Deflection of Molecules by a Homogeneous Electric Field: A New Effect

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Abstract

In this work we put forward a theoretical explanation of a peculiar effect found very recently by A. González Ureña et al. [3]. They have observed the deflection of a beam of molecules possessing a permanent electric dipole moment by a homogeneous electric field when a resonant oscillating field is superposed transverse to the static one.

INTRODUCTION

The molecular beam technique has significantly contributed to the development of the Atomic and Molecular Physics. Well known examples of this intellectual and scientific development are the molecular beam magnetic or electric resonance spectroscopy. There are excellent reviews [1, 2] on the subject emphasizing either spectroscopic or scattering applications. The basic principle exploited in these techniques is the magnetic or electric focussing and/or depletion due to the interaction between the permanent magnetic or electric moment of a molecule and a non-homogeneous magnetic or electric field, respectively.

The aim of the present work is to put forward an explanation to the effect reported in ref. [3].

In that experiment a N₂O supersonic beam that interacts with both a DC Stark field and a resonant radiofrequency radiation. During the flight of the molecular beam pulse from the source to the detector, the molecules pass through a homogeneous static electric field. Changes in the beam intensity were observed when a resonant oscillating electric field is superposed transverse to the static field. Thus, a new phenomenon was observed which consists of N₂O beam depletion upon its interaction with both a homogeneous electric field and a resonant radiofrequency, see ref. [3] for details.

THEORETICAL DISCUSSION

When a neutral particle with an electric dipolar moment, \( \mu \), goes through an electric field, \( E \), upon the particle is acting a force

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Hence, if the electric field is homogeneous the corresponding force vanishes and the particle’s trajectory will not be affected by the electric field.

For understanding the experimental results two types of interaction are of relevance. Namely, the interaction of the permanent dipole moment with the homogeneous electric field (Stark interaction) and the new interaction between the particle and both the static and the resonant oscillating field (depletion interaction). Let us consider them briefly:

(a) Stark interaction

The quantum levels of a molecule that enters a homogeneous electric field are split by the Stark effect. Then, a direction ‘that of the field’ is singled out. The rotational energy levels of a molecule (rigid rotor) are perturbed and given by:

\[ W_{JM} = hB \left[ J(J+1) + \left( \frac{\mu}{hB} \right)^2 \frac{J(J+1) - 3M^2}{2J(J+1)(2J-1)(2J+3)} E^2 \right] \]  

(2)

Where \( J \) is the rotational quantum number, \( E \) is the electric field, \( M \) is the component of the angular momentum along the quantization axis, \( < \mu > \) the permanent electric dipole moment of the molecule, and \( B \) its rotational constant. This equation is obtained by the second-order perturbation theory. (The odd terms in the series are identically zero and the fourth term is neglected because it is quite small at the conditions of the present experiment). As mentioned earlier the transition considered in the experiment is the \((1, \pm 1) \rightarrow (1,0)\). For this transition equation (2) yields an energy splitting, \( \Delta W \):

\[ \Delta W = W(1,0) - W(1,\pm 1) = \frac{3}{20} hB\lambda^2, \quad \text{with} \quad \lambda = \frac{\mu E}{hB} \]  

(3)

The oscillator frequency \( \omega \) for the transition is obtained applying the usual Bohr relation

\[ \omega = \Delta W/\hbar \]  

(4)

For example, for the \( \text{N}_2\text{O} \) molecule, with \( < \mu > = 0.161 \text{ D} \) and \( I=6.68 \times 10^{-46} \text{ Kg m}^2 \), the frequency of the transition \((1,\pm 1) \rightarrow (1,0)\) is equal to 286.9 kHz when the static field has an intensity of 191.3 kV m\(^{-1}\).

(b) Depletion interaction

In a previous study on the dynamics of a moving system, which also has an internal angular momentum, the main conclusion of that work was that the trajectory of a moving particle, possessing internal angular momentum, can be modified when a torque is applied with a perpendicular component to the rotational angular momentum vector. Specifically the following behaviour was predicted for a ‘particle’ with angular momentum \( \mathbf{J} \) and velocity \( \mathbf{v} \) to which a torque \( \mathbf{\Gamma} \) is applied the system would behave as if a central force given by equation (5) applied. See Appendix for the main points of the derivation and ref. for details.

\[ \mathbf{F} = m\mathbf{v} \times \mathbf{\Omega} \]  

(5)

where \( \mathbf{\Omega} = \frac{\mathbf{\Gamma}}{J^2} \) and \( \mathbf{\Omega} \) direction, is that of external field.
To test this force, an experiment for a microscopic system was suggested based on the interaction of a homogeneous magnetic field and electromagnetic radiation with a particle that has spin and magnetic moment. It was then predicted that the deviation from the original trajectory should take place when the radiation is resonant with a quantum transition between the energy levels of the particle.

