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Thermal effects on the electric deflection of toluene molecules

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ABSTRACT

A series of precise electric deflection experiments were done on a supersonic beam of toluene molecules in several expansion conditions and field strengths. We analyzed the effect of a gradual rotational cooling on the evolution of the beam profile by use of the available theories of asymmetric-top dipoles in electric fields. We have recorded from non-broadened (warm) to very broad and asymmetric (cold) profiles, and discussed this effect in terms of the Stark perturbation on the rotational motion.

1. Introduction

The force involved in the interaction of isolated particles with strong electric fields has been widely used over the years to determine the electrical properties of atoms, molecules and clusters [1]. In particular, electric deflection (ED) of highly collimated molecular beams is a well known method where the particles' electric moment can be deduced from the beam deviation and broadening caused by a static inhomogeneous electric field applied perpendicularly to the propagation axis. The procedure consists in using an adequate theoretical model to calculate the beam intensity profile in the direction of the field gradient, and have this simulation to match with the measured profile. If the energy is low enough to disregard vibration, the equations that describe the particles' rotational motion can be written in terms of the rigid body approximation, and the electric force is given by the instantaneous orientation of the particle with respect to the field in the laboratory frame. The rigid body approximation has been successfully applied to molecular beams generated by supersonic expansion [2] as well as to several systems thermalized to room temperature after the expansion [3–5]. Different methods were developed to simulate the beam profile of spherical [6], linear [7–9] and symmetric-top [4,10] (two equal rotational constants) rotors; for lower symmetry molecules, quantum [2,5] and classical [11] theories of asymmetric tops (three unequal rotational constants) were successfully applied.

At room temperature, field-induced symmetrical beam broadening was reported for a polar symmetric-top molecule like TiC_{60} [10] and for polar quasi-symmetric-top molecules like *p*-amino benzoic acid [4] and *p*-aminobenzonitrile [5,12], while very little changes were observed in the beam profile for polar asymmetric-top molecules like *o*-aminobenzonitrile [5] or *m*-dimethylaminobenzonitrile [12]. It was suggested that the lack of broadening is associated with the complex rotational motion of asymmetric tops; this makes the averaged projection of the molecular dipole on the field axis to vanish during the transit time across the deflection electrodes. As a result, the dipole moment of asymmetric molecular objects (most systems of interest) would not be accessible by ED studies on thermalized beams at room temperature. At lower temperatures (85 K), it was found beam broadening in non-symmetrical tryptophane-glycine peptides [3], although the authors attributed this observation exclusively to the flexibility of the molecule and did not consider the interaction of the field with the rotational motion. Recently, a substantial profile broadening was found in a supersonic beam of asymmetric-top water molecules [2], and the effect was attributed to the low rotational temperature (T_r, estimated in 84 K) achieved in the expansion. Under such conditions, low-lying rotational levels having in general the largest Stark-shift variation with the electric field would be more likely populated and consequently, would contribute most to the broadening. Evidently, the effect of temperature will be less significant when the molecules have smaller rotational constants and weak permanent dipoles; in such cases, lower values of T_r would be necessary to notice changes in the deflection profile.

In this study, we will give experimental evidence on the evolution of the profile of an asymmetric-top molecule when it gradually becomes rotationally-colder. All ED measurements and calculations were done on toluene, which was selected as a model asymmetric-top molecule with low polarity. Our investigation is not oriented to determine the electrical properties of toluene, which are well known [13], but to explore the significance of thermal effects on the orientation of the rotating dipole in the field. In this study, the extent of cooling was qualitatively controlled by varying the expansion conditions. We have recorded from non-broadened (warm) to very broad and asymmetric (cold) profiles that were analyzed using the available theories [5,11].

