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Laser-Induced NMR Shift for Hg^{199} Atom

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Laser-induced NMR shifts are studied theoretically by semiclassical treatment as a dynamic Stark effect of optical fields. It is proved that light shifts in optical pumping experiment and in NMR and ESR spectra are based on the identical fundamental principle. The calculated NMR shift for a Hg^{199} atom can be of the order of 1 MHz in a circularly polarized laser beam 10 W cm^{-2} at a frequency near the singlet−triplet transition absorption.

1. Introduction

Recently there has been interest in the laser-enhanced NMR and ESR effects.[1−11] Evans[1] theoretically predicted that a circularly polarized light beam could raise NMR frequencies to gigahertz levels. Warren et al.[2a] reported the experimental discovery that optical irradiation far from any absorption bands can shift the resonance in a NMR spectrum and that the shifts on the order of 1 Hz were produced in a 270 MHz spectrum. In addition, the laser-induced shifts in NMR resonance are site specific. This means that the technique is capable of providing an entirely new fingerprint of a sample.[3] Lately Warren et al.[2b] have revised their work on laser-induced NMR shifts presented in ref 2a. They found their previously reported shifts were largely due to heating effects; still, residual shifts due to other mechanisms appear to be 0.1 Hz.[2b] From Warren et al.'s experiment[2] multiple competing theories have resulted.[4−8] Evans postulated that there exists a static magnetic field parallel to the direction of propagation of a circularly polarized light beam and of strength proportional to the intensity,[4] but this would lead to huge NMR shifts, and Barron[5] pointed that it would violate charge conjugation symmetry. Harris and Tinoco[6] evaluated the change in the chemical shift of a nucleus induced by a polarized laser beam and deduced that it was far too small to be measured. Buckingham and Parlett[7,8] indicated there is an induced magnetic moment and a magnetic field at a nucleus which can produce NMR shifts when atoms and molecules subjected to a constant circularly polarized light beam, and pointed that significant shifts should be observable in atomic or molecular beam samples as resonance is approached. However, in Warren et al.'s experiments,[2] the frequency of incident light is far from any resonance of the singlet−singlet transition. So far there are no pertinent theoretical explanations of Warren et al.'s observations.[2] Much remains to be explored both theoretically and experimentally to determine the ultimate utility of this technique. In addition, theoretical investigations into the effect of a laser beam on ESR spectra indicated that observable shifts should be produced by the oscillating electric field of the laser near optical resonance,[9,10] including the laser-induced ESR shift effect occurring in a molecular or radical system.[11] All these results give us a hint and impel us to explore the internal relations of the laser-induced NMR and ESR shifts.

On the other hand, a relative phenomenon, the shifting of atomic energy levels by light, has long been studied.[12−17] Kastler's studies[12] have demonstrated that the ground-state energy level of an atom may be artificially shifted by the action of an intense beam of light. These "light shifts" were first observed in the course of detailed studies of the optical pumping of Hg^{199}.[14] The detailed experimental study of light shifts was also carried out by Arditi and Carver.[15] They showed that ordinary resonance lamps could cause light shifts as large as several hundred hertz in the 0−0 transition frequencies of rubidium and cesium. In view of the complexity of the quantum theory of optical pumping,[12] Pancharatnam[16] presented the semiclassical explanation as an optical Stark shift (or dynamic Stark shift[17]) occurring when the field is near resonance. Lately Simon and Bauch et al.[13] have verified the frequency shifts of hyperfine splitting transition in the $^2S_{1/2}$ state of cesium atom due to the blackbody radiation field.

This paper attempts to explore the influence of a laser beam on NMR spectra and obtains the following results. (i) Both the laser-induced NMR and ESR shifts and the light shifts in optical pumping are originated from the oscillating electric field of light beams. Comparing their fundamental formulas is instructive. It is verified in section 2 that Buckingham and Parlett's perturbation theory on the light-induced energy change of a polarizable atom or molecule[8,9] is consistent with that of the optical-pumping theory.[12,16] But Buckingham and Parlett emphasized correctly the contribution of antisymmetric polarizabilities. (ii) Though the previous optical-pumping theories of Hg^{199} atom provided the general formulas of light shifts, the concretely calculated results have not been found in the literature, especially on NMR spectra. As an example, the laser-induced NMR shifts for Hg^{199} atom are calculated with a laser intensity 10 W cm^{-2} at a frequency near the resonance of a singlet−triplet transition in section 3. The result shows that the shift of Hg^{199} atom near resonance can be of the order of 1 MHz, which may be detectable in a NMR experiment. (iii) The mechanism of laser-induced NMR shifts for Hg^{199} atom may be expanded to study the molecular system. We discuss this possibility in section 4 and propose that the similar NMR shift mechanism as that of Hg^{199} atom can occur in NMR spectra of a molecular or radical system, for example, which may be considered as one of possible explanations on Warren et al.'s observations.[2]

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2. Energy Level shift in an Optical Field

The oscillating electric field of a light wave can cause Stark shifts of the energy levels of an atom or molecule. The theoretical expression for this light shift may be derived using a semiclassical argument due to Pancharatnam.[16] This generalizes the expression for the energy of $-1/2\alpha E^2$ acquired by an atom of polarizability α in an external electric field E.