Notice that according to the current wisdom (i.e. standard mechanics and electromagnetic) no deviation of the particle should occur as it is moving in a homogenous magnetic field.

The present work deals with an experiment carried out with a N$_2$O supersonic beam that interacts with both a DC Stark field and a resonant radiofrequency radiation. From a physical point of view the (present) electric resonant beam experiment is equivalent to the one suggested in Ref. Indeed, a Stark field replaces the Zeeman field and the particle magnetic moment is replaced by the permanent dipole moment of the linear N$_2$O molecule, which for the present investigation is considered as a rigid rotor. Again according to standard mechanics and electromagnetism the trajectory of a molecule in the beam should be not affected by the electric field since this is homogeneous. So that, any eventual beam depletion would in principle indicate the presence of the new force mentioned above (unless some other ‘conventional’ interpretation, of which we are not aware, could be found).

As said above, we deal with the rotational quantum states $J=1\ M_J=0,\pm 1$. The Stark interaction ensures molecular polarization and therefore quantized orientations of the $J$ vector with respect to $E$ while the molecule keeps rotating at each of these polarized ($M_J$) states.

We will deal with the motion of the molecular beam under the applied fields, $E$, homogeneous and constant, and $E_1$, which is an oscillating field. To do it, we are going to use a semiclassical approach wherein it is assumed that such motion can be reasonably well described by studying how the mean values (for the relevant quantum states) of the dipole moment operator evolve in presence of the external fields and then applying Eq. (5) with the torque computed by using those mean values of the dipole operator.

Now when no external field is present the mean value of the dipole operator, $\hat{\mu}$, is zero for any rotational state, that is $< \psi_{JM} | \hat{\mu} | \psi_{JM} > = 0$, simply due to symmetry (parity) reasons. But if the molecule is interacting with a homogeneous electric field, $E=(0,0,E)$, there is a interaction hamiltonian

$$\hat{H}_{int} = -\hat{\mu} \cdot E = -\mu > E \cos \theta$$

where $\theta$ is the polar angle, and then $J$ is no longer a ‘good’ quantum number since $[\hat{H}_{int}, \hat{J}] \neq 0$.

Restricting our discussion to the relevant, $J=1$, non perturbed states, and in first order perturbation theory, the corresponding quantum states with $E$ present are

$$|\Psi_{1M} > = |\psi_{1M} > + \frac{< \psi_{00} | H_{int} | \psi_{1M} >}{\varepsilon_1 - \varepsilon_0} |\psi_{00} > \delta_{M0}$$

$$+ \frac{< \psi_{2M} | H_{int} | \psi_{1M} >}{\varepsilon_1 - \varepsilon_2} |\psi_{2M} > (M=0,\pm 1)$$

Where $|\psi_{JM} >$ are the ‘non perturbed’ (rotational) states and $\varepsilon_J = hBJ(J+1)$ are the unperturbed (no field) energies. (Note that, in spite of the notation, $|\Psi_{1M} >$ is not an eigenstate of $\hat{J}^2$; yet it is of $\hat{J}_z$, with eigenvalue $M$.)

Now the mean value of $\hat{\mu}$ in a state $|\Psi_{1M} >$ is no longer zero. In fact, one has
but

\[ < \Psi_{1M} | \hat{\mu}_X | \Psi_{1M} > = < \Psi_{1M} | \hat{\mu}_Y | \Psi_{1M} > = 0 \quad (8) \]

where \( W_{1M} \) is the energy corresponding to the state \( | \Psi_{1M} > \) (Eq. (2)).

Therefore, we see that, in presence of the constant field \( E \), the mean value of the dipole operator in any quantum state (that is, for all values of \( M=0, \pm 1 \)) is a vector directed along the field \( (Z) \) direction.

In this situation, the new effect does not operate because the corresponding torque (computed as stated before) is zero, and, consequently, no depletion of the molecular beam takes place.

However, the presence of an oscillating electric field, \( E_1 = (E_1 \cos \omega t, E_1 \sin \omega t, 0) \), perpendicular to \( E \), as shown in Figure 1, where this situation is been displayed just before the interaction takes place, gives rise to a torque, \( \Gamma_1 = < \mu > \times E_1 \) (where \( < \mu > \) is the mean value of \( < \hat{\mu} > \) in the corresponding quantum state), that makes the molecules dipole (its mean value, of course) to deviate from its previous direction (parallel to \( E \)) due to the nutation performed by the molecules angular momentum, the nutation velocity being (recall eq. (5))

\[ \Omega_1 = \frac{\Gamma_1}{< J >} \quad (10) \]

where \( \Omega_1 \) direction, is that of \( E_1 \).

