# Nuclear Quadrupole Resonance of Hg$^{201}$[†]

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Five nuclear quadrupole resonance lines have been observed in polycrystalline HgCl$_2$. From their frequencies, the magnitudes of the quadrupole coupling constants $eQq_{zz}(\text{Hg}^{201}) = 720$ Mc/sec and $eQq_{zz}(\text{Cl}^{35}) = 44.3$ Mc/sec were evaluated. Comparison of the Cl$^{35}$ coupling constant in HgCl$_2$ with that known for the free Cl atom from atomic beam experiments facilitates the discussion of the molecular structure. A quadrupole coupling constant of 1000 Mc/sec per $p$ electron in the $6s6p$ configuration of free Hg is deduced from the Hg$^{201}$ coupling in HgCl$_2$. This value can be directly compared with the coupling of the $6s6p$, $^2P_2$ HgI term, $eQq_{zz}(\text{Hg}^{201}, p_z) = 780$ Mc/sec, which is equivalent to the value of the quadrupole parameter $B = 0.27 \times 10^{-3}$ cm$^{-1}$ known from optical hfs investigations. Whereas a standard analysis of the hfs of the $^2P_2$ term had given $Q(\text{Hg}^{201}) = 0.5 \times 10^{-24}$ cm$^2$, a discrepant value $Q(\text{Hg}^{201}) = 0.2 \times 10^{-24}$ cm$^2$ was obtained from the $^1P_1$ term. Our results yield a value $0.6 \times 10^{-24}$ cm$^2$, in fair agreement with the larger value found for the $^2P_2$ term.

FIVE rf magnetic absorption lines caused by nuclear quadrupole resonance of the mercury isotope Hg$^{201}$ occurring with its natural abundance of 13.2 percent and the chlorine isotopes Cl$^{35,37}$ have been observed in polycrystalline HgCl$_2$. A number of other mercury-containing crystalline compounds have been tried also, so far without success. A superregenerative spectrometer, similar to that described by Dehmelt[1] but with increased sensitivity because of the use of narrow-band recording techniques, was employed.

Pure nuclear quadrupole resonance in solids detected first by Dehmelt and Kruger[2] is treated in a review
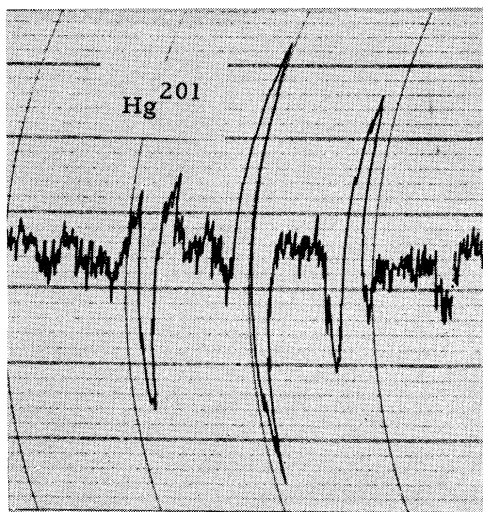


FIG. 1. Recording of the Hg$^{201}$ nuclear quadrupole resonance line at 354 207±60 kc/sec in HgCl$_2$ at room temperature. Besides the strong main line in the center, two strong and two weaker super-regeneration satellites appear on the recording; the distance between the lines is equal to the quench frequency of 200 kc/sec. Capacitive frequency modulation and detection of the second harmonic of the modulation frequency with a time constant of about 0.15 sec were used.

article by Dehmelt.[3] No previous detection of such resonance for Hg$^{201}$ has been reported, although a theoretical prediction of the Hg$^{201}$ resonance frequency in HgCl$_2$ was published by Bassompierre[4] after our measurements on this substance had been made. His predicted frequency, 230 Mc/sec, is appreciably lower than the actual frequency, 360 Mc/sec, observed in the present work (see Fig. 1). Bassompierre mentions the unpublished observations of two Cl$^{35}$ lines at 22.26 and 22.07 Mc/sec by Buyle-Bodin and Monfils. These independent observations are in essential agreement with our measurements of the Cl$^{35}$ frequencies.

The frequencies of the lines observed in HgCl$_2$ are given in Table I. They have been assigned on the assumption that only one line is expected per isotope and lattice site, as the spin of the Hg$^{201}$ isotope as well as that of the Cl isotope is $\frac{3}{2}$. The known quadrupole moment ratio of the Cl isotopes served to identify the Cl lines. Distinct, nearly linear, Cl−Hg−Cl molecules are discernible in the crystal.[5] However, the two Cl atoms do not have identical surroundings in the lattice. This explains the occurrence of two closely spaced lines for each Cl isotope.

