Experimental Demonstration of the Rotational Frequency Shift in a Molecular System

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The frequency shift expected to occur analogously to the Doppler effect when an emitting quantum system is forced to rotate [Phys. Rev. Lett. **78**, 2539 (1997)] has been detected for the first time, and verified quantitatively. The experimental conditions were chosen such that the most general case was realized where perturbation theory is not applicable. Circularly polarized visible laser light tuned to a rovibronic transition, and a rotating radio-frequency electric field were applied to the strongly polar molecule H_2CS in a gaseous sample.

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The dynamics of a quantum system which is placed in a rotating environment is of general interest. Adequate situations are found in connection with the Sagnac effect [1], the Berry phase [2], quadrupole nuclear resonance in a rotating sample [3], the mechanical Faraday effect [4], or perhaps in the maser action from a fast rotating astronomical source. Details of some of these are discussed elsewhere [5]. The time dependence introduced by the rotation needs special treatment. Białynicki-Birula and Białynicka-Birula [6] have formulated an adequate theory for systems of such a kind and their interactions with light. The light of frequency ν is exploited to monitor the system spectroscopically. A frequency change,

$$\Delta\nu_{\mathrm{RFS}} = \nu(\Omega) - \nu(\Omega = 0), \tag{1}$$

will occur under certain conditions where $\nu(\Omega)$ is the frequency where the spectroscopic transition takes place, as a function of the angular frequency of rotation, Ω. The theory predicts the value of the quantity $\Delta\nu_{\mathrm{RFS}}$, which bears information about the dynamics of the system at hand, in a rather general way. It is the purpose of the present Letter to provide evidence of this quantity for a selected experimental situation. We shall call $\Delta\nu_{\mathrm{RFS}}$ the rotational frequency shift (RFS).

The well-known translational Doppler effect leads to the frequency change $\Delta\nu = \pm kV/2\pi$ when a wave of wavenumber k is absorbed or emitted by an object moving with constant velocity V along the propagation line of the light. This holds for any type of wave. An analogous phenomenon is the rotational Doppler effect which occurs when the absorbing or emitting object rotates. However, here the wave must not show rotational symmetry around the propagation direction. In other words, the wave must possess nonvanishing angular momentum. Then, when we first think of a rigid classical source or receiver rotating clockwise or anticlockwise around the propagation direction with angular frequency Ω, the change of frequency will be $\Delta\nu = \pm\Omega L/h$ where L is the total angular momentum of the light. This classical rotational Doppler effect has been verified experimentally [7,8].

Since we are more interested in quantum objects like atoms or molecules with their internal degrees of freedom, we must take care of the dynamics caused by centrifugal and Coriolis forces [6]. It is important to note that rotation in our context cannot be provided by an intrinsic rotational quantum state. External means like the dipole forces of a rotating field will have to induce the rotation, in agreement with the notion of the traditional classical Doppler effects. An approximate exception to this rule is possible when the rotation can be treated quasiclassically, and separated from the degrees of freedom which interact with the incoming or outgoing light. Examples are the fluorescence doublets which are emitted by heavy diatomic molecules in rovibronic states of high rotational quantum numbers [9].

In special situations, the theory [6] can be shown to be in accordance with alternative treatments. For example, driving an atom by an optical laser field results in the well-known dynamical Stark effect which can be handled by time-dependent perturbation theory. In this Letter we present an experimental proof of the theory for a situation where no alternative treatment seems possible. Details of the selected system are given after the following short summary of the theory's essentials.

The theory [6] predicts measurable changes of transition frequencies of a quantum mechanical system in a rotating environment, say field, as compared with the same system at rest. The predicted frequency shifts depend on two parameters: the frequency Ω of the rotating environment and a constant measuring the coupling between the quantum system under consideration and the environment or field. The transformation of the Hamiltonian into the frame corotating with the field is the most important step in the calculations. It produces an additional angular momentum term in the Hamiltonian, and incorporates the classical rotational Doppler effect [7,8] of the electromagnetic wave used for spectroscopy.