2. Experimental

A scheme of the apparatus is presented in Fig. 1. The beam of toluene molecules was generated by pulsed supersonic expansion

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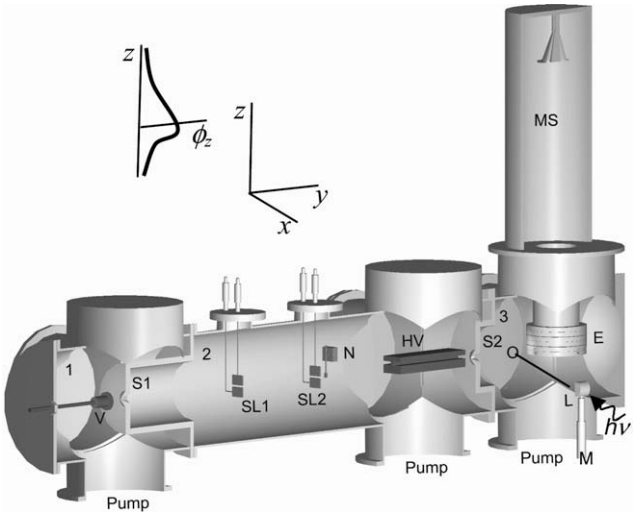

Fig. 1. Scheme of the molecular beam apparatus: differentially-pumped chambers, (1)–(3); solenoid-driven valve, V; skimmers, S1 and S2; collimation slits, SL1 and SL2; rotating beam stopper, N; deflection electrodes, HV; focusing cylindrical lens, L; focus of the ionization laser, O; motor stage for scanning L in the z axis, M; ion extraction plates, E; linear TOF mass spectrometer, MS.

in chamber (1), using helium and neon as carrier gases at pressures in the range of 1.0–3.0 bar. The exit hole of a fast solenoid-driven valve (V) acts as a nozzle of 750 μm in diameter, with a length of 2 mm. The gas pulse has a typical duration of 300 μs; it propagates in the y axis through the differentially-pumped chambers (1)–(3). The beam was collimated to a rectangular z–x section of respectively 200 μm × 2000 μm by use of two externally-controlled slits (SL1) and (SL2), located 1000 mm apart in chamber (2). The deflection electrodes (HV) are situated a few centimeters downstream, being their cross section accurately machined to adopt a 'two wire' [1] field geometry; this ensures a constant z-field-gradient at the beam position. We used electric fields up to $F_z = 13.6$ kV/mm, which corresponds to a field gradient $\nabla_z F = 3.3$ kV/mm^2.

For a molecule of mass m propagating with a speed v_y, the deviation caused by the field along z is given by the equation:

$$d_z = C\frac{\nabla_z F}{m v_y^2}\langle \mu_z \rangle \tag{1}$$

where C is a geometrical constant of the apparatus [1] and $\langle \mu_z \rangle$ represents the time-averaged projection of the molecular dipole moment on the laboratory's z axis. If the contribution of the polarizability to the dipole moment is ignored and the molecule is considered as a rigid rotor (two valid approximations under our experimental conditions) Eq. (1) can be written as

$$d_z = A\mu_0\langle \cos\theta \rangle \tag{2}$$

where $A = C(\nabla_z F/m v_y^2)$, μ_0 is the modulus of the permanent dipole of the molecule, and θ represents the angle between this vector and the laboratory's z axis. The overall beam profile, ϕ_z, is essentially a distribution function of the molecular deviations d_z. The determination of ϕ_z was done at the point (O) located 500 mm downstream from the deflector. The method consists in probing the molecular beam in several steps along the z coordinate. This is done by scanning the z position of a UV laser spot and analyzing the ion yield in a pulsed linear time-of-flight mass spectrometer (MS) operated under Wiley–McLaren conditions. Two 266 nm photons (fourth harmonics of a 1 mJ/pulse nanosecond Nd:YAG laser) were used to reach the ionization threshold of toluene; this photon energy is near a resonant absorption of the molecule [14]. The UV laser was focused on the molecular beam to 100 μm in the z direction by means of a cylindrical lens (L); a precision linear motor stage (M) is employed to drive the lens along z. Toluene molecular ions arrive at the MS some microseconds earlier than the background ions; this allows us to collect very clean mass spectra by adjusting the delay time of the ion extraction pulse. The detection efficiency of our apparatus was found to be independent of the position of the ionization spot within $z = \pm 1.5$ mm from the beam center. In all cases, the expansion conditions were adjusted so as to minimize the presence of toluene clusters in the mass spectrum.

