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Interaction of polar molecules with a resonant RF electric field: strong deflection of a NO molecular beam

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Abstract. Deflection of a cold supersonic NO beam seeded in He has been observed when these molecules interact with both static and a resonant oscillating electric field. The NO beam splits into two beams each one deflecting about 0.5° towards the positive and negative direction of the Stark field when the employed resonant frequency between the two Stark levels of the NO molecule is 1515 kHz. This deflection angle is about four orders of magnitude higher than the value one would expect from the NO dipole moment and the employed RF field gradient. This phenomenon suggests the possibility of a significant translational motion perpendicular to the beam axis, which is induced by the resonant RF electric field on the cold and high-density supersonic beam.

PACS. 32.60.+i Zeeman and Stark effects

1 Introduction

In a previous paper [1] our group has reported beam depletion spectra of a NO supersonic beam when the polar NO molecules interact with a resonant RF field. No experimental evidence has been yet presented about the origin of such a beam depletion leaving the subject open to either molecular deflection or cluster photofragmentation as possible sources of the observed phenomenon. In this letter we have investigated further this phenomenon using a modified experimental approach by which clear evidence of the nature of the beam depletion is provided confirming it is due to molecular deflection. In what follows the experimental set-up is briefly described and the deflection results are reported and discussed.

2 Experimental

Figure 1 shows a schematic view of the molecular beam deflection technique. The main features of the molecular beam apparatus have been extensively described elsewhere [2] and only a brief description is given here. The present experiment employs the same NO beam (80% diluted in He) as used in reference [1], but with a stagnation nozzle pressure of 4 bars instead of 2 bars used previously. The resonance unit is of the same type that described earlier [3]. Essentially it consists of two parallel Cu coated glass plates (length 10 cm along the beam, height 6 cm) separated by 0.67 cm. In one plate a 1 mm wide scratch insulates electrically a rectangle of 8 cm by 3 cm; the rectangle and the rest of the plate form the electrodes to which the RF is applied. The static voltage is applied to the rectangular electrode and the opposite plate. The molecular beam runs parallel to the scratch (along the x-axis) 0.34 cm away from the plate. At this distance the homogeneous static field (z-axis) is perpendicular to the RF field (y-axis). As sketched in Figure 1 a movable slit was used to record the beam profile. The slit position can be changed by a computer controlled step motor by increments of 0.01 cm along the z-axis (i.e. perpendicular to the beam direction).

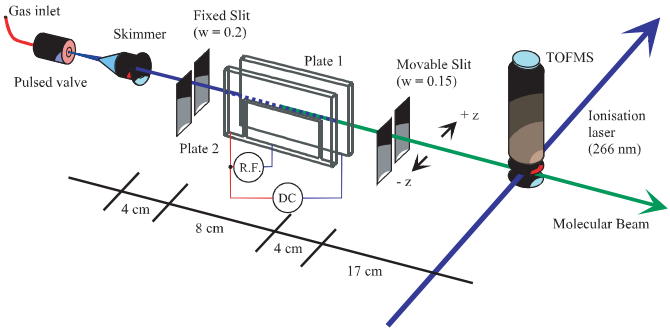

Fig. 1. Schematic view of the molecular beam apparatus. The NO beam passes through the resonant unit and is subsequently ionised and detected by a linear time-of-flight spectrometer. The present investigation used two possibilities regarding the experimental set-up: (a) the slit is used at a fixed position at the centre of the beam axis, and (b) the slit is moved towards the $+z$- and $-z$-directions to record the beam profile intensity. All dimensions in cm.

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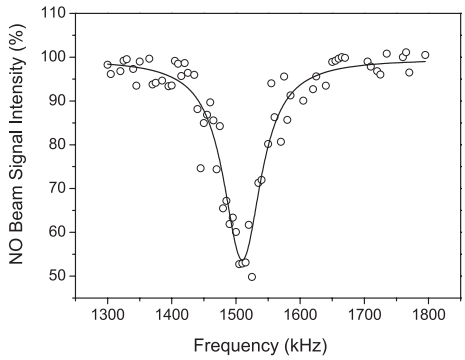

Fig. 2. NO beam depletion spectrum as function of the RF field frequency. Notice the dip resonance at 1515 kHz. The data was taken at $E = 14.28$ kV/m and $E_1 = 2.1$ kV/m. Stagnation pressure was 4 bars. See text for comments.

