

Measurement of a Quadrupole Transition Moment by Interference of Quadrupole and dc-Field-Induced Sum-Frequency Generation

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We show that, by measuring the interference between quadrupole and dc-field-induced sum-frequency generation, both the magnitude and the sign of a quadrupole matrix element can be obtained relative to the dipole matrix elements in atomic transitions. We use the measurement of $\langle 3s|z^2|4d\rangle$ of sodium to demonstrate the technique.

In recent years, there have been a number of calculations of atomic quadrupole transition moments.¹⁻⁴ The corresponding experimental work is however extremely rare. Bogaard and Orr³ have proposed measuring the quadrupole moments by observing the field-induced birefringence of an atomic vapor in a strong electric field gradient, but concluded the effect is much too small to allow a decent signal-to-noise ratio. Lambropoulos *et al.*⁵ have reported the observation of a multi-photon ionization process involving a quadrupole transition. By comparing the ionization rate of the $(3s \rightarrow 3p \rightarrow 4f \rightarrow \text{continuum})$ process with that of the $(3s \rightarrow 3p \rightarrow 4d \rightarrow \text{continuum})$ process, they were able to deduce the $3p \rightarrow 4f$ quadrupole moment; however, the accuracy depends critically on the dipole matrix elements of $3p \rightarrow 4d$, $4d \rightarrow \text{continuum}$, and $4f \rightarrow \text{continuum}$. In this Letter, we propose and demonstrate a new nonlinear optical technique to measure quadrupole transition moments relative to the known dipole matrix elements. The technique is based on the interference between quadrupole⁶ and dc-field-induced⁷ sum-frequency generation. It gives not only the magnitude but also the sign of the quadrupole matrix elements, and has an inherently high accuracy. A similar

method based on the interference between magnetic-dipole and dc-field-induced dipole transitions in single-photon absorption has been used to measure the magnetic-dipole matrix elements in atomic vapors.⁸ As a preliminary example, we have measured the $3s \rightarrow 4d$ quadrupole moment of sodium.

The idea is simple: Let \vec{E}_1 at ω_1 and \vec{E}_2 at ω_2 be the incoming pump fields. The nonlinear polarization \vec{P}^{NL} responsible for the sum-frequency generation at $\omega_3 = \omega_1 + \omega_2$ near a quadrupole resonance is given by⁶

$$\vec{P}^{\text{NL}}(\omega_3) = [-i\vec{k}_3 \cdot \vec{\chi}_Q^{(2)} + \vec{\chi}^{(3)} \cdot \vec{E}_0] : \vec{E}_1 \vec{E}_2, \quad (1)$$

where \vec{E}_0 is the applied dc field, $\vec{\chi}_Q^{(2)}$ is the quadrupole second-order nonlinear susceptibility, and $\vec{\chi}^{(3)}$ is the third-order nonlinear susceptibility. Since the sum-frequency signal is proportional to $|P^{\text{NL}}(\omega_3)|^2$, variation of the sum-frequency signal resulting from variation of E_0 should yield a value for the ratio $\chi_Q^{(2)}/\chi^{(3)}$, from which the particular quadrupole matrix element can be deduced in terms of dipole matrix elements.

More specifically, consider the case of sodium vapor with ω_1 close to ω_{3p} and $\omega_1 + \omega_2$ resonant with ω_{4d} . Insertion of the microscopic expressions for $\vec{\chi}_Q^{(2)}$ and $\vec{\chi}^{(3)}$ in Eq. (1) leads to

$$\vec{P}^{\text{NL}}(\omega_3) \cong \frac{Ne^3}{\hbar^2} [-i\vec{k}_3 \cdot \vec{M}_Q + \vec{M}_D \cdot \vec{E}_0] \frac{\langle 4d|\vec{r}|3p\rangle\langle 3p|\vec{r}|3s\rangle : \vec{E}_1 \vec{E}_2}{(\omega_1 - \omega_{3p})(\omega_3 - \omega_{4d} + i\Gamma)},$$

where⁹ $\vec{M}_Q = \langle 3s|\frac{1}{2}\vec{r}\vec{r}|4d\rangle$ and

$$\vec{M}_D = e \sum_n \left\{ \frac{-\langle 3s|\vec{r}|np\rangle\langle np|\vec{r}|4d\rangle}{\hbar(\omega_3 - \omega_{np})} + \frac{\langle np|\vec{r}|4d\rangle\langle 3s|\vec{r}|np\rangle}{\hbar\omega_{np}} \right\}. \quad (2)$$