Consider a circularly polarized plane wave propagating in the z-direction, parallel to the external magnetic field $\boldsymbol{B}$, whose electric field at the point z at time t is[9,19]

$$\mathbf{E}_{\pm} = E_{\pm}\exp[-\mathrm{i}2\,\pi\nu(t - nz/c)] \tag{1}$$

where $E_{\pm} = \pm 2^{-1/2}\,E^{(0)}(\mathbf{i}\mp\mathrm{i}\mathbf{j})$, $\mathbf{i}$ and $\mathbf{j}$ are unit vectors in the x and y directions. $E^{(0)}$ is the scalar electric field strength of the circularly polarized laser, n the refractive index, and c the velocity of light in vacuum. $\mathbf{E}_+$ and $\mathbf{E}_-$ refer to right and left circularly polarized light, respectively.

According to the semiclassical dispersion theory,[16] it is found that, as a result of virtual transitions to the excited-state sublevel $|j\rangle$, the ground-state sublevel $|n\rangle$ will be shifted by an amount[18,19]

$$\Delta W_{\pm}^{(\mathrm{n})} = Re\langle n|\delta H_{\pm}|n\rangle \tag{2}$$

where the effective Hamiltonian is

$$\delta H_{\pm} = -{}^{1}/_{2}E_{\pm}^{*}\,\hat{\alpha}E_{\pm} \tag{3}$$

which is related to the atomic or molecular polarizability operator $\hat{\alpha}$[19,20]

$$\hat{\alpha} = \frac{1}{h}\sum_{j}\frac{\hat{\mu}|j\rangle\langle j|\hat{\mu}}{(\nu_{jn} - \nu - \mathrm{i}\Gamma/2)} \tag{4}$$

where $\hat{\mu} = \sum e_i\boldsymbol{r}_i$ is the electric dipole moment operator, $h\nu_{jn} = W^{(j)} - W^{(n)}$ is the energy difference between the excited state $|j\rangle$ and the occupied state $|n\rangle$, and Γ is the radiative width of the excited state $|j\rangle$. By substituting eqs 3 and 4 into eq 2 and simplifying the result,

$$\Delta W_{\pm}^{(n)} = -\frac{(E^{(0)})^2}{2h}\sum_{j}\frac{\nu_{jn} - \nu}{(\nu_{jn} - \nu)^2 + \Gamma^2/4}Re(\langle n|\hat{\mu}_{\pm}^{*}\,|j\rangle\langle j|\hat{\mu}_{\pm}|n\rangle) \tag{5}$$

$$= -\frac{(E^{(0)})^2}{2}\alpha_{\pm}$$

where $\alpha_{\pm}$ is the induced polarizability for a right (+) or left (−) circularly polarized laser beam. $\hat{\mu}_{\pm}$ is the dipole moment operator

$$\hat{\mu}_{\pm} = \pm 2^{-1/2}(\hat{\mu}_x \mp \mathrm{i}\hat{\mu}_y) \tag{6}$$

and $\hat{\mu}_{\pm}^{*}$ is its complex conjugate. The expression of eq 5 indicates that the interaction of the polarizability tensor $\alpha_{\pm}$ with the electric field of a circularly polarized laser beam will give rise to an energy shift of the state $|n\rangle$, which depends on the frequency-dependent polarizability and intensity of the light. This is actually similar to the quadratic Stark effect of optical fields or dynamic Stark effect.[16,17]

On the other hand, when studying the effect of circularly polarized light on ESR spectra, Buckingham and Parlett have derived the time-independent energy change of a molecule in state $|n\rangle$ by using time-dependent perturbation theory [9]

$$\Delta W_{\pm}^{(n)} = -{}^{1}/_{4}(E^{(0)})^2[(\alpha_{xx} + \alpha_{yy}) \mp 2\alpha'_{xy}] \tag{7}$$

