Laser-induced splittings in the nuclear magnetic resonance spectra of the rare gases

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Circularly polarized laser field causes a shift in the nuclear magnetic resonance (NMR) spectra of all substances. The shift is proportional to the intensity of the laser beam and yields oppositely signed values for left- and right-circularly polarized light, CPL-/+ respectively. Rapid switching — in the NMR time scale — between CPL+ and CPL- gives rise to a splitting of the NMR resonance lines. We present uncorrelated and correlated quadratic response calculations of the splitting per unit of beam intensity in the NMR spectra of 21Ne, 83Kr, and 129Xe. We study both the regions far away from and near to optical resonance and predict off-resonance shifts of the order 0.01, 0.1, and 1 × 10−6 Hz for 21Ne, 83Kr, and 129Xe, respectively, for a beam intensity of 10 W/cm². Enhancement by several orders of magnitude is predicted as the beam frequency approaches resonance. Only then can the effect on guest 129Xe atoms be potentially useful as a probe of the properties of the host material.

Nuclear magnetic resonance (NMR) spectroscopy has become one of the most successful techniques for the analysis of molecular structure [1]. Irradiation by circularly polarized light (CPL) from a laser has been proposed as a potentially useful technique of enhancing the resolution of NMR spectra [2]. Early experiments searching for the effect, in a solution of chiral molecules, reported shifts of the order of 1 Hz in a 270 MHz NMR spectrum [3]. Much of that magnitude can, however, be explained by heating effects and only a residual of at most 0.1 Hz could be interpreted as originating in other mechanisms [4]. Theory for the laser field-induced NMR shifts was presented by Buckingham and Parlett [5, 6], in terms of the inverse Faraday effect [7], i.e., induced magnetization caused by the CPL beam propagating through any sample. Since the laser-induced shifts become proportional to the square of the electric field of the laser or, equivalently, the intensity of the beam [8], initial proposals involved using high-intensity pulsed lasers to obtain shifts of the order of GHz [9]. This is, however, ruled out in NMR experiments, even leaving aside the heating problem, due to the long lifetime of the nuclear spin states. Hence, intensities of the order of tens of W/cm², obtainable from continuous wave lasers, must be considered in estimates of the order of magnitude of the induced shifts. Left- and right-circularly polarized light cause opposite shifts. If the laser field is switched between the two modes rapidly in the NMR time scale, the spectral lines are doubled, with splitting proportional to the beam intensity.

NMR of guest rare gas atoms can be used as a sensitive probe of the microstructure of the surrounding medium [10]. In this work, we present ab initio electronic structure calculations of the laser-induced splitting per unit of beam intensity in the NMR spectra of free atomic 21Ne, 83Kr, and 129Xe, both at frequencies away from and near to optical resonance. In the off-resonance region, at standard laser wave lengths and intensities, the splittings in 129Xe are below the limit of current experimental capabilities, while a large enhancement is expected when approaching resonance.

A CPL beam of frequency ω induces a magnetic field at the position of the nucleus K in a molecule given by [2]

$$B_{K\alpha}^i = \frac{1}{2\alpha} \hat{b}_{\alpha\beta\gamma}^K \left( E_{\beta}^+ \tilde{E}_{\gamma}^- - E_{\gamma}^- \tilde{E}_{\beta}^+ \right).$$

Here, $E_{\alpha}^\pm$ represents the magnetic field of the right (+) or left (−) circularly polarized beam, and $\hat{b}_{\alpha\beta\gamma}^K$ can be calculated as a third-order perturbation expression from [10]

$$\hat{b}_{\alpha\beta\gamma}^K = -\frac{\alpha^2}{2} \text{Im} \langle \sum_i \ell_{i\beta\gamma}^K \hat{r}_{i\beta}^K, r_{\gamma} \rangle_{\omega, -\omega},$$

where we have used atomic units and the notation for the quadratic response function [11] $\langle \langle A; B, C \rangle \rangle_{\omega_1, \omega_2}$ equivalent to time-dependent third-order perturbation theory with the time-dependent operators B and C, as well as their respective frequencies $\omega_1$ and $\omega_2$. In Eq. [4], $\alpha$ is the fine structure constant, $r_{\beta}$ and $r_{\gamma}$ are the components of the electric dipole moment, $\ell_{i\beta\gamma}^K$ is the distance between the electron i and the nucleus K, and $\ell_{i\beta\gamma}^K$ is the α component of the angular momentum of the electron i around the nucleus K. While $-\alpha^2 \sum_i \ell_{i\beta\gamma}^K / r_{i\beta}^K$ is the magnetic field at nucleus K due to the orbital motion of the electrons, Eq. [4] corresponds to the modification

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of this quantity by the external, time-dependent electric field.

