Nuclear Quadrupole Coupling in Polar Molecules*

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The quadrupole moment induced in various ions by the nuclear electric quadrupole moment Q has been recalculated to higher accuracy than in a previous paper. Values are presented for the ratio γ_∞ of the induced moment to Q for the Na^+, Cl^-, Cu^+, Rb^+, and Cs^+ ions. These values of γ_∞ enter into the quadrupole coupling of polar molecules, which is given by $q \cong 2e(1+|\gamma_\infty|)/R^3$ (R=internuclear distance) provided that the exchange repulsion of the ions can be neglected. The calculated values of γ_∞ are of order 10–100, in agreement with experimental evidence from the measured values of q for several polar molecules.

IT has been previously shown[1] that the nuclear electric quadrupole moment induces a large quadrupole moment in the electronic shells of the surrounding atom or ion. The ratio γ_∞ of the induced moment Q_{iT} to the nuclear moment Q was shown to be of the order of 10–100 for a series of representative ions. The large magnitude of Q_{iT} affects the values of the quadrupole coupling in polar molecules which can be represented as consisting of two (or more) ions in interaction. Another way of interpreting this effect is to consider the perturbation of the ion involved by the field of the other ion in the polar molecule. The perturbation of the ion core makes a contribution to the field gradient at the nucleus which is $|\gamma_\infty|$ times the contribution of the external charge due to the other ion, i.e., $2e|\gamma_\infty|/R^3$, where R is the internuclear distance. Although the values of the quadrupole coupling q can be determined for only a few polar molecules at present, it was shown that in most of these cases, q is larger than $2e/R^3$ by a factor of the same order of magnitude as the calculated values of $|\gamma_\infty|$, in qualitative agreement with the present considerations.

The values of γ_∞ given in Table I of I were calculated rather crudely, and an estimated error of $\pm 50\%$ was assigned to these results. Recently we have discovered that some of the values of $\gamma_\infty(nl \to l)$ were unfortunately in error and that the accuracy of the results could be improved by more refined methods of calculation. In the present note we give the revised values of $\gamma_\infty(nl \to l)$, which are probably accurate to $\pm 10\%$. The contribution $\gamma_\infty(nl \to l)$ of the nl shell is given by

$$\gamma_\infty(nl \to l) = c_l \int_0^\infty u_0' u_1' r^2 dr, \tag{1}$$

where c_l is the coefficient due to the angular part of the wave function ($c_1 = 48/25$ for $np \to p$, $c_2 = 16/7$ for $nd \to d$), u_0' is r times the radial wave function normalized according to $\int_0^\infty u_0'^2 dr = 1$; u_1' is the radial part of the perturbation due to the nuclear moment, and is determined by

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_0 - E_0\right] u_1' = u_0' \left(\frac{1}{r^3} - \left\langle \frac{1}{r^3} \right\rangle\right), \tag{2}$$

where V_0 is the spherical potential, E_0 is the unperturbed energy, and $\langle 1/r^3 \rangle$ is the average of $1/r^3$ over the unperturbed function[2] u_0'. In order to check the calculation of γ_∞, this quantity was also obtained from the perturbation $\bar{u}_1'$ due to the external charge. The radial wave function $\bar{u}_1'$ is obtained from the equation

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V_0 - E_0\right] \bar{u}_1' = u_0' (r^2 - \langle r^2 \rangle), \tag{3}$$

where $\langle r^2 \rangle$ is the average of r^2 over u_0'. In terms of $\bar{u}_1'$, $\gamma_\infty(nl \to l)$ is given by

$$\gamma_\infty(nl \to l) = c_l \int_0^\infty u_0' \bar{u}_1' r^{-3} dr. \tag{4}$$

The fact that the two expressions (1) and (4) are equivalent has been shown previously.[3] Table I gives

TABLE I. Values of γ_∞ for the Na^+, Cl^-, Cu^+, Rb^+, and Cs^+ ions.

Ion	Na^+	Cl^-	Cu^+	Rb^+	Cs^+
$\gamma_\infty(2p \to p)$	−4.7	− 1.5	− 0.62	− 0.45	− 0.26
$\gamma_\infty(3p \to p)$		−56.5	− 7.9	− 4.4	− 1.7
$\gamma_\infty(3d \to d)$			− 8.5	− 1.4	− 0.38
$\gamma_\infty(4p \to p)$				−66.6	− 10.7
$\gamma_\infty(4d \to d)$					− 4.0
$\gamma_\infty(5p \to p)$					−129.3
γ_∞(ang)	+0.6	+ 1.4	+ 2.0	+ 2.2	+ 2.9
γ_∞	−4.1	−56.6	−15.0	-70.7	−143.5

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[1] R. M. Sternheimer, Phys. Rev. **80**, 102 (1950); **84**, 244 (1951); Foley, Sternheimer, and Tycko, Phys. Rev. **93**, 734 (1954). The last paper will be referred to as I.

[2] For Na^+ we used the wave functions of V. Fock and M. Petrashen, Phys. Z. Sowjetunion **6**, 368 (1934). For Cl^- and Cu^+, the Hartree-Fock wave functions were used, while for Rb^+ and Cs^+ only Hartree wave functions (without exchange) are available. The references for these wave functions are given in I. The effective values of $V_0 - E_0$ were obtained from the wave functions u_0' according to Eq. (4) of I.