This expression is general and not limited in the light shift of the electron spin energy levels of a system. The follows show that eqs 5 and 7 are equivalent. When substituting eq 6 into eq 5, the energy change $\Delta W_{\pm}^{(n)}$ can be written as

$$\Delta W_{\pm}^{(n)} = -\frac{(E^{(0)})^2}{4h}\sum_{j}\frac{\nu_{jn} - \nu}{(\nu_{jn} - \nu)^2 + \Gamma^2/4}[Re(\langle n|\hat{\mu}_x|j\rangle\langle j|\hat{\mu}_x|n\rangle + \langle n|\hat{\mu}_y|j\rangle\langle j|\hat{\mu}_y|n\rangle) \pm Im(\langle n|\hat{\mu}_x|j\rangle\langle j|\hat{\mu}_y|n\rangle - \langle n|\hat{\mu}_y|j\rangle\langle j|\hat{\mu}_x|n\rangle)] \tag{7a}$$

Because $\hat{\mu}_{\alpha}$ is Hermitian, this equation can be simplified and expressed in terms of the polarizability tensors

$$\Delta W_{\pm}^{(n)} = -{}^{1}/_{4}(E^{(0)})^2[(\alpha_{xx} + \alpha_{yy}) \mp (\alpha'_{xy} - \alpha'_{yx})] \tag{7b}$$

which is the same as eq 7 due to the antisymmetric polarizability $\alpha'_{xy} = -\alpha'_{yx}$. The equivalence of eqs 5 and 7 implies that the laser-induced NMR and ESR shifts and the light shift in optical pumping conform to the same fundamental principle. They may be applied to all light shifts of energy levels of an atom or molecule. In fact, eqs 5 and 7 in different forms had been applied respectively to the light shift in early optical pumping[12,16] and the shifts in NMR[8] or ESR[9−11] spectral lines recently.

Taking the transition between nuclear magnetic energy levels $|m_I = \pm{}^{1}/_{2}\rangle$ as an example, based on eq 5, the laser-induced NMR shift is

$$\Delta\nu_{\pm} = (\Delta W_{\pm}^{(-1/2)} - \Delta W_{\pm}^{(1/2)})/h = -[(E^{(0)})^2/2h](\alpha_{\pm}(-{}^{1}/_{2}) - \alpha_{\pm}(+{}^{1}/_{2})) \tag{8}$$

where $\alpha_{\pm}(-{}^{1}/_{2})$ and $\alpha_{\pm}(+{}^{1}/_{2})$ are the polarizabilities of the $|m_I = -{}^{1}/_{2}\rangle$ and $|m_I = +{}^{1}/_{2}\rangle$ states, respectively. On the basis of eq 7, eq 8 also can be written as

$$\Delta\nu_{\pm} = -\frac{E^{(0)2}}{4h}[(\alpha_{xx}(-{}^{1}/_{2}) - \alpha_{xx}(+{}^{1}/_{2})) + (\alpha_{yy}(-{}^{1}/_{2}) - \alpha_{yy}(+{}^{1}/_{2})) \mp 2(\alpha'_{xy}(-{}^{1}/_{2}) - \alpha'_{xy}(+{}^{1}/_{2}))] \tag{9}$$

$$= \Delta\nu^{s} \mp \Delta\nu^{a}$$

The first term $\Delta\nu^{\mathrm{s}}$ is dependent on the induced symmetric polarizability, and the second term $\Delta\nu^{\mathrm{a}}$ is related to the antisymmetric polarizability. They can be written as

$$\Delta\nu^{s} = {}^{1}/_{2}(\Delta\nu_{-} + \Delta\nu_{+}),\quad \Delta\nu^{a} = {}^{1}/_{2}(\Delta\nu_{-} - \Delta\nu_{+}) \tag{10}$$

It is known that the light shifts were first observed by Cohen−Tannoudji[14] in the experiment of optical pumping of Hg^{199} in the nuclear magnetic resonance signal $|m_I = {}^{1}/_{2}\rangle \rightarrow |m_I = -{}^{1}/_{2}\rangle$. As a concrete example, we calculate the laser-induced NMR shift for Hg^{199} atom in the next section.

3. Laser-Induced NMR Shift for Hg^{199} Atom

The laser-induced NMR shift is proportional to the laser intensity and the frequency-dependent polarizability tensors. It is necessary to know the wave functions and energy levels of a system first.

3.1. Hyperfine Structure Energy levels of an Atom.

Consider the *IJ* coupling approximation in which the central field and all electrostatic and magnetic interactions internal to the electron system are included in a zeroth-order Hamiltonian. We apply as a perturbation the nuclear magnetic dipole interaction and the Zeeman terms. The perturbation, then, is[21]

$$H = A\mathbf{I}\cdot\mathbf{J} + g_J\mu_B J_z B - g'_I\mu_B I_z B \tag{11}$$

where A is the magnetic hyperfine structure constant to be determined from experiment, μ_B the Bohr magneton, $g'_I = g_I\mu_N/\mu_B$ is a small number of order m_e/M (where m_e and M are the mass of an electron and proton, respectively), and the Landé g-value g_J is

$$g_J = \frac{J(J+1) + L(L+1) - S(S+1)}{2J(J+1)} + g_s\frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \tag{12}$$