The relevant quantity for NMR experiments in the isotropic gas or liquid phase is the isotropic rotational average

$$b_K = \frac{1}{6} \sum_{\alpha \beta \gamma} \epsilon_{\alpha \beta \gamma} b_{\alpha \beta \gamma} = \frac{1}{3} \left( b_{x_y z}^K + b_{y_z x}^K + b_{z_x y}^K \right),$$

(3)

where $\epsilon_{\alpha \beta \gamma}$ stands for the Levi-Civita tensor and $(x, y, z)$ is the molecule-fixed Cartesian frame. For spherically symmetric systems, Eq. (3) reduces to one of the components of $b_{\alpha \beta \gamma}^K$, e.g. $b_{x_y z}^K$. The induced field is stationary and oriented along the direction of propagation of the beam. It couples to the magnetic moment $\gamma_K I_K$ of nucleus $K$, and to give a term in the NMR spin Hamiltonian (in frequency units) in the high-field approximation as

$$H_{NMR} = \pm \frac{1}{4\pi} \gamma_K I_{K,Z} b_K E_0^2,$$

(4)

where $\gamma_K$ is the magnetogenic ratio of $K$, $I_{K,Z}$ is the component of $I_K$ along the external magnetic field, and $E_0$ is the amplitude of the electric field associated with the laser beam. Eq. (4) corresponds to equally large but oppositely directed frequency shifts, $\Delta$ and $-\Delta$, for the two differently polarized beams. $\Delta$ depends on the intensity $I_0$ of the beam, and becomes

$$\Delta = \frac{1}{4\pi c \epsilon_0} \gamma_K b_K I_0,$$

(5)

where $c$ and $\epsilon_0$ are the speed of light and permittivity of vacuum, respectively.

Calculations of $\Delta/I_0$ were performed with the DALTON program [13], using the implementations of analytic quadratic response functions of Ref. [14] at the ab initio self-consistent field (SCF) and multiconfiguration SCF (MCSCF) levels, and Ref. [15] using density-functional theory (DFT). We studied the basis set convergence of the laser-induced shifts, starting with the uncontracted Gaussian basis set denoted by HIVu in Ref. [15]. Diffuse (small-exponent) functions were added to each block of angular momentum until convergence of the results at the correlated MCSCF level [using the complete active space (CAS) CASSCF wave function, to estimate the range of frequencies where optical resonances occur. These ranges are 0.63–1.05 a.u. for Ne, 0.41–0.52 a.u. for Kr, and 0.35–0.45 a.u. for Xe. $\Delta/I_0$ was evaluated at frequencies approaching the resonance, too.

The results for $\Delta/I_0$ in $^{21}\text{Ne}$, $^{85}\text{Kr}$ and $^{129}\text{Xe}$ are presented in Table II. The range of the shifts, calculated at SCF level, due to a laser beam intensity of 10 W/cm$^2$ and wavelengths between 13190 and 4880 Å, is 1.7–4.7 nHz for $^{21}\text{Ne}$, 9.6–30 nHz for $^{85}\text{Kr}$, and 80–290 nHz for $^{129}\text{Xe}$. The corresponding values for $^{131}\text{Xe}$ are of the opposite sign and smaller than those for $^{129}\text{Xe}$, and can be obtained from the latter by multiplying by the quotient of the respective magnetogyratic ratios $\gamma_{131}\text{Xe}/\gamma_{129}\text{Xe} = -0.296$.