if we use the noncollinear geometry for sum-frequency generation shown in Fig. 1 with \vec{k}_1 and \vec{k}_2 in the \hat{x} - \hat{z} plane, \vec{k}_3 along \hat{z} , \vec{E}_0 and \vec{E}_1 along \hat{y} , and $\vec{E}_2 = (\hat{x} \cos\theta_2 + \hat{z} \sin\theta_2)E_{2h} + \hat{y}E_{2v}$, then from symmetry arguments, we can write

$$\begin{aligned} P_x^{\text{NL}}(\omega_3) &= (M_D)_{xy} F_{yx} E_0 E_1 E_{2h} \cos\theta_2, \\ P_y^{\text{NL}}(\omega_3) &= [-ik_3 (M_Q)_{yz} F_{yz} \sin\theta_2 + (M_D)_{yy} F_{yy} E_0 E_{2v}/E_{2h}] E_1 E_{2h}, \end{aligned} \quad (3)$$

where

$$F_{yx} = \frac{Ne^3}{\hbar^2} \frac{\langle 4d|y|3p\rangle\langle 3p|x|3s\rangle}{(\omega_1 - \omega_{3p})(\omega_3 - \omega_{4d} + i\Gamma)} = F_{yz} = (\sqrt{3}/2)F_{yy} = (\sqrt{3}/2)F_{zz},$$

$$(M_D)_{zz} = (M_D)_{yy} = (2/\sqrt{3})(M_D)_{xy}, \quad (M_Q)_{zz} = (2/\sqrt{3})(M_Q)_{yz}.$$
(4)

The sum-frequency field $\vec{E}_3(\omega_3)$ is now directly proportional to $[\hat{x}P_x^{NL}(\omega_3) + \hat{y}P_y^{NL}(\omega_3)]$. Thus, if \vec{E}_2 is circularly polarized so that $E_{2y}/E_{2h} = \pm i$, then the \hat{y} component of the output $\vec{E}_3(\omega_3)$ will vanish when

$$E_0 = \pm \frac{3}{4}k_3(M_Q)_{zz} \sin\theta_2 / (M_D)_{zz}. \tag{5}$$

If \vec{E}_2 is linearly polarized in the \hat{x} - \hat{z} plane, then the output \vec{E}_3 becomes circularly polarized when

$$E_0 = \pm k_3(M_Q)_{zz} \tan\theta_2 / (M_D)_{zz}. \tag{6}$$

In either case, from the measured value of E_0 , we can deduce the ratio $(M_Q)_{zz}/(M_D)_{zz}$, including the sign.

We have conducted an experiment to verify the above theoretical prediction. Our experimental setup was the same as the one described in Ref. 6 except that a pair of 1.8-cm \times 3.8-cm stainless steel plates separated by 0.095 cm were inserted in the heat pipe as electrodes. The dc voltage applied to the electrodes was in the form of a 10- μ sec square pulse synchronous to the 0.5- μ sec dye-laser pulses at $\omega_1 = 16\,900\text{ cm}^{-1}$ and $\omega_2 = 17\,649\text{ cm}^{-1}$. We operated the heat pipe at a vapor pressure of 1 Torr. In order to avoid heavy ionization of Na by resonant three-photon ionization processes, we limited the peak laser power at ω_1 to ~ 10 W and that at ω_2 to ~ 100 W. At these power levels, ionization of Na was less than 1% as judged from the induced current between the two electrodes. However, with the angle between \vec{k}_1

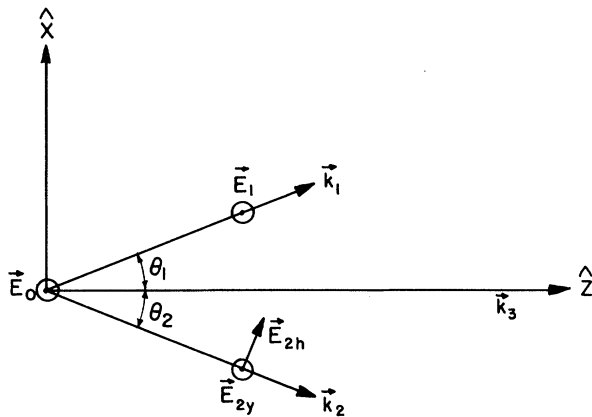


FIG. 1. Experimental geometry for sum-frequency generation. The dc field \vec{E}_0 and the laser field \vec{E}_1 are both directed along \hat{y} .

and \vec{k}_2 adjusted to phase matching for sum-frequency generation ($\theta_1 \cong \theta_2 = 13$ mrad), the output signal at $E_0 = 0$ still has a peak power of ~ 1 mW and could easily be detected.