3 Results

Two kinds of measurements were carried out. In the first one, depletion spectra are measured, when the slit position remains fixed at the centre of the molecular beam. In this case we want to emphasize that the measured signal consists of the NO beam intensity after it passes the resonant unit. Here the NO molecules interact with both an external Stark field and an oscillating electric field. The measured spectra consist of NO beam intensity as a function of the frequency of the oscillation field for a given fixed Stark field. In the second type of experiments, all experimental parameters, i.e. Stark, RF field and radiofrequency were fixed and only the slit position was changed. Thus the NO signal intensity can be monitored as a function of the slit position to measure a deflection spectrum.

The transmitted NO signal vs. the oscillating frequency for a DC field strength of 14.28 kV/m and a RF field strength of 2.1 kV/m with the slit allocated at the centre of the molecular beam is shown in Figure 2. A clear dip around 1515 kHz is observed, which represents a depletion of ca. 50% of the beam intensity. The width of the central dip is about 68 kHz, which is higher than 15 kHz the width observed in reference [1]. This difference could be due to higher broadening factors under the present experimental conditions. First, the RF field strength is now 1.5 times higher than the one used in [1]. Secondly, the factor of 10 higher in the static field strength of the current experiment compared with that of the attenuation experiment of references [1,3] could also play a role, particularly when considering imperfect homogeneities of the static C-field. The higher spectral width of the central dip would also explain why the two side peaks observed in Figure 1 of reference [1] are not reproduced in the spectrum.

Figure 3 shows the second type of measurements taken in the present investigation. The beam signal intensity is represented as a function of the slit position. Two beam profiles are displayed at two distinct RF frequencies; 1515 kHz (on Resonance) and 1400 kHz (off Resonance) conditions. Sixty laser shoots were averaged for each slit position, which was moved by 0.01 cm increments. To reduce possible effects due to signal drifts, one ON beam

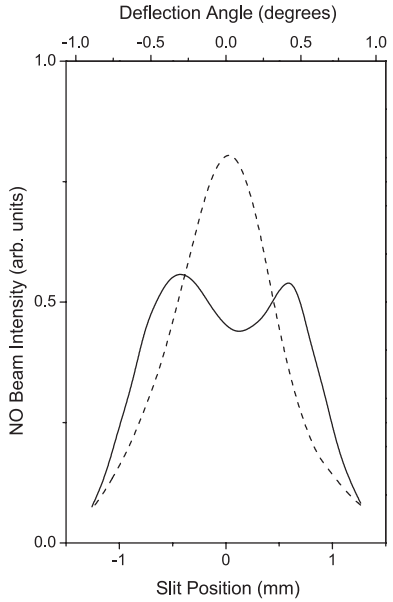

Fig. 3. NO signal intensity as a function of the slit position. Dot line refers to beam profile intensity measured under off conditions ($\nu_{off} = 1400$ kHz) and dot line refers to the same type of measurement taken at resonant conditions ($\nu_{on} = 1515$ kHz). Notice the splitting towards both $\pm z$-directions when the beam interacts with the resonant RF field. The DC and RF field strengths were the same as those used in Figure 2. See text for comments.

profile measurement was followed by one OFF beam profile measurement and so on.

As shown in the Figure the beam splits into two parts at resonant conditions. Each peak represents a deflection angle of 0.5° taking the centre of the resonant unit as the origin for the beam deflection [4]. Interestingly, the total beam signal, i.e. the signal integral over the slit position is, within the experimental error, the same for the two beam profiles. The latter indicates that the main difference between the two measurements is the beam splitting towards the negative and positive direction of the z-axis. Hence this beam deflection leads to signal depletion when one monitors the beam intensity with a fixed slit and detector located at the centre of the collimated beam.