Then, there is a torque induced by \( E \), \( \Gamma_2 = < \mu > \times E \) (because \( E \) and \( < \mu > \) are no longer parallel ) and, besides the said nutation, the angular momentum, \( < J > \), starts precessing about \( E \) with a velocity

\[ \Omega_2 = \frac{\Gamma_2}{< J >} \quad (11) \]

where \( \Omega_2 \) direction, is that of \( E \).

If the frequency of the precession induced by the homogeneous electric field is resonant with the frequency of the oscillating field, then the interaction keeps up coherence, that is, the plane defined by the homogeneous field \( E \) and the dipole moment \( < \mu > \) (to be called \( \alpha \) hereafter) precesses about \( E \) as depicted in Figure 2. In this Figure, the system evolution is shown after a time \( t \), together with the trajectory \( S \) followed by the molecule under resonant conditions. Notice how the oscillating field, \( E_1 \) (which is emulated experimentally by an electromagnetic radiation), remains perpendicular to \( \alpha \) during the interaction time. Indeed, the particle deflection from the original X direction is clearly noticed. On the other hand, if there is no resonance, the \( \alpha \) plane precession velocity, \( \Omega_2 \), and that of the oscillating field, \( \omega \), are different, and then the interaction is not coherent and the effect (averaged in time) turns out to be null. (Notice that, from (10), one has \( \Omega_1 = < \mu > E_1 \cos(\Omega_2 - \omega t) \).

Then (see Appendix and for a complete classical treatment, ref. [5]) there will be two forces (of analogous type) acting at the CM of the molecule that will modify its trajectory (recall eq. (5))

\[ F_1 = mv \times \Omega_1 \]
\[ F_2 = mv \times \Omega_2 \]
where $v$ is the velocity of the centre of mass of the molecule.

When the interaction begins, and because of the oscillating field, molecules in resonance start to follow a circular trajectory in plane $\alpha$, of radius $R_1 = \frac{v}{\Omega_1}$.

Simultaneously, $F_2$, causes the precession of plane $\alpha$, that contains the circular trajectory about $E$. This interaction can be visualized by regarding the said molecules as describing a circle in $\alpha$ while this plane is precessing about $E$ with velocity $\Omega_2$. This effect remains as long as such molecules are acted by both fields, and, consequently, they will not reach the detector.

To summarize: If the oscillating electric field $E_1$ is not resonating, that is its frequency is not that corresponding to the transition between the $M_J = 0$ and $M_J = \pm 1$ levels, then the new effect is absent and, consequently, no depletion of the molecular beam takes place. However, things are different when the oscillating field has a frequency which corresponds to the transition between the mentioned levels, for, in such a case, and as predicted in [9] an effect appears which deflects the trajectory of molecules in the $J=1$ state, as observed in the present experiment. The depletion depends on both the intensity of the homogeneous electric field and the resonant field. Nevertheless, the important point is that the oscillation between the two levels is the necessary ingredient for the new interaction to take place, not the transition between levels itself.

CONCLUSION

The effect reported in ref. [3] can be understood by a semiclassical model, presented here, based upon the work presented in ref. [9], which concerns only the classical domain. Up to our knowledge, there is no conventional explanation for this effect.
Figure 1: The frames X, Y, Z (laboratory), and X'Y'Z' (attached to the molecule) are shown. O is the origin of the laboratory system; O', that of system axis linked to the particle and also the location of the centre of mass of the particle. The mean dipole moment <μ> and angular momentum <J> are parallel to E (Z-axis). The situation is represented when, due to the interaction with E₁ the depletion of the molecule starts.
Figure 2: Detailed view of the particle’s trajectory from $t = 0$ until $t = t$ when the resonant conditions are fulfilled. The molecule moves from $O$ along the spherical surface with radius $r$ centred at $C$. $S$, the particle’s trajectory results from the combinations of (a) a circular path, $S_{\alpha}$, with radius $r$ and centred at $C$ along the $Y'Z'$ plane, called $\alpha$ hereafter, which contains $E$, $<\mu>$, $<J>$ and $v$, and (b) the rotation of $\alpha$ around the $OC$ axis with (angular) velocity $\Omega_2$. The $XYZ$ frame has been displaced to $O'$ for a better illustration of the rotational movements. The $X'Y'Z'$ plane is tangent to the sphere at $O'$; consequently the $Z'$ axis is perpendicular to the surface of the sphere at $O'$ and contains $C$. As indicated, the particle’s trajectory is always located on the sphere surface. Since the position of $O'$ is defined by $\theta$ and $r$, $\dot{\theta}$ defines the $O'$ angular velocity with respect to the laboratory axis. In addition $\Omega_1$ is the $XY'$ (mutation) velocity with respect to the laboratory axis. Notice how $\dot{\theta}$ and $\Omega_1$, always coincide as described in equation (A11). See text and appendix for further details.