Here we omit the nuclear electric quadruple interaction to simplify the problem. In fact, for Hg^{199} atom ($I = {}^1/_2$) the nuclear electric quadruple interaction is identically zero for the nuclear charge distribution is spherically symmetric.[19]

To evaluate the energy shift arising from the hyperfine interaction, in a weak field, that is, $g_J\mu_B B \ll A$, we take linear combinations of the uncoupled functions $|\gamma JIm_Jm_I\rangle$ to form new zeroth-order coupled wave functions $|\gamma JIFm_F\rangle$ for which the total angular momentum F and its projection $m_F = m_J + m_I$ are good quantum numbers. The total energy shift in the first-order perturbation of the hyperfine interaction and the Zeeman splitting is[21]

$$\Delta E_{F,m_F} = {}^1/_2 AK + g_F\mu_B Bm_F \tag{13}$$

where K is given by

$$K = F(F+1) - I(I+1) - J(J+1) \tag{14}$$

and g_F is an effective g-value analogous to eq 12

$$g_F = g_J\frac{F(F+1) + J(J+1) - I(I+1)}{2F(F+1)} - g'_I\frac{F(F+1) - J(J+1) + I(I+1)}{2F(F+1)} \tag{15}$$

The selection rules of electric dipole transitions between hyperfine levels are

$$\Delta J = 0, \pm 1\ (J = 0 \nleftrightarrow J = 0);\quad \Delta F = 0, \pm 1\ (F = 0 \nleftrightarrow F = 0);\quad \Delta m_F = 0, \pm 1 \tag{16}$$

These rules are related to the polarization of the electric vector: $\Delta m_F = 0$ corresponds to an electric dipole oscillating in the z-direction (π polarization), and $\Delta m_F = \pm 1$ corresponds to that oscillating in the $x-y$ plane (σ polarization).

For a strong field, $g_J\mu_B B \gg A$, the complete hyperfine Hamiltonian is evaluated in the uncoupled representation $|\gamma JIm_Jm_I\rangle$ and the energy obtained by using first-order perturbation theory is given by

$$\Delta E_{m_Jm_I} = g_J\mu_B Bm_J - g'_I\mu_B Bm_I + Am_Jm_I \tag{17}$$

The electric dipole selection rules are

$$\Delta m_I = 0;\quad \Delta m_J = 0\ (\pi\ \text{polarization}),\ \pm 1\ (\sigma\ \text{polarization}) \tag{18}$$

In addition, in an intermediate magnetic field, where the Zeeman interaction and the hyperfine interaction are of the same order of magnitude, all the elements of the hyperfine interaction must be evaluated and energy levels obtained by the solution of the secular equation. This is a complex case, but we can study this case approximately by using some kind of combination of weak and strong field results to approach to it.

In terms of the above discussion, we are able to draw the hyperfine splitting diagram of the singlet-triplet transition 6 $^1S_0 \rightarrow 6\ ^3P_1$ for Hg^{199} atom in a magnetic field, which is shown in Figure 1. At the left are the low-field states and at the right are the high-field states. In between, states of intermediate field. The absorption transitions are grouped according to the polarization, σ_+ and σ_-, and indicated by solid arrows pointing up.

3.2. Laser-Induced NMR Shift.

Consider the laser-induced NMR shift of Hg^{199} atom in ground state 6 $^1S_0$ by using the incident frequency near the singlet−triplet absorption transition (1.181681×10^{15} Hz, i.e., wavelength $\lambda = 253.7$ nm). It is known that if the incident frequency ν is near the absorption resonant regions, the corresponding terms in the absorption transitions will dominate over the polarizability tensors and other higher excited terms can be neglected. Thus we only study the contribution of the transition 6 $^1S_0 \rightarrow 6\ ^3P_1$ to the polarizabilities and shifts in the nuclear magnetic sublevel $|m_I = \pm{}^1/_2\rangle = |n^\pm\rangle$ of the ground state 6 $^1S_0$. Since the Zeeman splitting levels in the various cases of the magnetic field strength (see Figure 1) are different from each other, we calculate the NMR shift in two different cases: weak and strong fields.