Our results with \vec{E}_2 linearly polarized in the \hat{x} - \hat{y} plane are shown in Fig. 2 as $I_x(\omega_3)/I_y(\omega_3)$ vs E_0 , where $I_x(\omega_3)$ and $I_y(\omega_3)$ are the sum-frequency output intensities polarized along \hat{x} and \hat{y} , respectively. Following Eq. (3), we should have

$$\frac{I_x(\omega_3)}{I_y(\omega_3)} = |(M_D)_{zz}E_0[k_3(M_Q)_{zz}]^{-1}\tan\theta_2|^2, \tag{7}$$

which becomes unity when E_0 satisfies Eq. (6). When $I_x/I_y = 1$, the output should be circularly polarized. We found experimentally that this was indeed the case. In the absence of a uv circular polarizer, we did not analyze the sense of the circular polarization. Using Eq. (7) to fit the data points in Fig. 2, we obtained $|(M_Q)_{zz}/(M_D)_{zz}| = (4.4 \pm 0.4) \times 10^{-4}$ statvolt. The uncertainty was mainly due to laser power fluctuations.

We also used a Polaroid circular-polarizing

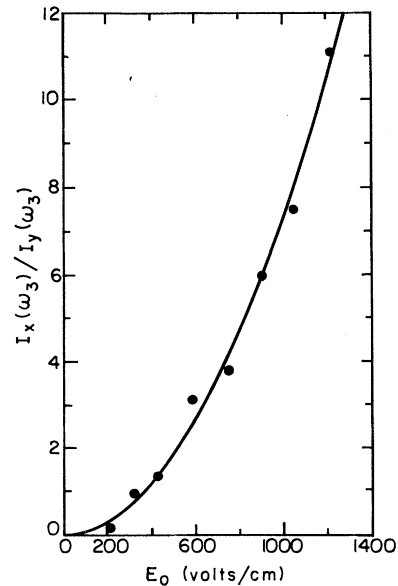


FIG. 2. $I_x(\omega_3)/I_y(\omega_3)$ as a function of the applied dc-field E_0 . $I_x(\omega_3)$ and $I_y(\omega_3)$ are phase-matched sum-frequency signals polarized along \hat{x} and \hat{y} , respectively. The solid curve is a theoretical curve obtained from Eq. (7) to fit the data points.

sheet to make \vec{E}_2 left circularly polarized so that $E_{2y}/E_{2h} \approx -i$, and measured $I_y(\omega_3)$ as a function of E_0 . According to Eq. (3), we should have

$$I_y(\omega_3) \propto \left| \frac{3}{2} k_3 (M_Q)_{zz} \sin\theta_2 / (M_D)_{zz} + E_0 \right|^2. \quad (8)$$

As E_0 increases to positive values from 0, $I_y(\omega_3)$ should first decrease if $(M_Q)_{zz}/(M_D)_{zz}$ is negative; this was the case that we found experimentally. Since the circular polarizer that we used was not perfect, $I_y(\omega_3)$ did not go exactly to zero at a certain value of E_0 as predicted by Eq. (8), but if we assume that E_0 of Eq. (5) corresponds to the observed minimum of $I_y(\omega_3)$, then we could deduce from the experimental data that $(M_Q)_{zz}/(M_D)_{zz} = -(4.45 \pm 0.8) \times 10^{-4}$ statvolt, which is very close to the value derived earlier.