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APPENDIX

In this Appendix we present a brief treatment of the classical motion of a rigid body— with internal angular momentum— that is moving with respect to a given (inertial) frame and is subjected to the action of a torque which is perpendicular to the angular momentum vector. This situation is clearly related to the classical motion of molecules as described in the text.

The corresponding equations of motion will be obtained by the Hamiltonian formulation. It should be noted that the Hamiltonian formulation is developed for holonomous systems and the forces derived from a potential that depends on the position or from generalized potentials. A torque is applied to the present system. The result of the forces is zero on the center of mass and, therefore, it is meaningless to refer to potential energy.

The Hamiltonian describing the centre of mass motion of the ‘body’ is, therefore, that of a free particle but for the fact that the motion is constrained by the presence of the torque. Such constrain is expressed by the equation

$$\left(\frac{dJ}{dt}\right)_{X'Y'Z'} = \left(\frac{dJ}{dt}\right)_{XYZ} + \Omega \times J$$

(A1)

in which $\Omega$ is the rotation velocity of the frame linked to the particle $(X',Y',Z')$ about the frame of inertial reference axes $(X,Y,Z)$ (see [10]).

We use polar coordinates in the plane of motion

$$v_r = \dot{r} ; v_\theta = r \dot{\theta} ; v_Z = \dot{Z}$$

(A2)
and the corresponding momenta

\[ P_r = m\dot{r} ; \ P_\theta = mr^2 \dot{\theta} ; \ P_Z = m\dot{Z} \]  \hspace{1cm} (A3)

The Hamiltonian is then

\[ H = \frac{P_r^2}{2m} + \frac{P_\theta^2}{2mr^2} + \frac{P_Z^2}{2m} \]  \hspace{1cm} (A4)

The Hamilton equations are

\[
\dot{r} = \frac{\partial H}{\partial P_r} = \frac{P_r}{m} ; \ \ \dot{\theta} = \frac{\partial H}{\partial P_\theta} = \frac{P_\theta}{mr^2} ; \ \ \dot{Z} = \frac{\partial H}{\partial P_Z} = \frac{P_Z}{m} \]  \hspace{1cm} (A5)

\[
-\dot{P}_r = \frac{\partial H}{\partial r} = -\frac{P_\theta^2}{mr^3} ; \ -\dot{P}_\theta = \frac{\partial H}{\partial \theta} = 0 ; \ -\dot{P}_Z = \frac{\partial H}{\partial Z} = 0 \]  \hspace{1cm} (A6)

From these equations (A6) it is shown that the angular momentum orbital \( P_\theta \) is conserved.

\[ P_\theta = P_Z = \text{const.} \]  \hspace{1cm} (A7)

The first equation in (A6) gives the radial equation of motion from (A3) it results that

\[ \dot{P}_r = \frac{m^2 r^4 \dot{\theta}}{mr^3} = mr\dot{\theta}^2 \]  \hspace{1cm} (A8)

The term \(-\frac{\partial V}{\partial r}\) normally appears in this radial equation of motion and represents the force derived from a potential. In the present case, this term does not exist.

Now we incorporate the constrain, Eq. (A1), taking into account that \( \frac{dJ}{dt} \equiv \frac{dJ_{XYZ}}{dt} = 0 \), because by assumption the torque is external (with respect to the body), and \( \Gamma = \frac{dJ}{dt} \equiv \frac{dJ_{XYZ}}{dt} \) Then we have

\[ \frac{dJ_{XYZ}}{dt} = \Omega \times J \]  \hspace{1cm} (A9)

From this,

\[ \Omega = \frac{\Gamma}{J} \]  \hspace{1cm} (A10)

\( \Omega \) direction is that of the electric field that produces the torque.

In polar coordinates, the variable defining the rotation about the system of axes is \( \dot{\theta} \) and it is concluded that

\[ \dot{\theta} = \Omega = \frac{\Gamma}{J} \]  \hspace{1cm} (A11)

substituting in the radial equation of motion, one obtains:

\[ m\ddot{r} = mr\dot{\theta}^2 = mr\Omega^2 \]  \hspace{1cm} (A12)

From (A3) it results that the initial moments equals,

\[ P_\theta = mr^2 \dot{\theta} = mr\dot{v} \]  \hspace{1cm} (A13)

as \( v \) is constant, it is concluded that \( r \) is also constant.

Finally one gets

\[ r = \frac{v}{\Omega} \ \text{and} \ m\ddot{r} = mv\Omega \]  \hspace{1cm} (A14)

A geometric treatment lets to conclude that:

\[ F = m\dot{v} \times \Omega \]  \hspace{1cm} (A15)