First we discuss the laser-induced NMR shift in the case of a weak field. To simplify, we abbreviate the wavefunctions $|\gamma JIFm_F\rangle$ of the excited 6 $^3P_1$ Zeeman sublevels to $|F,m_F\rangle$. For the right circularly polarized light, based on eqs 8, 16, and Figure 1, the laser-induced NMR shift of Hg^{199} atom in ground state 6 $^1S_0$ is

$$\Delta\nu_+ = -\frac{(E^{(0)})^2}{2h^2}\left[\frac{\nu_{3/2,-3/2} - \nu}{(\nu_{3/2,-3/2} - \nu)^2 + \Gamma^2/4} Re(\langle n^-|\hat{\mu}_+^*|{}^3/_2, -{}^3/_2\rangle\langle{}^3/_2, -{}^3/_2|\hat{\mu}_+|n^-\rangle) - \frac{\nu_{3/2,-1/2} - \nu}{(\nu_{3/2,1/2} - \nu)^2 + \Gamma^2/4} Re(\langle n^+|\hat{\mu}_+^*|{}^3/_2, -{}^1/_2\rangle\langle{}^3/_2, -{}^1/_2|\hat{\mu}_+|n^+\rangle) - \frac{\nu_{1/2,-1/2} - \nu}{(\nu_{1/2,-1/2} - \nu)^2 + \Gamma^2/4} \times Re(\langle n^+|\hat{\mu}_+^*|{}^1/_2, -{}^1/_2\rangle\langle{}^1/_2, -{}^1/_2|\hat{\mu}_+|n^+\rangle)\right] \tag{19}$$

In terms of the Wigner−Ekart theorem and Clebsch−Gordan coefficient,[22,23] eq 19 can be reduced to

$$\Delta\nu_+ = -\frac{(E^{(0)})^2}{h^2}|\langle 6S_0|\hat{\mu}_x|6P_1\rangle|^2\left[\frac{\nu_{3/2,-3/2} - \nu}{(\nu_{3/2,-3/2} - \nu)^2 + \Gamma^2/4} - {}^1/_3\frac{\nu_{3/2,-1/2} - \nu}{(\nu_{3/2,-1/2} - \nu)^2 + \Gamma^2/4} - {}^2/_3\frac{\nu_{1/2,-1/2} - \nu}{(\nu_{1/2,-1/2} - \nu)^2 + \Gamma^2/4}\right] \tag{20}$$

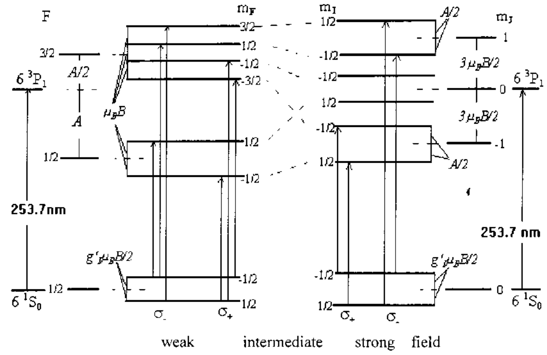

Figure 1. Zeeman splitting of hyperfine structure of the transition 6 $^1S_0 \rightarrow 6\,^3P_1$ for Hg^{199} atom in the various cases of magnetic field. At the left are the low-field states and at the right are the high-field states. The absorption transitions are grouped according to the polarization, σ_- and σ_+, and indicated by solid arrows pointing up.

Similarly, for the left circularly polarized light, we can also deduce

$$\Delta\nu_- = -\frac{(E^{(0)})^2}{h^2}|\langle 6S_0|\hat{\mu}_x|6P_1\rangle|^2\left[{}^1\!/_3\frac{\nu_{3/2,1/2}-\nu}{(\nu_{3/2,1/2}-\nu)^2+\Gamma^2/4}+{}^2\!/_3\frac{\nu_{1/2,1/2}-\nu}{(\nu_{1/2,1/2}-\nu)^2+\Gamma^2/4}-\frac{\nu_{3/2,3/2}-\nu}{(\nu_{3/2,3/2}-\nu)^2+\Gamma^2/4}\right] \quad (21)$$

On the other hand, in the case of a strong field the equations of the NMR shifts are different from eqs 20 and 21 for the various Zeeman splitting energy levels. The wavefunctions $|\gamma JIm_Jm_I\rangle$ of the excited 6 $^3P_1$ Zeeman sublevels are abbreviated to $|m_J,m_I\rangle$. Proceeding as above method, the shifts can be deduced

$$\Delta\nu_+ = -\frac{(E^{(0)})^2}{h^2}|\langle 6S_0|\hat{\mu}_x|6P_1\rangle|^2\left[\frac{\nu_{-1,1/2}-\nu}{(\nu_{-1,-1/2}-\nu)^2+\Gamma^2/4}-\frac{\nu_{-1,1/2}-\nu}{(\nu_{-1,1/2}-\nu)^2+\Gamma^2/4}\right], \quad (22)$$

$$\Delta\nu_- = -\frac{(E^{(0)})^2}{h^2}|\langle 6S_0|\hat{\mu}_x|6P_1\rangle|^2\left[\frac{\nu_{1,-1/2}-\nu}{(\nu_{1,-1/2}-\nu)^2+\Gamma^2/4}-\frac{\nu_{1,1/2}-\nu}{(\nu_{1,1/2}-\nu)^2+\Gamma^2/4}\right] \quad (23)$$