Inclusion of electron correlation at the CAS level increases $\Delta/I_0$ by about 15% for Ne, but decreases it by ca. 20% for Kr and Xe. Comparison of the results obtained with the different RAS and CAS wave functions shows that the choice of the active space is more important than using the multireference (CAS) wave functions. With CAS wave functions, correlation increases the shifts by up to around 15% for Ne and 25% for Kr and Xe, compared to the SCF level. For all atoms and frequencies, the DFT/B3LYP results are significantly larger than those corresponding to the ab initio methods. We have also tested the LDA and BLYP functionals, which resulted in even larger shifts.

The larger shifts obtained for Xe as compared to Ne and Kr can be attributed to the larger polarizability of xenon. The electron cloud is deformed in response to the external electric field, thus giving a corresponding larger induced magnetic field at the nuclear site. Results of correlated CAS calculations of $\Delta/I_0$ and the dynamic polarizability $\alpha(\omega)$, for Ne, Kr, and Xe as a function of the laser frequency $\omega$, are depicted in Fig. II. The frequency ranges from 0.1 a.u. to near the threshold of optical resonance, where the properties diverge because of the poles in linear and quadratic response functions. The growth of $\Delta/I_0$ with $\omega$, although qualitatively similar to $\alpha(\omega)$, is faster than in the latter property. There is an enhancement of $\Delta/I_0$ by several orders of magnitude when optical resonance is approached.

Finally, we have also carried out a preliminary investigation of the influence of relativistic effects on $\Delta$, by including the mass-velocity $H^{mv} = -\frac{1}{2} \alpha^2 \sum_i \nabla_i^2$, and Darwin $H^{Dar} = \frac{1}{2} \omega^2 \sum_i Z_K \sum_r \delta(r_{ik})$ Hamiltonians as additional perturbations. The relativistic corrections

$$b_K^{mv} = -\frac{\alpha^2}{2} \text{Im}(\sum_i \ell_{ik} x^2 |y, z, H^{mv})\omega, -\omega, 0),$$

(6)

$$b_K^{Dar} = -\frac{\alpha^2}{2} \text{Im}(\sum_i \ell_{ik} x^2 |y, z, H^{Dar})\omega, -\omega, 0).$$

(7)

were evaluated using cubic response functions [21] at the CAS level. The corresponding corrections to the shifts, $\Delta^{mv}$ and $\Delta^{Dar}$, have opposite signs and partially cancel each other. As expected, the relativistic effects
in $^{21}\text{Ne}$ are completely negligible. For $^{83}\text{Kr}$, $b_{\text{K}}^\text{Dar}$ and $b_{\text{K}}^\text{Kr}$ represent, individually, corrections of the same order of magnitude as the uncorrected value of $b_{\text{K}}$, although their partial cancellation finally leads to values approximately 25\% larger than the nonrelativistic value. Finally, $b_{\text{Xe}}^\text{Dar}$ and $b_{\text{Xe}}^\text{Kr}$ are larger than the nonrelativistic values, roughly by a factor of three. Their cancellation leads to a corrected value of about $-50 \text{ nHz}$ for all the frequencies studied, with $I_0 = 10 \text{ W/cm}^2$. No definitive conclusions may be drawn based on these results, however, as the response functions retain their nonrelativistic pole structure in this approach. Furthermore, picture change effects [22] on the hyperfine operator are also presently neglected. A fully relativistic quadratic response calculation would be more appropriate, and will be pursued in the future.

In summary, we have calculated the shifts induced by circularly polarized laser beam, to the NMR spectra for atomic $^{21}\text{Ne}$, $^{83}\text{Kr}$, and $^{129}\text{Xe}$ using first principles electronic structure methods. At typical beam intensities and laser frequencies, the shifts are much too small for observation, with the shift for $^{129}\text{Xe}$ predicted at the order of magnitude of 1 $\mu\text{Hz}$. Experimental techniques exploiting higher beam frequencies would benefit from the dramatic enhancement expected at near-resonant frequencies. If realised experimentally, the effect may provide a new characteristic signature of molecular structure in NMR spectroscopy.

