Vibration Induced Electric Dipole in a Weakly Bound Molecular Complex

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A strong electric susceptibility is measured as a function of temperature in a molecular dimer which is weakly bound by a pair of hydrogen bonds. This system is a remarkable example where the dominant term in the susceptibility is due to a vibration induced electric dipole. As a consequence, the averaged square of the dipole moment varies linearly with the temperature and the susceptibility does not follow the usual $1/T$ Curie law. this spectacular effect demonstrates the importance of dynamics to interpret the properties of weakly bound complexes.

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Charge transfers govern the structure and reaction mechanisms of large molecules. They are also crucial for the formation of weakly bound complexes [1,2]. For example, the hydrogen bond plays a key role in a large field of physical chemistry, including biomolecules. The measurement of electric dipole is an efficient method to probe these charge transfers in a given molecular system and has been successfully used to study dipole properties of molecules and atomic clusters through microwave spectroscopy [3] or electric beam deflection measurements [4–6]. Beyond single molecule studies, electric dipole measurements can give precise information on the electric properties or on the arrangement of molecules in supramolecular complexes. In the gas phase, an electron interacting with a molecular cluster which possesses a large dipole moment may bind to the cluster to form a dipolar anion. Rydberg electron transfer spectroscopy and photoelectron spectroscopy have allowed people to study such species and to identify their geometry [2]. In this Letter, we report the first electric deflection measurement on a weakly bound molecular complex: the para-amino-benzoic-acid dimer (PABA dimer). The PABA molecule has a strong permanent dipole moment ($\sim$ 3.9 D [7]) but the dimer has a symmetrical structure, which is bound by a pair of hydrogen bonds [8], and the two dipoles cancel each other at equilibrium. A specificity of weakly bound complexes is that they can undergo large deformations. Because of the vibrational motion, the average of the square of the dipole moment is non-null, which leads to a high electric susceptibility. This is the first observation of a vibration induced dipole moment in a gas phase molecular complex. This spectacular effect was predicted [9], but to our knowledge never observed for an isolated system yet. The results are interpreted by a simple and general model in the framework of linear response theory. It constitutes a nice and original example of a system with an electric susceptibility that does not follow the well-known Curie law. Finally, the observed susceptibility as a function of the temperature is quantitatively interpreted by Monte Carlo simulations, which probe the deformation of the complex with temperature and the charge repartition in the complex.

The experimental setup is shown in Fig. 1. It consists of a matrix assisted laser desorption source coupled to an electric beam deflector setup [5,6,10]. PABA and cellulose were mixed in a 1:10 mass ratio and pressed to form a rod. The PABA molecules are desorbed in the source by the third harmonic of a Nd^{3+}:YAG laser (355 nm) into a pulsed helium flow. At the exit of the source, the molecules are thermalized in a 5 cm long nozzle that can be heated by thermocoax wires or cooled by liquid nitrogen. The molecular beam is collimated by two rectangular slits and then it travels through a 15 cm long electric deflector with a "two wires" electric field configuration. The electric field F and the field gradient $\frac{\partial F}{\partial z}$ are perpendicular to the beam axis (the direction of the field defines the z axis). One meter after the deflector, the molecules are ionized with the fourth harmonic of a second Nd^{3+}:YAG laser (266 nm) in the extraction region of a position sensitive time of flight mass spectrometer [5]. The pulse width of the laser is 6 ns and its fluence $\sim$3 $\mathrm{mJ/cm^2}$. The ionization potential of the PABA molecule is equal to 8.0 eV and the ionization potential of the dimer is slightly below 7.9 eV [8]. Two photons are needed to ionize the PABA molecule and the PABA_2 complex (resonant two photon ionization process [8]). Measurements of the molecular beam profile in the extraction

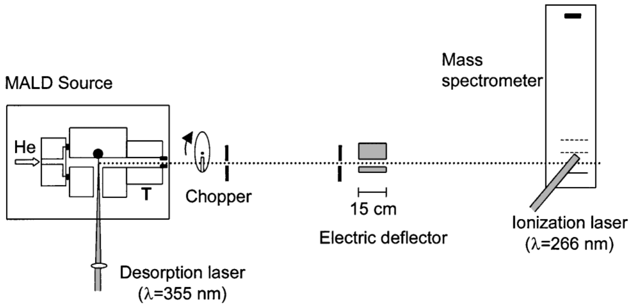

FIG. 1. Schematic of the apparatus.

region of the time of flight are performed as a function of the electric field in the deflector. The beam velocity was determined with a mechanical chopper. At 300 K, the beam velocity is 720 ms^{-1}, which corresponds to a transit time in the deflection region of 208 μs.