We can now find the quadrupole transition moment $(M_Q)_{zz} = \langle 3s | \frac{1}{2} z^2 | 4d \rangle$ of sodium if $(M_D)_{zz}$ is known. The latter can actually be calculated from the tabulated transition frequencies and dipole matrix elements for sodium.¹⁰ According to Ref. 10, all dipole matrix elements between $3s$ and $n p$ and between $n p$ and $4d$ with $n = 3, 4, 5$, and 6 are negative except $\langle 5p | z | 4d \rangle$ which is positive. Using these matrix elements, we obtained from Eq. (2) $(M_D)_{zz} = +5.1 \times 10^3 a_0^2/\text{statvolt}$ and hence $(M_Q)_{zz} = -2.2 a_0^2$, where a_0 is the Bohr radius. This is about 50% larger than the value¹¹ of $|(M_Q)_{zz}| = 1.36$ a.u. calculated by Tull *et al.*¹ Aside from possible large uncertainty in the calculation, we do not know other causes for the discrepancy.

The technique described here can, of course, be used to measure other $s-d$ quadrupole transition moments. It can also be used to measure $p \rightarrow p$ quadrupole moments by observing interference between $s \rightarrow p \rightarrow p \rightarrow s$ quadrupole sum- (or difference-) frequency generation and $s \rightarrow p \rightarrow d \rightarrow p \rightarrow s$ or $s \rightarrow p \rightarrow s \rightarrow p \rightarrow s$ dc-field-induced sum- (or difference-) frequency generation.

The dc-field-induced sum-frequency generation is of some interest by itself. Unlike the quadrupole case, the nonlinear susceptibility $\chi^{(3)}$ gives nonvanishing sum-frequency generation for the collinear beam geometry. As a result, dc-field-induced sum-frequency generation with collinear phase matching is possible. The process is in fact more efficient than the quadrupole process at a dc field of $E_0 \approx 500$ V/cm. However, the efficiency of resonant optical mixing in metal vapor is always limited at high laser intensities by saturation, multiphoton ionization, and self-

defocusing. In order to improve the efficiency, the pump beams must be expanded. This requires greater electrode-plate separation and higher voltage across the plates in the dc-field-induced case. Consequently, the problem of avalanche breakdown initiated by multiphoton ionization of atoms in the dc field becomes much more severe and may prevent the use of the dc-field-induced process for very efficient sum- or difference-frequency generation.

We have proposed here a new technique for measuring both the magnitude and the sign of atomic quadrupole transition moments relative to the dipole matrix elements. The technique is inherently very accurate. In the present work, it is limited by the pulsed laser power fluctuations. However, since the sum-frequency signal is far above noise, it is possible that stable cw dye lasers can be used for such measurements. The accuracy of the measurements can then be greatly improved.

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¹C. E. Tull, M. Jackson, R. P. McEachran, and M. Cohen, *Can. J. Phys.* **50**, 1169 (1972).

²L. L. Boyle and J. Murray, *J. Phys. B* **2**, 433 (1969).

³M. P. Bogaard and B. J. Orr, *Mol. Phys.* **14**, 557 (1968).

⁴B. Warner, *Mon. Not. Roy. Astron. Soc.* **139**, 115 (1968).

⁵M. Lambropoulos, S. F. Moody, S. J. Smith, and W. C. Lineberger, *Phys. Rev. Lett.* **35**, 159 (1975).

⁶D. S. Bethune, R. W. Smith, and Y. R. Shen, *Phys. Rev. Lett.* **37**, 431 (1976).

⁷See, for example, J. F. Ward and I. J. Bigio, *Phys. Rev. A* **11**, 60 (1975); R. S. Finn and J. F. Ward, *Phys. Rev. Lett.* **26**, 285 (1971).

⁸M. A. Bouchiat and L. Pottier, *J. Phys. (Paris)*, *Lett.* **36**, L-189 (1975), and **37**, L-79 (1976); S. Chu, E. D. Commins, and R. Conti, to be published.

⁹In Ref. 6, we left out the factor $\frac{1}{2}$ in the quadrupole matrix element.

¹⁰R. B. Miles and S. E. Harris, *IEEE J. Quant. Electron.* **9**, 470 (1973); D. R. Bates and A. Damgaard, *Philos. Trans. Roy. Soc. London, Ser. A* **242**, 101 (1969); E. M. Anderson and V. T. Zilitis, *Opt. Spektrosk.* **16**, 177 (1964) [*Opt. Spectros. (U. S. S. R.)* **16**, 99 (1964)].

¹¹ $\langle 3s | z^2 | 4d \rangle = (2/\sqrt{45}) \langle 3s | r^2 | 4d \rangle \equiv (2/\sqrt{45}) \int_0^\infty R_{3s} r^2 R_{4d} dr$, where the radial function for the state $|nl\rangle$ is R_{nl}/r .