For a better illustration of both the extent and direction of the beam deflection Figure 4 displays the (ON–OFF) beam signal. Here ON and OFF refer to the measured beam signal at 1515 kHz and 1400 kHz conditions, respectively. In this plot the beam deflection towards the $\pm z$-direction is clearly noticed. Notice how the area of the negative part (corresponding to the depleted beam) is about the same as that of the positive part (i.e. that of the deflected beam).

4 Discussion

When a molecule with a permanent electric dipole moment, μ, interacts with a homogeneous static Stark field,

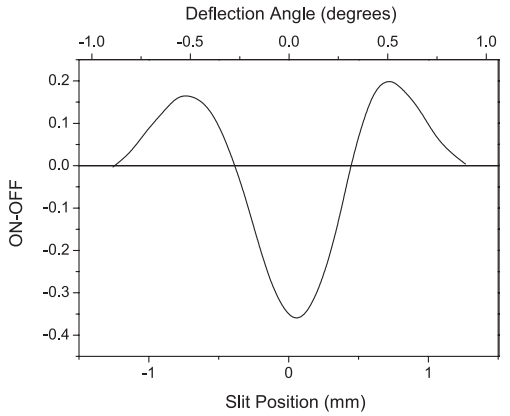

Fig. 4. Variation of the NO beam as a function of the slit position. At each position the (ON–OFF) beam signal is plotted. ON and OFF stand for the NO signal measured at 1515 kHz and 1400 kHz conditions, respectively.

with E as field strength the energy of the molecule is perturbed and given by [5–7]

$$W = W_0 + W_{stark} \tag{1}$$

in which W_0 is the energy of the unperturbed system (i.e. when $E = 0$) and $W_{Stark} = -\overline{\mu}_E E$. Here $\overline{\mu}_E$ is the mean component of the electric moment in the field direction. If the linear molecule is in a Σ-state the dipole moment is perpendicular to the total angular momentum (we neglect spin effects) and therefore $\overline{\mu}_E = 0$. In other works, there is no first order Stark splitting [7]. However, there is a second order effect when one considers the action of the Stark field on the molecular rotation.

If the molecule is in a Π, Δ, etc., state $\overline{\mu}_E$ is not longer zero and a linear Stark effect arises given by [5–7]:

$$W_{stark} = -\mu E \frac{\Omega M}{J(J+1)}. \tag{2}$$

Here μ is the permanent electric dipole moment which in the case of the NO molecule equals $\mu = 0.158$ D [8], J the total angular momentum, Ω the magnitude of the projection of J on the internuclear axis and M the projection of J on the space fixed axis, i.e. the direction of the static E field. In this work we restrict ourselves to the $\Omega = 1/2$ case of the electronic ground state. Consequently, the Stark interaction is given by

$$W_{stark} = -\frac{1}{2}\,\mu E \frac{M}{J(J+1)}. \tag{3}$$

Thus, the $\Delta M = \pm 1$ transition corresponds to an energy splitting of:

$$\Delta W_{stark} = h\nu_0 = \frac{1}{2}\mu E/(J(J+1)). \tag{4}$$

Inserting $J = 3/2$, $\Delta M = 1$ and the experimentally observed resonant frequency of $\nu_0 = 1515$ kHz one obtains a dipole moment value of $\mu = 0.1580$ D which is within the range estimated in our previous work [1] given by $\mu = 0.1579 \pm 0.0004$ D. In addition this value compares very well, within our experimental errors, with that of reported in reference [8] of $\mu = 0.15782 \pm 0.00002$ D.

The unexpected linear Stack effect found in our investigations still remains to be explained. Here we only consider some arguments, which may shed some light in the interpretation of this anomalous linear Stack behaviour.