In ED studies, the propagation speed has to be determined precisely. For doing this, we produced a mechanical interruption of about 10 μs in the molecular pulse and then we measured the time elapsed before detecting the corresponding intensity drop in the MS, located 900 mm downstream. Molecular velocities were measured with accuracy better than 2% in the range of 800–1800 m/s, depending on the carrier gas used and on the source conditions. In agreement with previous studies with supersonic beams [15] we

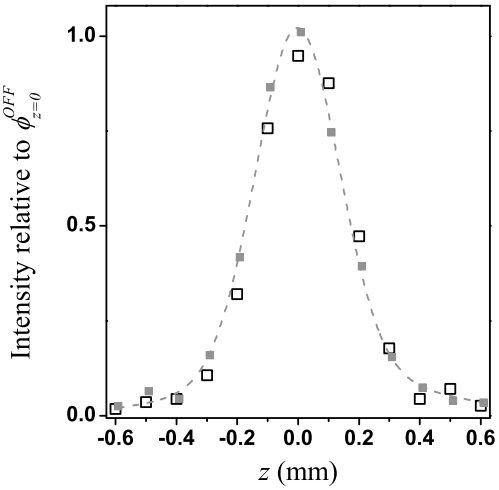

Fig. 2. Intensity profile of rotationally-warm toluene molecules for an electric field strength of $F_z = 6.8$ kV/mm ($\nabla_z F = 1.7$ kV/mm^2), open squares; ϕ_z^{OFF}, solid squares joined by a dashed line to guide the eyes; $v_y = 1520$ m/s; expansion mixture, 1 mol% toluene in helium (1.1 bar).

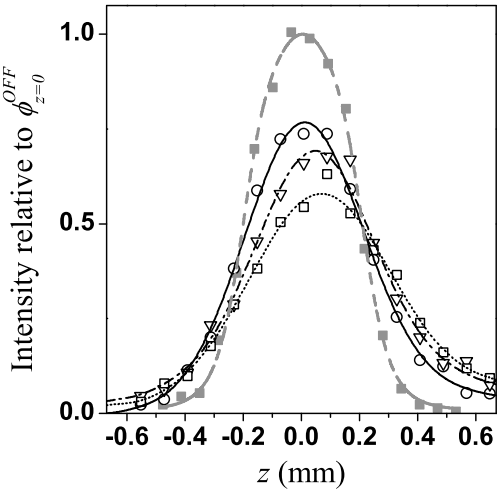

Fig. 3. Intensity profile of rotationally-cold toluene molecules for the following electric field strengths and gradients: $F_z = 6.8$ kV/mm ($\nabla F_z = 1.7$ kV/mm^2), circles; $F_z = 10.2$ kV/mm ($\nabla F_z = 2.5$ kV/mm^2), triangles; $F_z = 13.6$ kV/mm ($\nabla F_z = 3.3$ kV/mm^2), open squares; ϕ_z^{OFF}, solid squares; $v_y = v_y^{\infty}$; expansion mixture, 0.1 mol% toluene in helium (1.1 bar). Lines are drawn to guide the eyes.

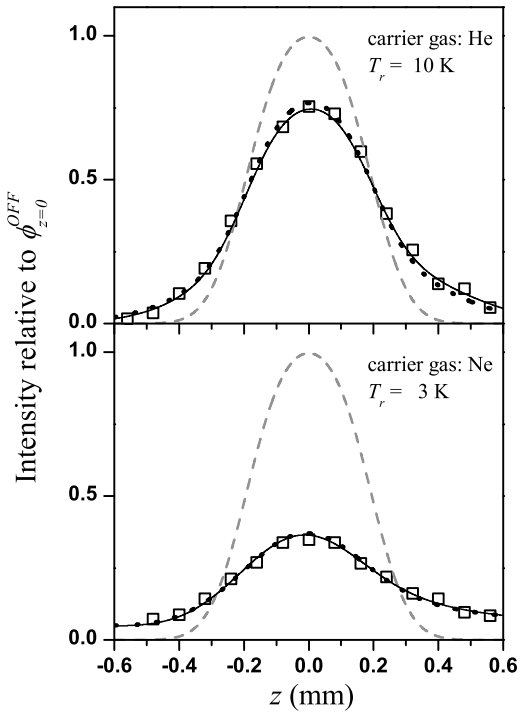

Fig. 4. Experimental profiles of rotationally-cold toluene molecules (squares) and the corresponding classical (full line) and quantum (dotted line) simulations. Field strength, F_z = 6.8 kV/mm ($\nabla F_z = 1.7$ kV/mm^2); T_r values, determined by getting the simulations to match with the experimental results; ϕ_z^{OFF}, dashed line; $v_y = v_y^{\infty}$; expansion mixture, 0.1 mol% toluene in the carrier gas (1.1 bar).

observed, within the accuracy of our method, no velocity spread in the pulse.

