced with respect to accuracy and reliability than that in the gas phase. In parallel to the improvement of calculations in the condensed phase, experimental results in the gas phase are needed for a better understanding of the fundamental properties of these molecules. In this article, we present the first measurement of the permanent electric dipole of a gas-phase doubly substituted benzene molecule: the *p*-amino benzoic acid molecule (PABA). The permanent dipole is a direct probe of the internal charge transfer in the ground state and its determination is important to understand the electronic and optical properties of the molecule. Moreover, comparison between gas-phase and condensed-phase measurements may allow a better description of the effects of a solvent on a dipolar push−pull molecule. More generally, electric dipole measurements may provide experimental data to assess the validity of theoretical methods to compute the electronic properties of a π-conjugated system. Different calculations are compared to experimental results in the last part of this article.

Experimental Section

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.[14] PABA is purchased from SIGMA (purity > 99%) and mixed with cellulose in a 1:10 mass ratio. The sample is pressed under 10^4 bars in a cylindrical mold 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. The molecules leave the source through a 5 cm long nozzle in which the temperature can be adjusted. Otherwise stated, all the experiments described in this article were performed at room temperature.

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. 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]

One meter after the deflector, the molecules are two-photon ionized with the fourth harmonic of a Nd^{3+}:YAG (266 nm) and mass-selected with a time-of-flight mass spectrometer. We use a position-sensitive time-of-flight.[16] The profile of the beam in the ionization region is determined from the arrival time distribution at the detector. The beam profile is measured as a function of the electric field in the deflector.

Results

Figure 1 shows a mass spectrum of PABA recorded at room temperature. The dominant peak is observed at the parent mass 137 and is attributed to the PABA molecule. The small peak observed at mass 138 is due to the isotopic distribution. The source conditions were adjusted in order that no dimer was produced. Small fragmentation peaks are also observed at mass 120 and mass 93. They correspond to OH and COO losses occurring during the two-photon ionization process. The gas-phase PABA molecule was first studied by G. Meijer and

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10.1021/jp022247j CCC: $25.00

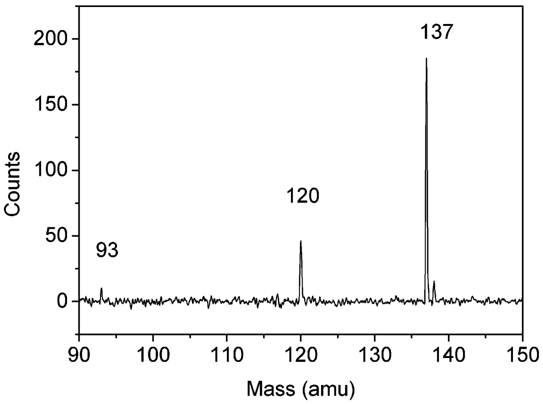

Figure 1. Mass spectrum of PABA molecules recorded with a photoionization energy of 4.66 eV (266 nm). The signal obtained with the source off has been subtracted.

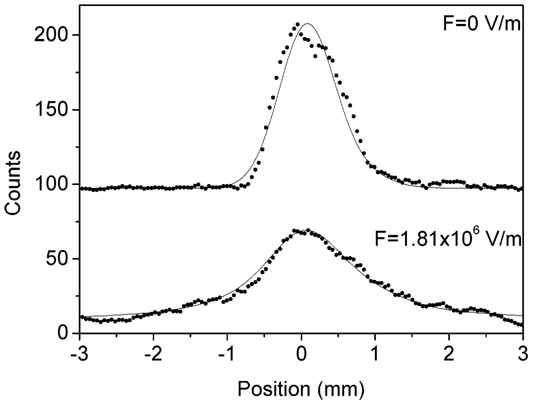

Figure 2. Experimental (circles) and simulated (full line) profiles of the molecular beam with $F = 0$ and $F = 1.81 \times 10^6$ V/m in the electric deflector (the two profiles are offset for clarity). $\mu_a = 2.79$ D, $A = 0.13$ cm^{-1}, $B = C = 0.024$ cm^{-1} were used for the simulation.

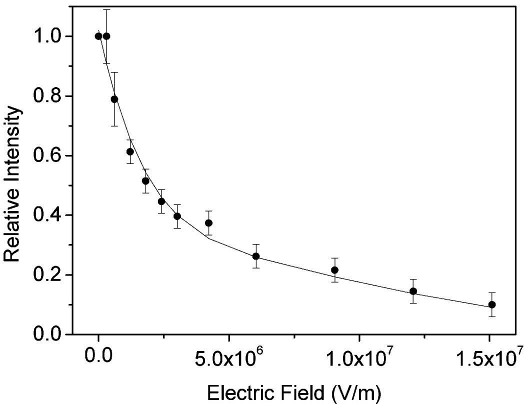

Figure 3. Relative intensity of the beam profile on the beam axis as a function of the electric field in the deflector. The circles correspond to experimental data and the line to the simulation. $\mu_a = 2.79$ D, $A = 0.13$ cm^{-1}, $B = C = 0.024$ cm^{-1} were used for the simulation.