Friedrich and Herschbach [9] have demonstrated the occurrence of a (pseudo) first order Stark effect for a linear polar molecule under the action of a non-resonant laser field combined with an even small static electric field. First the non-resonant strong laser pulse creates a significant alignment of the rotational angular momentum distribution. Subsequently, the action of a static electric field converts the rotational alignment distribution into an oriented distribution. This new method to orient a polar molecule has been used in the study of the HXeI photofragmentation dynamics by Buck and coworkers [10,11].

Taking into consideration this combined action of the two fields one could think in the possibility to achieve molecular orientation by the combination of the rotational alignment originated by strong collisions in supersonic expansions followed by the action of a static electric field, rotational alignment in supersonic expansions has been evidence by Aquilanti et al. [12]. Therefore it is not far from expectation to think that we may have an oriented NO distribution as a result of the combined action of the strong alignment during the supersonic expansion plus the action of the static and/or resonant RF field.

One crucial question also raised by the present results, is the mechanism for the beam deflection, i.e. the observed symmetrical deflection of the order of ca. 0.5°. The splitting of the molecular beam into two beams towards the positive and magnetic z-directions can be rationalised by the transverse Stern-Gerlach deflection. While in the classic Stern-Gerlach experiment the beam deflection is due to the gradient of the (static) non-homogeneous field in the present case it should be originated by the gradient of the resonant RF field. In fact deflection of a CsF beam by a resonant RF field has been observed by Hill and Gallager [12]. According to these authors a spatially inhomogeneous oscillating field tuned to the transition frequency between adjacent rotational states of a polar molecule exerts a force onto the molecule that leads to a resonance deflection. The force is due to the interaction of the oscillating field with the permanent dipole moment both of which rotates with the same frequency at resonance and is given by the negative gradient of the interaction energy. The authors observed resonance deflection of molecules in the $v = 0$, $J = 0$, $J = 1$ states of CsF by passing a molecular beam of CsF through an inhomogeneous electric field and when the $J = 0 \rightarrow 1$ rotational transition was induced. The observed deflection can be well described by this model. If applied to the present system it provides the largest force conceivable in the framework of electrostatic interaction $F < -\mu_z d/dz(E_1)$ where μ_z is the mean z-component of μ. The maximal deflection angle is then given by $\theta_{max} = FL/(2E_{tr})$. With $L = 0.08$ m (the length

of the interaction region), $E_{tr} = 0.1$ eV (the mean translational energy of NO), $d/dz(E_1) = 10500$ kV/m [2] and $\mu_z = \mu$ one obtains $\theta_{max} < 10^{-4}$ degrees, a value that is by orders of magnitude too small with respect to the observed one. Thus the RF gradient force acting on a free molecule cannot be responsible for the particle deflection. The observed deflection angle of ca. 0.5° represents a strong force acting on the NO molecule considering its average beam velocity of 755 m/s and an average residence time (i.e. the molecule spends inside the resonant unit) of 100 μs.

5 Concluding remarks

In this letter we have reported measurements on the NO beam signal intensities recorded by Laser ionisation coupled with time-of-flight mass spectrometry. The beam signal was measured after the NO molecules passed through a RF unit in which the cold molecules interact with both a static DC and an oscillating RF electric fields. Essentially, two types of measurements were recorded (i) beam depletion spectra and (ii) beam profile signal. In the former the beam transmission signal is recorded as a function of the frequency of RF field for a fixed DC field. In the second case the beam profile is measured using a computer controlled beam silt allocated before of the laser ionisation region.

The main finding of the present investigation is the observation of a significant beam deflection when the polar and cold NO molecule interacts with a resonant RF frequency between the two Stark levels split by the DC field. The beam splits into two beams each one deflected by 0.5° to both the positive and negative z-direction. The deflection is responsible for the beam depletion spectrum taken when the slit is fixed at the central beam position.

Of major relevance is the extent of the observed deflection. The measured deflection angle of 0.5° is several orders of magnitude higher than the calculated value based on the NO dipole moment and the experimental RF field gradient. At present we cannot offer an explanation to justify these experimental observations. More experiments are in progress to investigate all features of this phenomenon.

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