[3] R. M. Sternheimer and H. M. Foley, Phys. Rev. **92**, 1460 (1953).

the results of the calculations. For all of the cases shown in this table, the values of $\gamma_\infty(nl\to l)$ obtained from Eqs. (1) and (4) agree within $\sim 10\%$. The result listed in the table represents the average of the two values. The contribution $\gamma_\infty(\text{ang})$ of the angular modes was taken from our previous work.[1]

In comparing the values of γ_∞ in Table I with those obtained previously, two points may be noted. (1) The earlier values of $\gamma_\infty(2p\to p)$ for Na^+ and $\gamma_\infty(3d\to d)$ for Cu^+ had been unfortunately affected by rounding errors. (2) In the present calculations the method of numerical integration was somewhat different from that used in the previous work. For both Eqs. (2) and (3) a solution (u_1' or $\bar{u}_1'$) which is regular at $r=0$ was first obtained by outward numerical integration starting from the origin, as in the previous work. In addition, a solution which is regular at $r=\infty$ was obtained by inward numerical integration starting from large r. The two solutions were joined at an intermediate radius, generally in the vicinity of the outermost (principal) maximum of the unperturbed wave function u_0'. The procedure of using both solutions is necessary, particularly for u_1', in order to obtain reliable values of γ_∞ from Eq. (1). As mentioned above, the values of γ_∞ thus obtained from Eq. (1) are in good agreement with those of Eq. (4). This comparison probably provides a reliable check, since the calculations of the functions u_1' and $\bar{u}_1'$ from the differential equations (2) and (3) are completely independent of each other.

It is seen from Table I that the main conclusions of our earlier paper about the antishielding are entirely unaffected by the revised values of γ_∞ which are actually larger in all cases. Since the publication of I, additional evidence for the existence of a large antishielding has been obtained by Van Kranendonk[4] from the relaxation time in magnetic resonance experiments.

Recently Das and Bersohn[5] have obtained values of γ_∞ for Na^+ and Al^{3+} by a variational calculation in which the function $\bar{u}_1'$ is written as $u_0'r^2$ times a quadratic function of r with three undetermined coefficients. These coefficients were varied so as to minimize the second-order perturbation energy due to the external charge. For Na^+ they find $\gamma_\infty(2p\to p)=-5.23$. As shown in Table I, we obtain $\gamma_\infty(2p\to p)\cong -4.7$ using the $2p$ function of Fock and Petrashen.[2] (Actually the values obtained from Eqs. (1) and (4) were -4.68 and -4.78, respectively.) Das and Bersohn used the analytic Löwdin[6] wave functions. The small difference between their value and ours is due to the use of the different zero-order wave functions. This was established by recalculating u_1' and $\bar{u}_1'$ using the Löwdin function for u_0'. In this case, Eqs. (1) and (4) gave $\gamma_\infty(2p\to p)=-5.18$ and -5.14, respectively. These values are in satisfactory agreement with the result of Das and Bersohn, within the accuracy of the numerical calculations.

The second-order perturbation energy E_2 for the $2p\to p$ excitation due to the external charge is given by

$$E_2=-(48/25R^6)\int_0^\infty u_0'\bar{u}_1'r^2dr, \tag{5}$$

if E_2 is in Rydberg units and R is in units a_H. For the integral of Eq. (5), to be called I, Das and Bersohn have obtained $I=0.2792$. Our value as obtained with the Fock-Petrashen function is $I=0.2180$. With the function $\bar{u}_1'$ calculated using the Löwdin wave function, we found $I=0.2738$, in satisfactory agreement with the result of Das and Bersohn. The rather large difference between the values of I for the two zero-order functions u_0' (as well as the corresponding difference of the values of γ_∞) is due to the fact that the Löwdin function is somewhat more external than the function of Fock and Petrashen. Thus, although the maximum values of u_0' which occur at $r\cong 0.55a_H$ differ very little [$u_0'(0.55a_H)=1.064$ for the Löwdin function and 1.078 for the Fock-Petrashen function], there is an appreciable difference in the region of large r, which is of primary importance for E_2. Thus the Löwdin and Fock-Petrashen values of u_0' are, respectively: 0.217 and 0.205 at $r=2a_H$; 0.0481 and 0.0388 at $r=3a_H$; 0.0092 and 0.0065 at $r=4a_H$. The corresponding values of $\bar{u}_1'$ are: 0.213 and 0.189 at $r=2a_H$; 0.158 and 0.116 at $r=3a_H$; 0.068 and 0.044 at $r=4a_H$. Since the integrand of E_2 is proportional to $u_0'\bar{u}_1'$ and is weighted heavily ($\propto r^2$) for large r, this small difference of the wave functions leads to an appreciable difference of the values of E_2.

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[4] J. Van Kranendonk, Physica **20**, 781 (1954).

[5] T. P. Das and R. Bersohn, Phys. Rev. **100**, 1792(A) (1955); **102**, 733 (1956), and private communication. We are very much indebted to Dr. Bersohn and Dr. Das for informing us of their calculations in advance of publication.

[6] P. O. Löwdin, Phys. Rev. **90**, 120 (1953).