M. S. de Vries et al. in 1990.[17] Similar mass spectra were obtained, except that they observed the loss of COOH instead of COO (the molecules were ionized with a different wavelength).

Figure 2 shows the profiles of the beam recorded for PABA molecule (mass channel 137) with $F = 1.81 \times 10^6$ V/m and without electric field in 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 1.5×10^7 V/m. Figure 3 shows the evolution of the normalized intensity on the beam axis as a function of the field in the deflector. The diminution of the intensity on the axis reflects the increase in the broadening due to the interaction with the electric field.

In the deflector, the force due to the interaction between the electric field F_z and the permanent dipole μ of the molecule can be written as

$$f = \langle \mu_z \rangle \frac{\partial F_z}{\partial z} = \langle \mu_a \cos(az) + \mu_b \cos(bz) + \mu_c \cos(cz) \rangle \frac{\partial F_z}{\partial z} \quad (1)$$

where μ_a, μ_b, *and* μ_c are the components of the permanent dipole of the molecule along the three principal axes of the molecule, and cos(*az*), cos(*bz*), and cos(*cz*) represent the cosines of the angles between the principal axes of the molecule and the axis of the electric field. For a molecule of mass m and of velocity v, the deviation d induced by this force is

$$d = K \frac{f}{mv^2} \quad (2)$$

where K is a geometrical constant. Its value was determined by calibration with the polarizability of the sodium atom for which the value is known with a high accuracy from interferometry measurements.[18] The average force depends on the rotational level and Stark levels of the molecule, which explains the broadening of the beam that is experimentally observed.

To determine the experimental value of the dipole one needs to simulate the rotational motion of the molecule in the electric field. The rotational constants obtained from ab initio calculation are $A = 0.13$ cm^{-1}, $B = 0.026$ cm^{-1}, $C = 0.022$ cm^{-1} (every calculation described in the following section leads to the same values). The PABA molecule is very slightly asymmetric and it was approximated by a symmetric top rotor with $A = 0.13$ cm^{-1} and $B = C = 0.024$ cm^{-1}. The force in the deflector was obtained by a classical calculation of the rotational motion of the symmetric rotor in the electric field.[19] The final beam profile is obtained by taking into account every possible initial rotational motion with a Boltzmann weight factor.[19] Within the symmetric top approximation, the force on the molecule depends only on the value of the dipole moment along the principal axis of the molecule (μ_a). The value of μ_a was adjusted on the experimental results plotted in Figure 3. A least-squares fit leads to $\mu_a = 2.8 \pm 0.2$ D. A very good agreement between the calculated and experimental profiles is observed for every value of the electric field in the deflector (see Figures 2 and 3). Similar experiments were performed at liquid nitrogen temperature. The results are within the error bars.

To confirm the validity of the symmetric rotor approximation we have compared, for low electric field values, the results of this calculation to results of quantum calculation performed for the asymmetric rotor. The force on a molecule was determined by an exact calculation of the rotational levels and a perturbation calculation of the effect of the electric field.[20] First, the Hamiltonian of the asymmetric rotor, without electric field, is diagonalized to determine the rotational levels of the molecule. The molecule is slightly asymmetric and the splitting between K_+ and K_- states is small. The effect of the electric field is calculated in two steps. An exact calculation of the interaction induced by the electric field between nearby levels is obtained by diagonalization of 2×2 matrixes.[21] Then, the force is computed with the resulting wave functions (first-order or second-order perturbation theory). $A = 0.13$ cm^{-1}, $B = 0.026$ cm^{-1}, $C = 0.022$ cm^{-1}, $\mu_a = 2.79$ D, $\mu_b = -1.22$ D, and $\mu_c =$

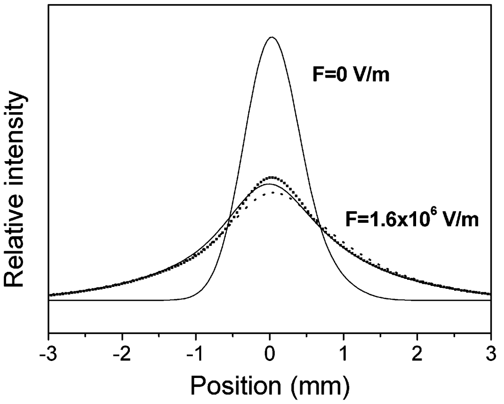

Figure 4. Comparison of beam profiles obtained for the asymmetric top rotor (**...** first-order perturbation theory, - - - second-order perturbation theory) and the approximate symmetric top rotor (—) (see text for details). Only the sublevels of the rotational level $J = 50$ have been included in the simulations.