The most intense peak in the mass spectrum corresponds to the PABA molecule. By adjusting the helium pressure in the source and the delay between the helium pulse and the vaporization laser pulse, it is possible to produce PABA dimers with a high efficiency. With the right source conditions, the count on the dimer channel is of the same order of magnitude as the count on the monomer channel. Some fragmentation is observed in the mass spectrum, in particular, part of the signal recorded on the monomer channel is due to the dissociation of the complex. Profiles of the beam were measured on the PABA dimer mass channel as a function of the electric field in the deflector. Figure 2 shows profiles measured with and without an electric field in the deflector. The electric field induces a global shift of the beam toward the high electric field region. The deviation d of the beam was measured as a function of the value of the electric field in the deflector. The deviation is proportional to the square of the applied field (inset of Fig. 2). It is related to the electric susceptibility of the molecule by

$$d = \frac{K}{mv^2}\langle\mu_z\rangle\frac{\partial F}{\partial z}, \tag{1}$$

and

$$\langle\mu_z\rangle = \chi F, \tag{2}$$

where K is a geometrical factor, m is the mass of the molecule, and v is its velocity. The experiment was calibrated on the sodium atom whose polarizability is known with a high accuracy from atomic interferometry [11]. The experimental susceptibility χ is determined from a linear fit of the deviations measured as a function of the square of the electric field in the deflector using Eqs. (1) and (2). The results obtained at different values of the nozzle temperature are reported in Fig. 3. The susceptibility is in the range of 100 Å^3. It is almost constant with temperature. While it cannot be attributed to pure electronic polarizability (see below), this behavior is different from the usual $1/T$ Curie law expected for polar molecules [12–14]. It is, in particular, different from what we have recently observed for the KC_{60} molecule in a similar experiment [15]. In this latter case, the usual $1/T$ law was observed.

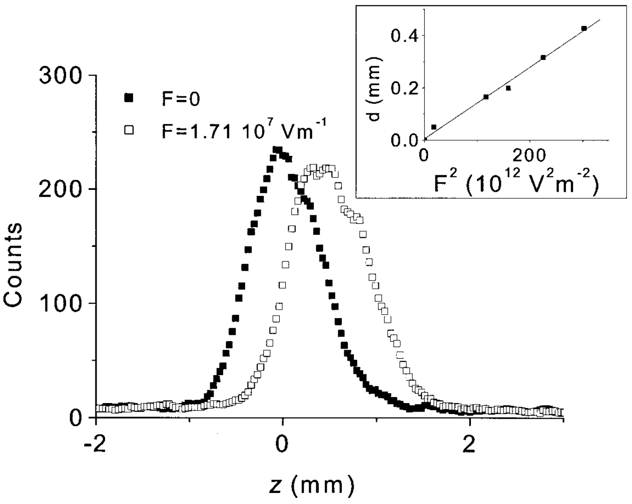

FIG. 2. Profiles of the beam measured for the PABA dimer at room temperature with $F = 0$ and $F = 1.71 \times 10^7\ \mathrm{V\,m^{-1}}$ in the deflector. With the electric field on, the beam is shifted toward the positive z direction. The inset displays the shift d of the beam as a function of the square of the electric field. The line is a linear fit of the experimental values.

Paraelectric or paramagnetic susceptibility of atomic or molecular systems independent of the temperature is known as Van Vleck susceptibility and is associated with systems that have no dipole moment in their ground state [14]. The Van Vleck susceptibility is due to couplings with excited states induced by magnetic or electric fields [14]. The equilibrium structure of the PABA dimer as determined by resonance enhanced multiphoton ionization [8] is shown in Fig. 4(b). The two molecules are held together by a pair of hydrogen bonds between the two carboxyl groups (an estimation of the binding energy of the complex at the HF/6-31G* level of theory leads to 0.5 eV). The structure is symmetrical and has no permanent dipole at equilibrium. Here, the susceptibility is due to couplings between vibrational states: the vibration of the molecule modifies its permanent dipole. A model of independent harmonic oscillators allows one to discuss the physical reasons for the effect that is reported in this Letter. This model is described below and is completed at the end of the article by molecular mechanics simulations.