The deflection unit and the skimmers were arranged in a line by mechanical adjustment using a telescope positioned collinearly to the y axis. The alignment of each collimation slit is done one at a time by scanning its z position until obtaining a perfectly symmetric field-off profile, ϕ_z^{OFF}, like those indicated as dashed curves in Figs. 2–4.

3. Simulation of intensity profiles

We used two methods. The first one, recently proposed by Dugourd et al. [11] considers an asymmetric top with given dipole and rotational constants, and simulates the particle's motion in presence of the electric field. We simulated about 20 000 trajectories having different initial molecular orientations and Boltzmann-weighed rotational energies, which were randomly distributed among the components of the angular velocity. In this method, the dipole orientation is calculated as $\cos\theta$ and averaged within each trajectory; when all trajectories are taken into account, it is possible to obtain a histogram of deviations, $\{d_z\}$, using the scaling factor $A\mu_0$ of Eq. (2). Finally, the profile ϕ_z is computed by convolution of $\{d_z\}$ with a function representing the field-off profile; this function was obtained by fitting the experimental field-off profile ϕ_z^{OFF}. We have repeated the whole procedure for different values of T_r to get the best fit between simulation and the experimental results. This procedure is frequently used [2,6] to estimate the value of T_r in a supersonic expansion.

A second approach [5] considers the electric field dependence of the energy of a quantum state i, $\varepsilon_i(F_z)$; it can be calculated by numerical diagonalization of truncated Stark + rotational Hamiltonians that are written on the $|JKM\rangle$ basis of the eigenvectors of the prolate symmetric rotor, using a sufficiently large number of states (J = 50). The z-deviation of a molecule in this state is calculated using the expression $d_{zi} = -A(\partial\varepsilon_i/\partial F_z)$. The histogram of deviations required to simulate the beam profile is made by weighing the series of values d_{zi} with the factor $\exp(-\varepsilon_i^{OFF}/kT_r)$, where T_r is left as a fitting parameter.

In the calculations, the toluene molecule was considered a rigid body with a dipole moment of 0.375 D [16] oriented along the molecular symmetry axis (a-inertial axis), and with the following rotational constants: A = 5.72933 GHz, B = 2.51745 GHz and C = 1.74887 GHz [16].

4. Results and discussion

As mentioned before, no field-induced broadening is expected for an asymmetric rotor like toluene for high rotational temperatures. We found this behavior when we probed the middle part of a beam pulse generated by expanding a 1.0 mol% mixture of toluene in helium at a pressure of 1.1 bar. Under these conditions, we show in Fig. 2 that the measured beam profiles in presence and in absence of the field almost coincide. The propagation speed of the beam was found to be markedly lower than the terminal velocity of helium [17] at the source temperature ($v_y^{\infty} = 1750$ m/s), indicating that a limited cooling occurred in the expansion. Likewise, we also found absence of broadening when studying another asymmetric-top molecule like *meta*-xylene, in similar conditions.

However, as soon as we reduced the concentration of toluene in the expansion mixture to 0.1 mol% and focused our attention to the molecules at the front of the supersonic beam pulse, the narrow and symmetrical field-off profile was asymmetrically broadened in presence of the electric field (see Fig. 3). We attribute this behavior to the presence of colder molecules in the beam, which is compatible with the fact that in this case v_y was found identical to v_y^{∞}. The remarkable change found in ϕ_z points out the importance of thermal effects on the ED of asymmetric molecules. In spite of the weak dipole moment of toluene, the profiles exhibit long tails to higher fields ($z > 0$) that extend to about 1.5 mm from the beam center (not shown in the figure) when the field strength is 13.6 kV/mm. We found that the z position of the profile's maximum shifts systematically to the right at higher field strengths, and the intensity gradually decreases.