Let the total quantum system be governed by the Schrödinger equation,

$$i\hbar\frac{\partial}{\partial t}\Psi = H\Psi, \tag{2}$$

where the Hamiltonian, $H = H(x, y, z, t)$, is time dependent because of the coupling to a rotating field. Transformation into the corotating frame gives [5,6]

$$i\hbar\frac{\partial}{\partial t'}\Psi' = [H(x', y', z') - \Omega J_{z'}]\Psi' = H'\Psi', \tag{3}$$

where Ω is the angular frequency of rotation, and $J_{z'}$ is the total angular momentum operator along the rotation axis. The term $\Omega J_{z'}$ causes energetic effects which can be expressed as shifts on the frequency scale. It stands in analogy to Vp_z for the translational Doppler effect, where p_z is the z component of the linear momentum operator. Another important part of the formalism is the transformation of the electromagnetic wave of angular frequency ω_0 used for spectroscopy. The angular frequency of the wave in the rotating frame is $\omega_0 \pm \Omega$, depending on the sign of the circular polarization. This again is the classical rotational Doppler effect [7,8]. Both frequency shifts cancel completely when the system is not coupled to the rotating field [6]. Comparing the two parameters, the coupling energy $E_c = \langle\Psi|\hat{O}|\Psi\rangle$ and the driving angular energy $\hbar\Omega$, one can distinguish three cases: (i) the *fast-rotation* case where $E_c \ll \hbar\Omega$, (ii) the *strong-field* case when $E_c \gg \hbar\Omega$, and (iii) the *intermediate* case, where both parameters are comparable in magnitude.

$\hat{O}$ is an operator describing the coupling between the quantum system and the field. A more detailed discussion can be found in [5]. In this Letter we report on the experimental demonstration of the *intermediate* RFS—for a thioformaldehyde molecule put in a rotating rf electric field. We have employed high resolution, Doppler-free laser spectroscopic techniques. Thioformaldehyde, H_2CS, has been chosen for several reasons. It is one of the few molecules absorbing visible light and possessing a strong permanent electric dipole moment needed for interaction with the electric vector of the rf driving field. The optical transition $3_3\,4^1\tilde{A}^1A_2 \leftarrow 2_2\,0^0\tilde{X}^1A_1$ at 16 808.71 cm^{-1}(595 nm), a coinciding asymmetry doublet showing first-order static Stark effects [10], is well suited. Its strength is sufficient for single-scan observation, its field splittings are clearly resolved, and the rotational quantum numbers involved are low enough for an analytical RFS treatment (see below). The Hamiltonian of the free molecule subject to an electrical field rotating in the xy laboratory plane is

$$H_{g,e} = H_0(x, y, z) - \varepsilon\mu_{g,e}(\Phi_{yZ}\cos\Omega t + \Phi_{xZ}\sin\Omega t),$$

where H_0 is the molecular Hamiltonian in the rigid-rotor approximation, Φ_{xZ} and Φ_{yZ} are the direction cosine operators connecting the molecular Z with the laboratory x and y axes, respectively [11]. The indices g and e refer to the electronic ground and the excited state, respectively, ε is the electric field strength, and $\mu_g = 1.6491(4)$ D and $\mu_e = 0.815(20)$ D [10] are the electric static molecular dipole moments for the two states. In the frame corotating with the field we have

$$H'_{g,e} = H_0(x', y', z') - \varepsilon\mu_{g,e}\Phi_{y'Z} - \Omega J_{z'}, \tag{5}$$

where the last term arises from the transformation to the rotating frame, and $J_{z'}$ is the nuclear frame angular momentum component operator along the rotation axis of the rf field. The explicit form of the energy, in the prolate symmetric rotor basis for the $2_2\,0^0\tilde{X}^1A_1$ ($J = 2, K = 2$) state, reads [11]

$$H'_g(2_2) = H'_0 + \begin{pmatrix} -2\hbar\Omega & \frac{\sqrt{4}}{6}\mu_g\varepsilon & 0 & 0 & 0 \\ \frac{\sqrt{4}}{6}\mu_g\varepsilon & -\hbar\Omega & \frac{\sqrt{6}}{6}\mu_g\varepsilon & 0 & 0 \\ 0 & \frac{\sqrt{6}}{6}\mu_g\varepsilon & 0 & \frac{\sqrt{6}}{6}\mu_g\varepsilon & 0 \\ 0 & 0 & \frac{\sqrt{6}}{6}\mu_g\varepsilon & \hbar\Omega & \frac{\sqrt{4}}{6}\mu_g\varepsilon \\ 0 & 0 & 0 & \frac{\sqrt{4}}{6}\mu_g\varepsilon & 2\hbar\Omega \end{pmatrix}. \tag{6}$$

