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Molecular beam electric resonance without A- and B-fields

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Abstract. We report on a novel phenomenon observed during the passage of a pulsed NO beam seeded in He through a combined homogeneous, static electric and RF field, denoted as C-field in a standard molecular beam electric resonance (MBER) experiment. Although we refrain from the state selective A- and B-fields, which are considered crucial for a MBER experiment, the transmitted intensity exhibits as a function of the RF frequency conspicuous dips at resonance frequencies that depend strictly linearly on the static field strength E_0. Their spectral width is by a factor of 4 smaller than the time of flight broadening. Both, the resonance frequencies and their linear field dependence can be precisely predicted applying a simple expression for the Stark effect to a $\Delta M = \pm 1$ transition of a single rotational state ($J = 3/2$) of the electronic ground state $^2\Pi_{1/2}$. However, this formula is valid only in the high field limit ($E_0 > 1000$ kV/m) while the employed field ($E_0 = 1.47$ kV/m) was in the extreme low field domain where the large Λ type doubling and hyperfine coupling lead to a purely quadratic Stark effect. We assume that the phenomenon is due to a yet unknown collective rather than to an isolated particle process.

PACS. 33.20.Bx Radio-frequency and microwave spectra – 32.60.+i Zeeman and Stark effects

1 Introduction

The interaction of atoms and molecules with external magnetic and electrical fields has played a central role in our understanding of the structure of matter and constitutes one of the most widely used spectroscopic methods both in chemistry and physics [1]. Perhaps one of the most important techniques employed in the investigation of these interactions has been and continues to be the molecular beam technique, which significantly contributed to the development of atomic and molecular physics [2–5]. Well-known examples of this scientific development are the molecular beam magnetic or electric resonance spectroscopy [4]. There are excellent books and reviews [5–9] on the subject emphasising either spectroscopic or scattering applications.

In a molecular beam electric resonance (MBER) experiment [7] rotational states of polar molecules are prepared or analysed by exploiting the state dependent interaction between the electric dipole moment and an inhomogeneous electric field [8,9]. First, the molecular beam is state prepared in the A-field, then passes the resonance unit (C-field) and finally the state analyser (B-field) operated such that only molecules in the prepared state reach the detector. In the C-field the molecules are subjected to two mutually perpendicular fields, a homogeneous static and an oscillating field. If the oscillating field is tuned to a transition frequency between Stark substates a fraction of the molecules is removed from the prepared state and the intensity at the detector drops (flop out).

In contrast to the standard MBER method we use in our experiment only the resonance unit (C-field) and refrain from the A- and B-fields that are considered crucial for the MBER method. But, although the molecules are neither state prepared nor analysed, we find very sharp resonance structures in the intensity of the transmitted molecular beams as a function of the oscillating field (RF field) frequency. The intensity drops significantly if the RF field is tuned to certain resonance frequencies similar to a flop out type MBER experiment. This phenomenon has been observed so far for pulsed nozzle beams of N_2O [10], NO and Ba–FCH_3 seeded in He as carrier gas.

In the present letter we report the results of our first experiments with a diatomic namely NO. The depletion spectrum measured at a static field strength of $E_0 = 1.47$ kV/m exhibits an intense main dip at a RF frequency of 157 kHz surrounded by two weaker dips at 151 and 163 kHz. The resonance frequency varies strictly linearly with the static field within the studied range from 0.5 kV/m to 20 kV/m. The full width at half maximum of the central dip amounting to 2.1 kHz is by a factor of 4.2 smaller than expected for the passage time of the molecules through the field of 10^{-4} s. Very surprisingly, the resonance frequency as well as the linear dependence

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on the static field is quantitatively predicted by a simple expression that should be valid only for very high fields ≫1000 kV/m. To date neither the validity of the high field approximation nor the extremely narrow shape of the dip nor the mechanism causing the depletion are understood.