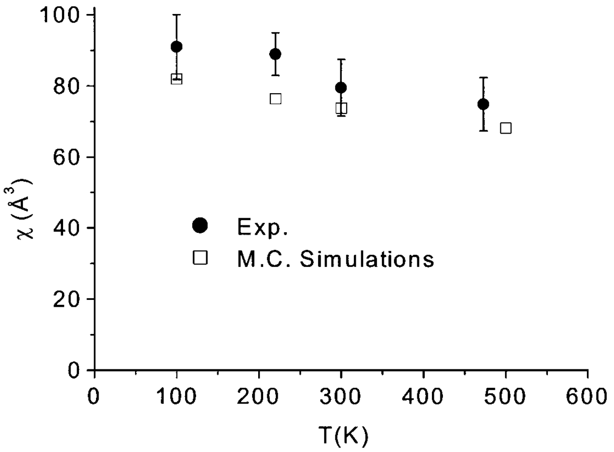

FIG. 3. Experimental and calculated susceptibilities for the PABA dimer plotted as a function of the temperature.

The classical linear susceptibility per molecule is given by the Langevin-Debye formula [12,13,16]:

$$\chi = \frac{\langle \mu^2 \rangle_T}{3kT} + \alpha_e, \tag{3}$$

where $\langle \mu^2 \rangle_T$ is the average value of the fluctuation of the dipole at equilibrium at temperature T (without the electric field) and α_e is the static electronic polarizability of the complex. We have assumed that the probability of having a given conformation is determined by a Boltzmann distribution. The temperature T is equal to the nozzle temperature. The average electronic polarizability of the complex, calculated at the HF/3-21G* level of theory, is 22 Å^3. Its contribution to the susceptibility is small. The main contribution is coming from the fluctuations of the permanent dipole. To evaluate the first term on the right-hand side of Eq. (3), we expand the dipole on the 96 normal coordinates Q_i of the complex:

$$\mu = \sum_i \left(\frac{\partial \mu}{\partial Q_i} \right)_0 Q_i + \ldots \tag{4}$$

(μ is equal to zero at equilibrium). For independent harmonic oscillators, the average value of the square of the dipole is

$$\begin{aligned} \langle \mu^2 \rangle_T &= \sum_{i,j} \left(\frac{\partial \mu}{\partial Q_i} \right)_0 \left(\frac{\partial \mu}{\partial Q_j} \right)_0 \langle Q_i Q_j \rangle_T + \ldots \\ &= \sum_i \left(\frac{\partial \mu}{\partial Q_i} \right)_0^2 \langle Q_i^2 \rangle_T + \ldots . \end{aligned} \tag{5}$$

For each normal coordinate, $\langle Q_i^2 \rangle_T$ is proportional to T, and then $\langle \mu^2 \rangle_T$ is proportional to T. The evolution of the average value of $\langle \mu^2 \rangle_T$ with the temperature cancels with the $1/T$ term in Eq. (3). This very simple model predicts a susceptibility that is independent of the temperature. A different behavior would be observed if the dipole at equilibrium [term of zero order in Eq. (4)] was not null. In this interpretation, the susceptibility is independent of the temperature, because $\langle \mu^2 \rangle_T$ is roughly proportional to T. This is different from the case discussed by Van Vleck where the susceptibility is independent of the temperature when the energy distances ΔE between the ground state and the excited states are large as compared to kT [14,17]. Corrections to the susceptibility due to the distortion of the molecule have already been observed for simple polar molecules but, in most systems, these distortions induce small corrections to the dipole and the dominant term in the susceptibility remains proportional to $1/T$ [13,18]. Our result corresponds indeed to a new textbook example of susceptibility behavior.

For a quantitative interpretation of the experimental results and a more realistic description of the vibrational motion of the complex, we have estimated the value of $\langle \mu^2 \rangle_T$ with Monte Carlo simulations. The simulations were done using the CHARMM force field as implanted in Hyperchem 7.0 [19] with CHARMM 22 parameters [20]. The atomic charges for the PABA molecule were derived from the electrostatic potential calculated at the MP2/6-31G* level with Gaussian 98 [21] using the RESP model [22]. These charges lead to a dipole value of 3.7 D, close to the theoretical value of Ref. [7]. The equilibrium structure shown in Fig. 4(b) is used as the initial structure for the Monte Carlo simulation. Each Monte Carlo run consisted of 1.2×10^8 steps. During the course of the Monte Carlo simulation, the electric dipole was calculated every 2000 steps (after an initial run of 10 000 steps) using the position of the atoms and their atomic charge ($\vec{\mu} = \sum_i q_i \vec{r}_i$). The simulations were performed at four different temperatures (100, 220, 300, and 500 K). The value $\alpha_e = 22$ Å^3 was used in Eq. (3).