The matrix for the $3_3\,4^1\tilde{A}^1A_2$ state has a similar form. Higher order terms are negligible for the H_2CS molecule. The transition frequencies for the selection rules $\Delta m = \pm1$, calculated after diagonalizing the two matrices, are

$$\nu_{m+1\leftarrow m} = \nu_0 + \frac{1}{h}\bigg(m\sqrt{\frac{\mu_g^2\varepsilon^2}{9} + \hbar^2\Omega^2} - (m+1) \times\sqrt{\frac{\mu_e^2\varepsilon^2}{16} + \hbar^2\Omega^2} + \hbar\Omega\bigg) \tag{7}$$

and

$$\nu_{m-1\leftarrow m} = \nu_0 + \frac{1}{h}\bigg(m\sqrt{\frac{\mu_g^2\varepsilon^2}{9} + \hbar^2\Omega^2} - (m-1) \times\sqrt{\frac{\mu_e^2\varepsilon^2}{16} + \hbar^2\Omega^2} - \hbar\Omega\bigg), \tag{8}$$

respectively, where ν_0 is the zero-field transition frequency and m is the orientation quantum number of the lower state. The last terms, $\pm\Omega/2\pi$, arise from the back transformation of the light frequency to the laboratory frame. It has to be emphasized that the selection rules for the different signs of the circular polarization arise because of the rotation of the rf field, which is one of the fingerprints of the RFS. In other words, the molecule driven by the rotating field sees the frequency of the laser light shifted to higher or lower frequency depending on the handedness of the circular polarization. Another manifestation of the RFS for this system is that the frequency shift dependence on the field amplitude is not linear, see Eqs. (7) and (8) as well as Fig. 2, opposite to the static case, where the zero-field line splits proportional to the field [10]. The rotational frequency shift, for a given resonance, is then as defined in Eq. (1) where the same field strength and the same selection rules ought to be applied in the rotating and static-field situations. In Ref. [6], the quantity ΩJ_z was termed the rotational frequency shift. We prefer our definition, Eq. (1), as it is identical to the quantity measured in the experiment.

The transitions were investigated in the saturation mode guiding the 350 mW laser beam back and forth through the vapor cell, and focusing it to a diameter of about 20 μm. A cw Spectra Physics 380 D dye laser pumped by an argon-ion laser was in use. The lenses as well as the cell windows were antireflex coated in order to reduce the stray light. The cell windows were oriented perpendicular to the beam in order to not affect the purity of the polarization state of the light. The electrical field, rotating with the arbitrarily chosen frequency of $\Omega/2\pi = 80.63$ MHz, was generated by a quadrupole setup of electrodes [5]. This value is sufficiently large compared to the full width of about 5 MHz of the saturation signals, thus allowing the expected frequency shifts to be observed. In order to fulfil the condition $\hbar\Omega \approx \mu_{g,e}\varepsilon$, a maximum field of $\varepsilon = 30$ kV/m was then required. This was achieved with two rectangular oriented pairs of electrodes each separated by 3.0 mm. Starting with a common rf source, the maximum rf voltage of 100 V per electrode pair was produced in two separate selective amplifiers. In one of the two input stages, the signal passes a parallel-resonant circuit (without phase shift), while in the other it is lead through two transformer-coupled resonant circuits with a phase shift of 90°. The two output stages consist of two transformer-coupled resonant circuits, with the centers of the two secondary coils set at ground. The pairs of electrodes form part of the capacities of the secondary resonant circuits and are connected, via short cables, to these coils in parallel. Fine adjustment, which is necessary to ensure identical sinusoidal time flow of each of the two 90° out-of-phase signals, is possible by changing the damping and staggering of the two secondary resonant circuits. The transformer coupling in each of the two signal paths was carried out using a normalized coupling coefficient close to 1 which allows a largely independent adjustment of amplitude and phase separately in each path. It is possible to monitor the potential of each electrode, in an almost nonreactive manner, with the aid of a capacitive voltage divider which works with respect to ground [5]. The broadband fluorescence was observed perpendicular to the laser beam. The signals were recorded via a lock-in amplifier using effect modulation. For that the rotating electric field was amplitude modulated (switched on and off) with a frequency of about 10 kHz. A typical scan is shown in Fig. 1.