3.3. Calculation and Results. By using eqs 20–23 we have calculated the laser-induced NMR shifts of Hg^{199} atom in the ground state 6 $^1S_0$ in weak, strong, and intermediate magnetic fields, respectively. In the calculations, the value of $E^{(0)}$ is obtained from the laser intensity $I_0 = 1/2\epsilon_0(E^{(0)})^2c$. For a laser intensity 10^5 W m^{-2}, $E^{(0)} = 8.66 \times 10^3$ V m^{-1}.[9] The values of transition frequencies ν_{F,m_F} (in eqs 20 and 21) and ν_{m_J,m_I} (in eqs 22 and 23) can be calculated in terms of Figure 1 and eqs 13 and 17, where the hyperfine structure constant A is 14750.7 MHz[19] and the magnetic field B is chosen as 10^{-3} T for the weak field case, 10 T for the strong field and 1 T for the intermediate field, respectively. The "natural line width" Γ of the optically excited state 6 $^3P_1$ in the ν-scale is connected to the lifetime $\tau = 1.2 \times 10^{-7}$ s of this state by the uncertainty relation $\Gamma = 1/\tau$.[12] The matrix element $\langle 6S_0|\hat{\mu}_x|6P_1\rangle$ can be obtained from the corresponding oscillator strength and frequency. Neglecting the influence of the static magnetic field upon the matrix element $\langle n|\hat{\mu}_\alpha|j\rangle$ and assuming isotropy for the transition $n \rightarrow j$, we have for the oscillator strength[24]

$$f_{n\rightarrow j} = \frac{8\pi^2 m_e}{h}\nu_{jn}|\langle n|x|j\rangle|^2 \quad (24)$$

For the singlet–triplet transition 6 $^1S_0 \rightarrow 6\,^3P_1$ of Hg^{199} atom, the oscillator strength is 2.45×10^{-2}.[19] So the matrix element $\langle 6S_0|\hat{\mu}_x|6P_1\rangle$ is 2.21×10^{-30} C m.

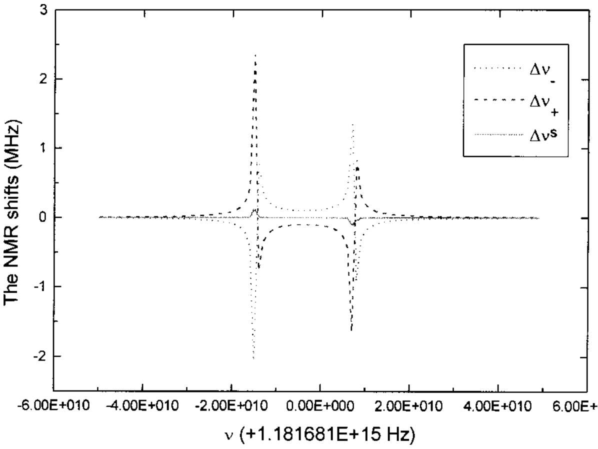

Figure 2. The NMR shifts induced in Hg^{199} atom by circularly polarized light with intensity 10 W cm^{-2} as resonance of singlet-triplet transition is approached. $\Delta\nu^s$ is the shift due to the symmetric polarizability. The magnetic field B = 10^{-3} T.

Taking the magnetic field B to be 10^{-3} T which can satisfy the criterion of weak fields, we first calculate the laser-induced NMR shifts by using eqs 20, 21, and 10 at a frequency near resonance of singlet–triplet transition. Figure 2 plots the curves of $\Delta\nu_+$, $\Delta\nu_-$, $\Delta\nu^s$ versus ν. From Figure 2, in the case of a weak field, the laser-induced NMR shifts can be of the order of 1MHz. The shifts in right and left circularly polarized beams $\Delta\nu_+$ and $\Delta\nu_-$ are nearly equal but of opposite sign, as demonstrated in optical pumping experiment of Hg^{199} atom.[14] The result indicates that the shift $\Delta\nu^s$ due to the symmetric polarizability is 3 orders of magnitude smaller than $\Delta\nu^a$ due to the antisymmetric polarizability; that is, the NMR shifts are mainly due to the contribution of the antisymmetric polarizability. This can be proved from eqs 20, 21, and 10 also. For a weak field $g_J\mu_B B \ll A$, we may neglect the energy change due to Zeeman effect and then obtain $\nu_{F,m_F} \approx \nu_{F,-m_F}$. On the basis of eqs 20 and 21, it is easy to deduce $\Delta\nu_+ \approx -\Delta\nu_-$. From eq 10 the shift from the contribution of the symmetric polarizability $\Delta\nu^s \approx 0$.