2 Experimental

The molecular beam apparatus, and method used in the present work together with most significant experimental conditions have been described already elsewhere [10]. Thus, we only describe the experimental conditions relevant to the study presented here. Essentially, NO diluted in He as carrier (20% NO and 80% He) is expanded into the separately pumped vacuum chamber through a pulsed nozzle (diameter 0.5 mm) operated at a repetition rate of 10 Hz. At a stagnation pressure of 2 bar and a temperature of 300 K we measure a most probable velocity of *ca.* 755 m/s and a full-width-half-maximum of 10% from which a parallel beam temperature of 15 K is extracted. The beam is collimated first by a skimmer (diameter 1 mm) mounted 1.5 cm downstream from the nozzle, and, then, by another collimator (diameter 3 mm) located at 23.5 cm from the skimmer. This gives a beam full divergence of 0.7°. It passes through the resonance unit and a subsequent slit that hinders all molecules that are deflected in the resonance unit by more than 0.7° from entering the quadrupole mass spectrometer detector. The resonance unit is very similar in design to the one used in earlier MBER [11,12] experiments. It consists of two parallel Cu coated glass plates (length 10 cm along the beam, height 6 cm) separated by 0.64 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) 0.2 cm away from the plate. At this distance the homogeneous static field (z-axis) is perpendicular to the RF field (y-axis) (see Ref. [10] for further details).

3 Results

Figure 1 shows the intensity of the NO beam (mass spectrometer set to mass 30) as a function of the RF frequency. The homogeneous static field was set to $E_0 = 1.47$ kV/m and the amplitude of the RF field at the beam centre to $E_1 = 1.4$ kV/m. The intensity is normalized to unity for the RF field turned off. Four remarkable and very surprising features have to be emphasized:

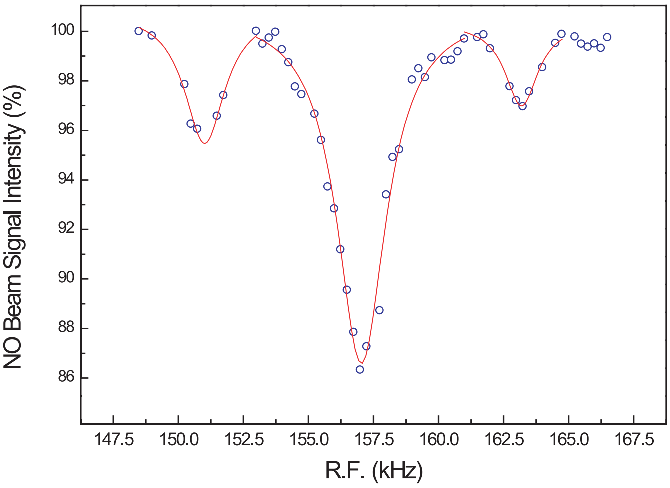

Fig. 1. NO beam intensity measured by the quadrupole mass spectrometer set to mass 30 as a function of the RF oscillating field frequency. The nozzle stagnation pressure and NO/He mol ratio are 3 bar and 20%, the static and RF field 1.47 and 1.4 kV/m, respectively. The data are normalised to 100% at off resonant conditions. Notice the two side bands and the maximum depletion of about 14%. The frequency of the central dip is exactly given by equation (1) for a $\Delta M = \pm 1$ transition of the $J = 3/2$ state of the ${}^2\Pi_{1/2}$ electronic ground state of NO.

(i) the measured curve exhibits three well resolved dips at 151, 157 and 163 kHz similar to the flop out spectra of standard MBER experiments. This finding is most surprising since the present setup is equipped neither with a state preparing nor a state selecting device both of which are, according to the usual interpretation of such spectra, considered crucial for the appearance of resonance structures;

(ii) the intensity of the phenomenon is very large and well outside any error margin. At the central frequency the depletion is most intense and amounts to roughly 14%; the attenuation of the satellites is smaller but clearly visible and reaches values about 4 and 3%;

(iii) the spectral width of the resonance features (full width at half minimum) amount to 1.6, 2.1 and 1.3 kHz at 151, 157 and 163 kHz, respectively. Most remarkably, these widths are considerably smaller than the time-of-flight broadening which, for an average time of 10^{-4} s, amounts to 8.9 kHz [13];

(iv) the position of all dips exhibits a clear dependence on the static field. Figure 2 displays the resonance frequency of the central feature as a function of E_0. We find that over a dynamical range of two orders of magnitude from 0.2 to at least 20 kV/m the dependence is absolutely linear.