The central peak is the inverted zero-field *Lamb dip*, and the two dips on either side are the signals observed with the rotating field in action. The fifth expected dip ($1 \leftarrow 0$ in this special case) is not resolved because it is overlapped by the zero-field line. This causes one of the zero-field peak shoulders to be sharper than the other.

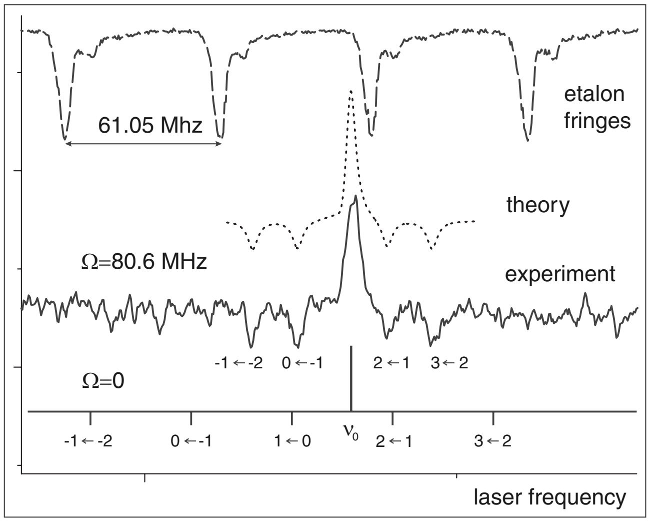

FIG. 1. Scan of the saturated optical transition $3_3\,4^1\tilde{A}^1A_2 \leftarrow 2_2\,0^0\tilde{X}^1A_1$ of H_2CS in a rotating amplitude modulated (see text) electric field (solid line). The direction of circular polarization is chosen here to cause $\Delta m = +1$ selection rules, and the rf field rotates in the same direction as the optical field vector. The simulated theoretical shape (dotted line) is shown on top of the measured signal. The static-field positions ($\Omega = 0$) of the resonances are indicated at the bottom. The $1 \leftarrow 0$ transition is hidden under the zero-field signal. The interferometer transmission signal (etalon fringes, dashed line on top) was recorded simultaneously. ε: 22.5 ± 1.2 V/mm, ν_0/c: 16 808.71 cm^{-1}, thioformaldehyde pressure: 3×10^{-2} mbar.

The results for several scans and varying electric rf field amplitude are plotted in Fig. 2. The single measurement precision of the transition frequencies is 1 MHz but instabilities of the laser system reduce the accuracy after repeated scans by about a factor of 5. The field amplitude error is estimated to ±5%. The experimental results are compared with the predictions from Eqs. (7) and (8) and satisfactory agreement is found. The measured rotational frequency shifts for the maximum achievable field strength of 30.0 V/mm are compared with the theory in Table I.

Finding an appropriate system which allowed the unambiguous discrimination of the RFS was one of the challenges of the present investigation. The rotational frequency shift, a general phenomenon like the standard Doppler shift, requires a specific set of experimental parameters in order to be observable. The experimental setup proposed in [6] for the observation of the so-called *Trojan states* [12] in atomic hydrogen could not be realized at present in our laboratory.