A question arises whether the simulation methods described earlier will be able to reproduce the observed field-induced broadening and height reduction. In Fig. 4, we compare the simulated profiles (lines) against those observed in the experiment (symbols) for a field strength of 6.8 kV/mm. We found that the measured broadening is adequately reproduced by models that consider the interaction of dipolar rotors in electric fields. The values given for T_r in Fig. 4 correspond to the best fit between the simulations and the experimental results; classical and quantum simulations yielded very similar values of T_r. We found that the rotational temperatures achieved in these experiments are in the range 3–10 K. From the profile analysis we noticed that a better cooling was achieved using neon as carrier gas, in accordance to previous studies [18] about the rotational relaxation of simple molecules like N_2 or CO. Cold supersonic beams of Fig. 4 were generated like before, expanding highly diluted mixtures of toluene in helium and in neon. The extent of broadening decreased rapidly when larger amounts of toluene were used in the expansion, resulting in higher T_r values. However, we observed that above 30 K the rotational temperature of toluene can hardly be determined by ED due to the similarity of field-on and field-off profiles.

A stronger deformation of the profile, including the appearance of a slow vanishing tail on the high-field side ($z > 0$), occurs when the field strength is increased and the expansion conditions are adapted in order to intensify the rotational cooling. In Fig. 5, we

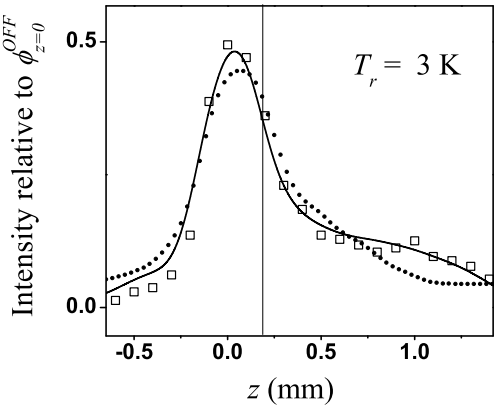

Fig. 5. Experimental profiles of rotationally-cold toluene molecules (squares) and the corresponding classical (full line) and quantum (dotted line) simulations. Field strength, F_z = 13.6 kV/mm (∇F_z = 3.3 kV/mm^2); T_r values, determined by getting the simulations to match with the experimental results; $v_y = v_y^{\infty}$; expansion mixture, 0.1 mol% toluene in helium (3.0 bar). Vertical line: mean displacement of the experimental profile, $\overline{d_z}$.

show a 13.6 kV/mm ED profile obtained using a 3.0 bar expansion of a 0.1 mol% toluene–helium mixture. The presence of an asymmetric profile broadening is an indication that the field–dipole interaction perturbs the rotational motion. We observed that the profile's height decreased to less than half of the maximum intensity of ϕ_z^{OFF}, being this effect more pronounced than that shown previously in Fig. 3, where the value estimated for the rotational temperature was higher (T_r = 10 K). The shape of the measured ϕ_z is reproduced well enough by the simulations shown in Fig. 5. However, a closer inspection allows us to identify a second peak on the right that appears as a shoulder in the quantum simulation and, surprisingly, is better reproduced by the classical approach. The existence of a structured deflection pattern was recently suggested for a beam of water molecules [2].

The net orientation of the beam ensemble of molecules, $\overline{\langle\cos\theta\rangle} = \overline{\langle\mu_z\rangle}/\mu_0$, can be evaluated from the experimental mean displacement of the profile, $\overline{d_z}$ (vertical line in Fig. 5), by using the expression $\overline{\langle\cos\theta\rangle} = \overline{d_z}/A\mu_0$ derived from Eq. (2). The experimental values of the orientation cosine are 0.144 (T_r = 3 K) and 0.056 (T_r = 10 K), which compare well with the predictions of the Langevin–Debye theory [19], where the cosine is calculated as $\mu_0 F_z/3kT$, giving the values 0.137 for T_r = 3 K and 0.041 for T_r = 10 K.

In conclusion, we found that: (i) toluene beams produce broad and asymmetric profiles only if T_r is of the order of a few Kelvin, (ii) the profiles are strongly dependent on the degree of cooling achieved in the expansion, (iii) when the beam is warm, higher rotational levels become populated and the beam broadening is rapidly lost, and (iv) the available theories for asymmetric tops [5,11] are able to reproduce the measured profiles.

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