Next to take the magnetic field B to be 10 T we calculate the NMR shifts in the case of a strong field by using eqs 22, 23, and 10. The calculated values are given in Table 1, which shows that the magnitude of $\Delta\nu^s$ is of the same order as that of $\Delta\nu^a$; that is, both symmetric and antisymmetric polarizabilities make an important contribution to the shifts in NMR spectra. The shifts can be of the order of 1 MHz, which is as large as that predicted by Buckingham and Parlett for a sodium atom at the resonance to the singlet–singlet transition.[8]

In an intermediate field $g_J\mu_B B \sim A$ take B to be 1 T. We evaluate approximately the NMR shift of this case by using two methods, i.e., using eqs 20 and 21, or eqs 22 and 23, respectively. The results are given in Table 2. Comparing the two kinds of values of shifts, we find they have the same order of magnitude. This implies that the change of laser-induced NMR shifts is a gentle and continuous process as the magnetic field varies from weak, intermediate to strong.

TABLE 1: Circularly Polarized Laser-Induced NMR Shift for Hg^{199} Atom at a Frequency Near the Singlet−Triplet Transition (1.181681×10^{15} Hz) in a Strong Magnetic Field $B = 10$ T

ν (10^{15} Hz)	$\Delta\nu_+$ (kHz)	$\Delta\nu_-$ (kHz)	$\Delta\nu^s$ (kHz)	$\Delta\nu^a$ (kHz)
1.181 432	8.44	-5.90×10^{-2}	4.193	−4.252
1.181 456	72.4	-6.57×10^{-2}	36.2	−36.3
1.181 461	2.65×10^{2}	-6.72×10^{-2}	1.32×10^{2}	-1.33×10^{2}
1.181 463	1.20×10^{3}	-6.79×10^{-2}	6.00×10^{2}	-6.00×10^{2}
1.181 464	-3.19×10^{3}	-6.82×10^{-2}	-1.60×10^{3}	1.60×10^{3}
1.181 467	-3.25×10^{2}	-6.92×10^{-2}	-1.62×10^{2}	1.62×10^{2}
1.181 478	-2.15×10^{3}	-7.29×10^{-2}	-1.07×10^{3}	1.07×10^{3}
1.181 479	1.51×10^{3}	-7.32×10^{-2}	7.56×10^{2}	-7.56×10^{2}
1.181 483	1.41×10^{2}	-7.47×10^{-2}	70.4	−70.5
1.181 492	32.4	-7.81×10^{-2}	16.1	−16.2
1.181 515	6.64	-8.79×10^{-2}	3.27	−3.36
1.181 721	0.199	−0.430	−0.116	−0.315
1.181 854	8.48×10^{-2}	−9.50	−4.71	−4.79
1.181 877	7.54×10^{-2}	−88.5	−44.2	−44.3
1.181 880	7.43×10^{-2}	-1.95×10^{2}	−97.5	−97.6
1.181 883	7.32×10^{-2}	-1.51×10^{3}	-7.56×10^{2}	-7.56×10^{2}
1.181 884	7.29×10^{-2}	2.15×10^{3}	1.07×10^{3}	1.07×10^{3}
1.181 895	6.92×10^{-2}	3.24×10^{2}	1.62×10^{2}	1.62×10^{2}
1.181 898	6.82×10^{-2}	3.19×10^{3}	1.60×10^{3}	1.60×10^{3}
1.181 899	6.79×10^{-2}	-1.20×10^{3}	-6.00×10^{2}	-6.00×10^{2}
1.181 901	6.72×10^{-2}	-2.65×10^{2}	-1.32×10^{2}	-1.33×10^{2}
1.181 912	6.39×10^{-2}	−31.9	−15.9	−16.0
1.181 930	5.90×10^{-2}	−8.45	−4.19	−4.25

TABLE 2: NMR Shift of Hg^{199} as a Resonance of the Singlet−Triplet Transition Approached in a Magnetic Field $B = 1$ T