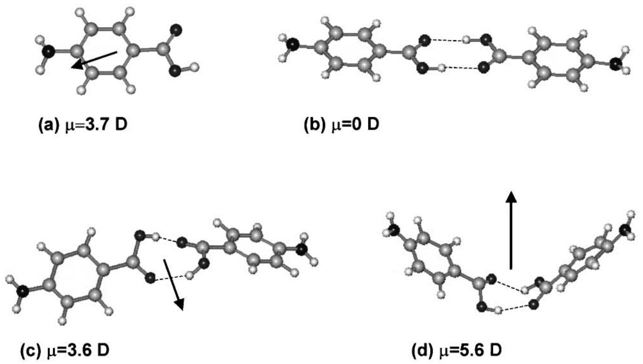
(a) μ=3.7 D
(b) μ=0 D
(c) μ=3.6 D
(d) μ=5.6 D

FIG. 4. (a) Para-amino-benzoic-acid molecule ($NH_2C_6H_4COOH$). (b) Equilibrium structure for the $(PABA)_2$ complex. Hydrogen bonds (between O and H atoms) are indicated by dashed lines. (c) and (d) Examples of structures found during the course of the Monte Carlo simulations that have a large dipole. The value of the electric dipole moment obtained from $\vec{\mu} = \sum_i q_i \vec{r}_i$ is specified for each structure. The arrows show the direction of the dipole.

Figure 5 displays the results of the Monte Carlo simulations. $\langle \mu^2 \rangle_T$ is in first approximation proportional to the temperature, which is in agreement with the prediction of the simple model of independent harmonic oscillators. However, the Monte Carlo simulation leads to a behavior that is more complicated than a simple linear increase. This probably reflects anharmonicities and couplings between the different modes. Results for the susceptibility are compared to experimental values in Fig. 3. These simulations provide the right order of magnitude for the electric susceptibility and the simulations reproduce the slight decrease in χ as the temperature increases. The agreement suggests that these simulations provide a good sampling of the conformations that are explored at a given temperature. The large susceptibility is due to the fact that the complex explores conformations in which the two dipoles do not cancel each other. Figure 4 shows examples of such conformations that were found during the course of the Monte Carlo run at 500 K. In this figure, the most visual deformations of the complex are due

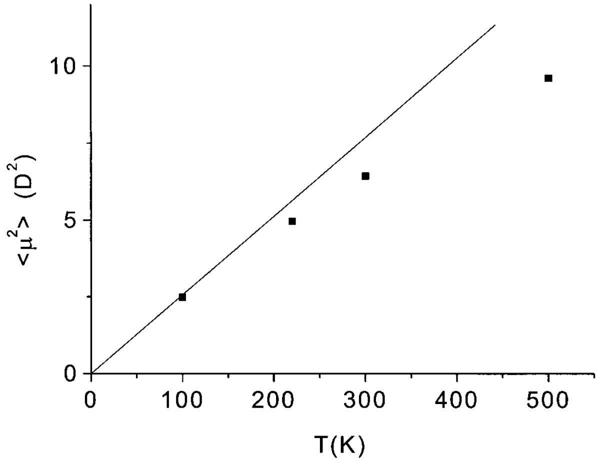

FIG. 5. Results of the Monte Carlo simulations performed for the PABA dimer complex as a function of the temperature. The line is a guide for the eyes.

to the bending and twisting of the two hydrogen bonds that connect the two molecules. These deformations correspond to low frequency modes of vibration (the HF/3-21G* calculation leads to an estimation of 18 cm^{-1} and 42 cm^{-1} for these two modes of vibration), which are populated even at 100 K. Two polar rigid subsystems in interaction are a good picture to illustrate this complex.

In conclusion, we have measured the electric susceptibility of isolated PABA dimer complexes over a large range of temperature. This is the first report of the susceptibility of a weakly bound complex in the gas phase. The results confirm that the dimer adopts a symmetrical structure with no permanent dipole. The susceptibility is mainly due to vibrational contributions. Dynamics has to be taken into account to explain the response of the complex to a static electric field. Generally, the effect of dynamics on $\chi(0)$ is negligible or adds small corrections to the value calculated at equilibrium [13,18]. An exception was observed in films with large values associated with proton transfers [23]. Here, it is another nice example where the dynamic plays a key role. This is expected to be a general feature of weakly bound complexes in which deformations and motions of large amplitude are possible as compared to covalently bound systems. As shown in this Letter, the flexibility of loose aggregates that are held by weak interactions is important in determining their physical and biochemical properties.

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