Summarizing, we have provided the electronics for a circulating electric field vector in the radio-frequency region to interact with the polar molecule H_2CS. The rotational frequency shift was then investigated studying the

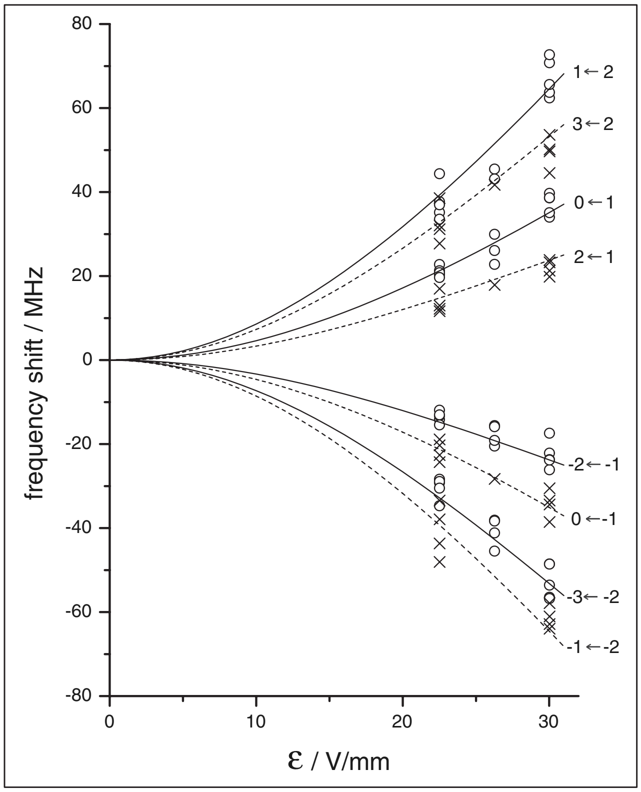

FIG. 2. Observed resonances relative to ν_0 vs electric field amplitude. The crosses indicate transitions where the direction of circular polarization was the same as that of the driving-field rotation, whereas the circles show the opposite. The m quantum transitions are indicated. The solid and dashed lines show predictions for these two cases as carried out with the aid of Eqs. (8) and (7), respectively.

TABLE I. Measured RFS as defined in Eq. (1) vs theory for the maximum achievable field strength of 30.0 V/mm in MHz. The values for the $m + 1 \leftarrow m$ transitions are mean values of four scans, those for $m - 1 \leftarrow m$ of five. The uncertainties in parentheses are the statistical standard deviations.

Transition	$-3 \leftarrow -2$	$-2 \leftarrow -1$	$0 \leftarrow 1$	$1 \leftarrow 2$
RFS measured	20.4(41)	−1.6(32)	−45.8(25)	−68.1(45)
Theory	20.0	−2.7	−47.9	−70.6
Transition	$-1 \leftarrow -2$	$0 \leftarrow -1$	$2 \leftarrow 1$	$3 \leftarrow 2$
RFS measured	73.7(27)	48.8(33)	1.0(18)	−23.7(37)
Theory	70.6	47.9	2.7	−20.0

$\Delta m = \pm 1$ selection rules of the Stark effect of a rovibronic transition of this molecule in the optical frequency range, by means of circularly polarized radiation. The frequency shifts $\Delta\nu_{\mathrm{RFS}}$ measured with respect to the static Stark effect pattern were found to be in agreement with the predictions of the theory [6]. This is an absolute comparison, parameter adjustments are not involved. The frequency Ω and the field strength ε were chosen such that the intermediate coupling case, $E_c \approx \hbar\Omega$, was realized. From Eqs. (7) and (8) we see that $\Delta\nu_{\mathrm{RFS}}$ is roughly proportional to $\sqrt{E_c^2 + \hbar^2\Omega^2} - \hbar\Omega$. For both limiting cases, $E_c \gg \hbar\Omega$ (strong field) and $E_c \ll \hbar\Omega$ (fast rotation), a perturbation treatment is possible, in terms of the parameters $\hbar\Omega/E_c$ and $E_c/\hbar\Omega$, respectively. For the strong-field case this reduces to the standard rotational Doppler effect [7,8] plus a static shift, and can also be interpreted as the energetic manifestation of the Berry phase [3,5]. The perturbation treatment of the fast-rotation case leads to the usual dynamic Stark effect [5]. Thus, the experiment has covered the most general, nonperturbative situation. If the system was placed far away from the rotational axis, relativistic corrections could become important.

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