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TABLE I: Active atomic orbital spaces of the MCSCF wave functions used.

| Atom | Wave Function | $N_e$ | Active Space |
|------|---------------|------|--------------|
| Ne   | CAS           | 8    | 2s2p → 3s3p3d |
|      | RAS-I         | 8    | 2s2p → 3s3p3d |
|      | RAS-III       | 10   | 1s2s2p → 3s3p3d4s4p4d4f5s5p |
| Kr   | CAS           | 8    | 4s4p → 4d   |
|      | RAS-I         | 8    | 4s4p → 4d   |
|      | RAS-II        | 18   | 3d4s4p → 4d4f5s5p5d |
|      | RAS-III       | 26   | 3s3p3d4s4p → 4d4f5s5p5d5f6s6p |
| Xe   | CAS           | 8    | 5s5p → 5d   |
|      | RAS-I         | 8    | 5s5p → 5d   |
|      | RAS-II        | 18   | 4d5s5p → 4f5d6s6p6d |
|      | RAS-III       | 26   | 4s4p4d5s5p → 4f5d5f6s6p6d7s7p |

$N_e$ is the number of correlated electrons.

TABLE II: Calculated laser-induced NMR line shifts per unit of laser beam intensity, $\Delta / I_0$ [in $10^{-9}$ Hz/(W cm$^{-2}$)] in rare gas atoms Ne, Kr, and Xe.

| Nucleus | $\omega$ (a.u.) | SCF   | CAS   | RAS-I | RAS-II | RAS-III | B3LYP |
|---------|-----------------|-------|-------|-------|--------|---------|-------|
| $^{21}$Ne | 0.0345439       | 0.17  | 0.19  | 0.19  | –      | 0.19    | 0.31  |
|         | 0.0428227       | 0.21  | 0.24  | 0.23  | –      | 0.24    | 0.38  |
|         | 0.0656249       | 0.32  | 0.37  | 0.36  | –      | 0.37    | 0.60  |
|         | 0.0773571       | 0.38  | 0.44  | 0.43  | –      | 0.44    | 0.71  |
|         | 0.0885585       | 0.44  | 0.51  | 0.50  | –      | 0.51    | 0.83  |
|         | 0.0932147       | 0.47  | 0.53  | 0.52  | –      | 0.53    | 0.87  |
| $^{83}$Kr | 0.0345439       | 0.96  | 0.80  | 0.80  | 0.85  | 1.49    | 1.76  |
|         | 0.0428227       | 1.17  | 1.01  | 1.01  | 1.06  | 1.86    | 2.24  |
|         | 0.0656249       | 1.92  | 1.60  | 1.60  | 1.76  | 2.98    | 3.62  |
|         | 0.0773571       | 2.34  | 1.97  | 1.97  | 2.13  | 3.57    | 4.42  |
|         | 0.0885585       | 2.82  | 2.34  | 2.34  | 2.56  | 4.26    | 5.27  |
|         | 0.0932147       | 2.98  | 2.50  | 2.50  | 2.77  | 4.53    | 5.70  |
| $^{129}$Xe | 0.0345439       | 7.99  | 5.32  | 5.32  | 9.58  | 10.65   | 19.17 |
|         | 0.0428227       | 10.11 | 6.92  | 6.92  | 12.25 | 13.31   | 24.50 |
|         | 0.0656249       | 17.04 | 12.25 | 12.25 | 20.24 | 22.90   | 41.00 |
|         | 0.0773571       | 21.83 | 15.44 | 15.44 | 25.56 | 28.22   | 51.12 |
|         | 0.0885585       | 26.62 | 19.17 | 19.70 | 31.42 | 34.61   | 62.84 |
|         | 0.0932147       | 29.29 | 20.77 | 21.30 | 34.08 | 37.81   | 68.16 |

$^a$ The frequencies correspond to wavelengths $\lambda = 13190, 10640, 6943, 5890, 5145, \text{and } 4888 \text{ Å}$, in the respective order.
FIGURE CAPTIONS

FIG. 1: Results of correlated CAS calculations of (a) the laser-induced NMR shift per unit of beam intensity $\Delta/I_0$, and (b) frequency-dependent polarizability $\alpha(\omega)$, as a function of the frequency $\omega$, for atomic Ne, Kr, and Xe.
Fig. 1, Romero and Vaara, Phys. Rev. A.