ν (10^{15} Hz)	$\Delta\nu_+{}^{a}$ (kHz)	$\Delta\nu_-{}^{a}$ (kHz)	$\Delta\nu_+{}^{b}$ (kHz)	$\Delta\nu_-{}^{b}$ (kHz)
1.181 635	12.6	−5.73	21.7	−2.80
1.181 649	1.353×10^{2}	−10.1	1.86×10^{2}	−4.51
1.181 659	-1.710×10^{2}	−17.4	-2.32×10^{2}	−6.92
1.181 665	-3.803×10^{2}	−27.1	-4.21×10^{2}	−9.44
1.181 667	-2.227×10^{3}	−32.4	-2.27×10^{3}	−10.6
1.181 669	5.089×10^{2}	−39.7	4.68×10^{2}	−12.1
1.181 674	1.39×10^{2}	−79.1	87.8	−17.0
1.181 678	1.40×10^{2}	-2.39×10^{2}	46.1	−23.8
1.181 681	7.86×10^{2}	7.53×10^{2}	32.1	−32.1
1.181 686	−32.1	1.03×10^{2}	20.0	−61.6
1.181 693	−5.05	−22.8	12.0	-4.68×10^{2}
1.181 695	−3.25	-6.55×10^{2}	10.6	2.27×10^{3}
1.181 699	−1.30	1.88×10^{2}	8.465	2.73×10^{2}
1.181 706	−0.040	2.98×10^{2}	6.02	3.24×10^{2}
1.181 709	0.178	2.32×10^{3}	5.29	2.34×10^{3}
1.181 711	0.273	-4.80×10^{2}	4.87	-4.65×10^{2}
1.181 717	0.420	−82.0	3.89	−72.6

[a] Shift calculated by using eqs 20 and 21. [b] Shift calculated by using eqs 22 and 23.

On the whole, in three cases of weak, strong and intermediate fields, the calculated laser-induced NMR shifts for a Hg^{199} atom can be of the order of 1MHz in a circularly polarized laser beam $I = 10^5$ W m^{-2} at a frequency near the singlet−triplet transition absorption, which can be detectable in NMR experiment.

4. Discussion

We now consider whether similar shifts to those of Hg^{199} will be produced in the NMR spectra of a radical or molecule. A key factor is that nearly resonant light is involved. Another important factor is the magnitude of the corresponding polarizabilities. Their magnitude will depend on certain general properties. First the frequency-dependent polarizabilities are proportional to the square of the transition dipole matrix element, i.e., the oscillator strength for the transition. Second the line width Γ is a crucial parameter affecting the magnitude of the polarizabilities near resonance, where they are proportional to Γ^{-2}.[11] This shows that the shifts decrease rapidly with increase of the line width.

If radicals or molecules meet the foregoing requirements, the laser-induced NMR shifts can be observed. For example, shifts of order of 0.1 Hz are produced in 270 MHz NMR spectrum of organic molecule *p*-methoxyphenyliminocamphor with incident laser in the 10 ∼ 20 W cm^{-2} range.[2b] The used laser wavelength 488 nm is far from the absorption peak of the singlet−singlet transition of *p*-methoxyphenyliminocamphor, but may be near the resonance of its singlet−triplet transition peak.[25,26] The favorable facts are (i) the groups $-OCH_3$, $=O$, and $-N=$ in *p*-methoxyphenyliminocamphor are favorable to relaxing the spin restrictions on singlet−triplet transition,[25−27] thus enhance the singlet−triplet absorption of the molecule. (ii) The typical peak of phosphorescence and singlet−triplet transition spectra of aromatic compounds cover the range from 450 nm to 600 nm around 500 nm[25,26] which involves the 488 nm wavelength used by Warren et al.[2b] In fact the visible and ultraviolet absorption spectrum of *p*-methoxyphenyliminocamphor in Figure 1 of ref 2a shows prominent absorption in this range. In addition, the ring protons and the methyl groups of the molecule have shown the largest laser-induced NMR shift in Figures 2 and 3 of ref 2. This is associated with the point of view of that the NMR shifts are proportional to the induced polarizabity by the hyperfine interaction, since the spin polarization in aromatic ring and the hyperconjugation system such as methyl group make them have larger hyperfine splitting respectively.[27] From the foregoing discussion, we suppose that the similar shift mechanism to that of Hg^{199} atom might play a role in Warren et al.'s experiment among multiple competing mechanisms.[2] Analogous to the phosphorescence−microwave double-resonance (PMDR) techniques,[28] this might develop to be a new technique applying to determine properties of the triplet state.

5. Conclusion

This paper studies the effect of circularly polarized laser beam on NMR spectra of an atomic or molecular system. It is proved that the laser-induced NMR or ESR shifts and the light shifts in optical pumping are due to the same physical essence, i.e., dynamic Stark effect of optical fields. Taking Hg^{199} atom as an example, we calculate the laser-induced NMR shifts in the various cases of magnetic field strength. With a circularly polarized beam of intensity 10 W cm^{-2} and frequency near resonance of singlet−triplet transition, the NMR shift of Hg^{199} can be of the order of 1 MHz, which should be observable in NMR experiment. The mechanism of laser-induced NMR shifts for Hg^{199} atom may be expanded to apply to the molecular or radical system and be considered as one of possible explanations on Warren et al.'s observations[2] among multiple competing mechanisms.

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