The resonant loss of beam intensity could be due to a deflection of the detected species by an angle larger than 0.7°, their partial removal from the beam or an RF induced substantial modification of their mass spectrum. However a physical mechanism that leads to one of these causes has not been found as yet. In order to get more information about the mechanism and to further solidify our observations we carried out additional experiments under modified experimental conditions. We found that a neat He beam created just by turning off the NO valve, an NO beam diluted by Ar, and a neat NO beam

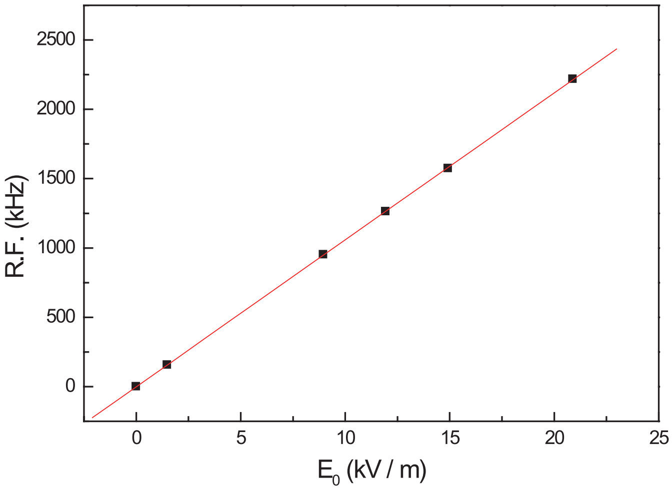

Fig. 2. Measured resonant frequency as a function of the static field strength. The experimental conditions are the same as in Figure 1. Notice the linear behaviour. The solid line is the best fit of equation (1) to the data with μ as adjustable parameter; the fitting returns $\mu = 0.1579 \pm 0.0004$ D.

exhibit no resonance structure within the probed frequency range (50–2500 kHz). Only an NO–He mixture exhibits the phenomenon essentially independent on the mol ratio NO/He within the studied range from 5 to 30%. Furthermore, in experiments performed with other polar molecules (N_2O, Ba–CH_3F) — He mixtures we observed clearly resolved resonance structures while none was observed in experiments with non-polar molecules. Although the number of systems studied so far is very limited these findings suggest that the existence of a permanent dipole moment as well as the simultaneous presence of He are prerequisites for the appearance of the phenomenon.

4 Discussion

Both, the permanent electric dipole moment as a prerequisite of the phenomenon and the linear dependence of the resonance frequency on the static field E_0 suggest that the resonance is due to a RF transition between states split by a linear Stark effect. And indeed, ignoring Λ-doubling and the nuclear spin $I = 1$ of N the ro-vibrational states of the $^2\Pi_{1/2}$ electronic ground state of NO feature a linear Stark shift according to

$$W_{\text{stark}} = \mu E_0 \frac{\Omega M}{J(J+1)} \tag{1}$$

where μ is the permanent electric dipole moment, Ω denotes the component of the electronic angular momentum with respect to the molecular axis, J the rotational quantum number and M the projection quantum number with respect to the electric field as quantization axis [9]. Inserting $\Omega = 1/2$ for the ground state, $J = 3/2$, $\mu = 0.158$ Debye and $E_0 = 1.47$ kV/m the Stark splitting of two adjacent M states amounts to 157 kHz which agrees exactly with the resonance frequency of the observed central dip. Moreover, fitting equation (1) with μ as a free parameter to Figure 2 one obtains $\mu = 0.1579 \pm 0.0004$ D, a value which is consistent with the best one available in the literature [14].

Besides the resonance frequency the second crucial question concerns the mechanism of the depletion. According to Hill and Gallagher [15] a spatially inhomogeneous oscillating field tuned to the transition frequency between adjacent rotational states exerts a force onto a polar 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 rotate with the same frequency at resonance and is given by the negative gradient of the interaction energy. The authors studied a CsF beam and observe at a frequency resonant with the $J = 0$ and $J = 1$ transition of the vibrational and electronic ground state a significant deflection that can be fairly well described by this model. If applied to the present system it provides the largest force conceivable in the framework of electrostatic interaction, $F < -\mu_z \mathrm{d}/\mathrm{d}z(E_1)$, where μ_z is the mean z-component of $\boldsymbol{\mu}$. The maximal deflection angle is then given by $\theta_{\max} = FL/(2E_{\text{tr}})$. With $L = 0.08$ m (the length of the interaction region), $E_{\text{tr}} = 0.1$ eV (the mean translational energy of NO), $\mathrm{d}/\mathrm{d}z(E_1) = 700$ kV/m^2 and $\mu_z = \mu$ one obtains an upper bound $\theta_{\max} < 5 \times 10^{-5}$ degree, a value that is by orders of magnitude too small to rationalize the observed depletion. Thus the usual gradient force acting on a free molecule cannot be responsible for the resonance feature.