TABLE 1: Relative Energies and Calculated Electric Dipole of the PABA Molecule Obtained at Different Levels of Theory

method	basis set	energy (Hartree)	dipole components (Debye) μ_a	μ_b	μ_c	total
HF	6-31G*	−473.3569	3.11	−1.52	1.14	3.64
HF	6-311++G**	−473.7875	3.23	−1.57	0.97	3.72
MP2	6-31G*	−475.7500	2.79	−1.22	1.25	3.29
DFT/B3LYP	6-31G*	−476.1790	3.54	−1.34	1.00	3.91
DFT/B3LYP	6-311++G**	−476.3286	3.82	−1.39	0.80	4.14
DFT/BPW91	6-311++G**	−476.2765	4.04	−1.34	0.79	4.33
experiment			2.8 ± 0.2			

1.25 D were used for the quantum simulations. Profiles obtained with the classical calculation (symmetric top rotor), the quantum calculation with first-order corrections (asymmetric top rotor), and the quantum calculation with second-order corrections (asymmetric top rotor) are shown in Figure 4 (only the sublevels of the rotational level $J = 50$ have been included in these simulations). The different profiles are similar: this shows that the asymmetry of the molecule does not modify significantly the effect of the electric field. For high electric field, the perturbative approach is no longer valid for this molecule and the quantum calculation cannot be used.

Discussion and Conclusion

Vaschetto et al. have performed a systematic theoretical study of substituted anilines with different DFT methods.[22] For PABA molecules they obtained a non planar geometry (NH_2 out of the benzene ring plane) with a total dipole of 3.92 D. The authors outlined that the B3LYP-DFT/6-31G* level of theory leads to accurate structural properties but that electronic properties are more difficult to predict. In Table 1, we compare the results of calculations obtained at different levels of theory to the experimental value. All the calculations were performed with Gaussian 98.[23] Hartree−Fock, Hartree−Fock with second-order Møller−Plesset corrections, and hybrid density functional theory calculations (B3LYP[24,25] and BPW91[26,27]) were performed with two different basis sets 6-31G* and 6-311++G**. A full geometry optimization was performed at every level of theory. The geometry and the direction of the dipole obtained at the MP2/6-31G* level of theory are shown in Figure 5. The phenyl ring and the acid function are in the same plane, the NH_2 group is out of the plane. This geometry is very similar to the geometry obtained by Vaschetto et al. and was obtained with every calculation described in this article. Table 1 shows that, even with hybrid functionals, DFT calculations significantly overestimate the value of the permanent electric dipole and should be used cautiously to predict the electronic properties of conjugated systems. HF calculations also lead to values that are slightly too high ($\mu_a = 3.23$ D with the large basis set). The introduction of correlation with the second-order Møller−Plesset corrections reduces the calculated values and leads to a value in agreement with the experiment. We were not able to perform MP2 calculations with the 6-311++G** basis set, but comparison of the HF results with the two basis sets suggests that the addition of diffuse functions would only slightly increase the calculated values.

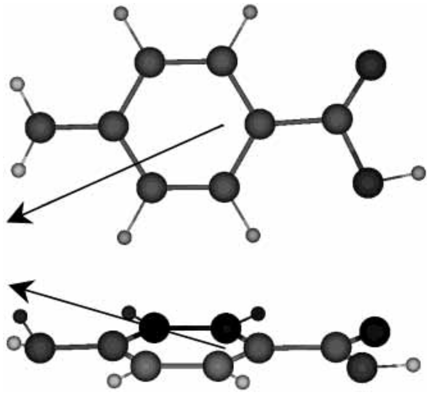

Figure 5. Geometry of the lowest energy conformation found at the MP2 6-31G* level of theory. The arrows show the direction of the electric dipole.

In conclusion, we have measured the value of the permanent electric dipole of the PABA molecule on its principal axis. This is the first measurement of the permanent electric dipole of a disubstituted benzene. This value gives a reference to test the accuracy of theoretical methods to predict the electronic properties of simple π -conjugated systems. More experiments are clearly needed to conclude on the validity of theoretical methods.

Acknowledgment. Experiments on PABA molecules were inspired by stimulating discussions with R. R. Hudgins.

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