Provided the applicability of equation (1) is not sheer coincidence it implies an interesting aspect. The expression is derived for a freely rotating symmetric top with degenerate Λ doublet and zero nuclear spin. However, NO has a rather complicated energy level scheme due to a substantial Λ-doubling (0.0237 cm^{-1} for $J = 3/2$ in the $^2\Pi_{1/2}$ state) and a strong quadrupole coupling of the nuclear spin $I = 1$ of the N atom [16–19]. With rising electric field all levels exhibit a quadratic Stark effect due to the fact that the field starts mixing the two components of the Λ doublet [20,21]. Deviations from the quadratic behaviour are expected to occur if the electric interaction energy (μE) becomes comparable to the hf splitting. From the smallest splitting of 27 MHz between two out of the six hf states for $J = 3/2$ one obtains the upper boundary of $E_{\max} = 33$ kV/m. That is, within the entire range of electric fields studied (see Fig. 2) the Stark effect of a free NO molecule in the $J = 3/2$ state is quadratic; equation (1) is applicable only if the electrostatic interaction energy becomes larger than the splitting of the Λ doublet, that is at fields beyond 1000 kV/m. Consequently, the amazing precision of equation (1) in predicting the resonance frequency and its linear field dependence cannot be due to an interaction with a free NO molecule.

The NO molecules obviously interact with other particles in the beam in a way that equation (1) becomes valid, in other words that Λ-doubling becomes completely quenched and the nuclear spin decoupled from rotation. It is conceivable that these conditions are met by He clusters formed during the expansion with (near) symmetric top geometry. For a given J these clusters would rotate much slower which would reduce or even suppress the decoupling of the electron angular momentum from the axis responsible for the Λ-doubling and influence the hf splitting. And indeed there is an experimental indication that cluster formation may play a role. The lack of a resonance dip in experiments with NO–Ar mixtures or with pure NO but its appearance in He–NO mixtures suggest that NO–He_n clusters might be the candidates. It is conceivable that such clusters are formed in states barely below the dissociation limit and are photo-fragmented by the RF. The extremely narrow width of the dips far below the time-of-flight broadening would then suggest even multi-photon processes. The depletion of the mass 30 signal could then result from a change of the mass spectrum of the clusters in the course of their dissociation.

Recently, Klos *et al.* [22] carried out an *ab initio* calculation on the NO–He dimer. They found various bound He–NO states some of them very close to the dissociation limit but no significant decrease of the Λ splitting. The latter result is not necessarily applicable to higher oligomers but raises doubts that the splitting becomes fully quenched. Another more severe argument against the oligomer model follows from population statistics. If we ignore Λ doubling and hf splitting the population of a single $J = 3/2$, M state at a rotational beam temperature of 15 K amounts to 4.5% provided the ${}^2\Pi_{3/2}$ population has not relaxed during the expansion of the gas. The probability for oligomer formation and the large number of rotational states of these species further reduces the population of individual states. As a consequence, the observed 15% depletion of the total NO intensity is absolutely out of reach of a single particle process.

We conclude that the striking magnitude of the observed dip is a strong indication for the presence of a collective process. Presently we consider the model of an NO gas that consists of two species inside an electric field, the one with positive Stark effect associated with one Λ component the other with negative Stark effect associated with the second Λ component. If the two components are separated they develop a restoring force due to the (field induced) dipole interaction and establish in this way a resonance frequency. Due to the quadratic Stark effect the induced dipole moment is linearly dependent on the field E. Thus the interaction energy and the restoring force depend on E^2 and hence the resonance frequency on E in perfect agreement with Figure 2. The RF field exerts an oscillating force via the field gradient and may cause a resonance whose transversal extensions are sufficiently large to prevent the molecules from reaching the detector. However, the model provides no explanation for the line width and for the validity of equation (1). Further collective mechanisms based on the strong dipole-dipole interaction may be more appropriate. Also the possibility that the NO becomes aligned due to the strong supersonic expansion with the light He carrier and, subsequently, oriented by the interaction with the electric fields cannot be ruled out. We are now working with several models that will be applied to the present as well as to other experiments going on in our laboratory. The results will be the subject of a future publication.

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