For further interpretation of the experimental results, we shall make the assumption that the HgCl$_2$ crystal is made up of essentially separate Cl−Hg−Cl molecules. The justification is provided by the smallness of the heat of evaporation, 14 kcal/mole, as compared with the heat of formation of the molecule from the elements, about 110 kcal/mole, and by the fact that the Cl coupling is almost identical to that found[6] for Cl in gaseous CH$_3$HgCl ($eQq$ for Cl$^{35}$ = −42 Mc/sec). Furthermore, the observed coupling in solid HgCl$_2$ (44 Mc/sec) is that expected for free HgCl$_2$ from the relation of the number of unbalanced $p$ electrons to the electronegativity difference of the bonded atoms.[7]

[1] H. G. Dehmelt, Z. Physik 130, 356 (1951).
[2] H. G. Dehmelt and H. Kruger, Z. Physik 129, 401 (1951).
[3] H. G. Dehmelt, Am. J. Phys. (to be published); see also R. V. Pound, Phys. Rev. 79, 685 (1950).
[4] M. A. Bassompierre, Compt. rend. 236, 596 (1953).
[5] C28 type, *Strukturbericht* (Akademische Verlagsgesellschaft M.B.H., Leipzig, 1937), Vol. III, p. 23.
[6] W. Gordy and J. Sheridan, J. Chem. Phys. (to be published).
[7] W. Gordy, J. Chem. Phys. 19, 792 (1951).

The treatment of the electronic structure of the molecule which will yield information on the nuclear quadrupole moment of $Hg^{201}$ is facilitated by the following: the nuclear quadrupole coupling constant per unbalanced atomic $p$ electron for the free $Cl^{35}$ atom is known from atomic beam experiments[8] to be $-109.746$ Mc/sec, and the $Cl^{35}$ coupling of $-44.3$ Mc/sec found in $HgCl_2$ can be compared with it. To describe the structure of the molecule, we assign a localized molecular orbital occupied by two electrons with antiparallel spins to each of the two $Hg-Cl$ bonds. These molecular orbitals can be expressed approximately as

$$\Psi_{HgCl} = a(1/\sqrt{2})(s\pm p_z)_{Hg} \mp b(p_z)_{Cl}. \quad (1)$$

The $(s\pm p_z)_{Hg}$ denotes a hybrid consisting of equal parts of normalized real atomic $6s$ and $6p$ eigenfunctions of the mercury atom; $(p_z)_{Cl}$ is a corresponding Cl $3p$ eigenfunction. The $a$ and $b$ are positive real numbers; and the upper signs hold for one bond, the lower ones for the other bond. One should expect $\Psi_{HgCl}$ to represent the true molecular orbital best in the immediate neighborhood of the nuclei. Fortunately, the quantities we are interested in, namely, the gradients of the electric fields at the sites of the nuclei, are mainly determined by the parts of the molecular electron cloud near to the nuclei, where the approximation is best. If we try to normalize $\Psi_{HgCl}$, we get

$$1 = \int \Psi_{HgCl}{}^2 dV = a^2 + b^2 + 2ab$$
$$\times \left[ \mp \int (1/\sqrt{2})(s\pm p_z)_{Hg}(p_z)_{Cl}dV \right], \quad (2)$$

where the factor in brackets, the "overlap integral," is a positive quantity and may have a value as large as 0.5. However, the approximation of the true molecular orbital by atomic orbitals is necessarily rather crude in the overlap region. The experimental evidence for elemental molecules like $Cl_2$ [9] and $Br_2$,[10] of which the quadrupole couplings agree within 1 percent with the couplings found by atomic beam methods for the free chlorine[8] and bromine[11] atoms, does not support the thinning out of the electron cloud around the nuclei which would be demanded by normalization in this form. Taking away electronic charge from the neighborhood of the nuclei in order to build up a concentration of charge in the overlap region of the bonding orbitals should result in an increase in the molecular quadrupole coupling over that in the free atoms, which is observed for neither $Cl_2$ nor $Br_2$.

For the reasons given above, we assume the normalizing conditions, $a^2 + b^2 = 1$, to apply for the present purposes. Now $b^2$ is connected with the expression for

[8] V. Jaccarino and J. G. King, Phys. Rev. **83**, 471 (1951).
[9] R. Livingston, J. Chem. Phys. **19**, 803 (1951).
[10] H. G. Dehmelt, Z. Physik **130**, 480 (1951).
[11] J. G. King and V. Jaccarino (private communication).

TABLE I. Nuclear quadrupole resonance frequencies in $HgCl_2$.

| Isotope | Lattice site | Temperature °C | Frequency of resonance lines kc/sec | Line width kc/sec | Frequency ratio of Cl isotopes |
|---|---|---|---|---|---|
| $Hg^{201}$ | | $-186 \pm 4$ $26.1 \pm 0.5$ | $361\,966 \pm 40$ $354\,207 \pm 60$ | 75 50 | |
| $Cl^{35}$ $Cl^{37}$ | I | $30 \pm 0.5$ | $22\,230.3 \pm 0.8$ $17\,519.7 \pm 0.9$ | 1 | $1.26887$ $\pm 0.0001$ |
| $Cl^{35}$ $Cl^{37}$ | II | $30 \pm 0.5$ | $22\,050.5 \pm 0.7$ $17\,378.9 \pm 1$ | 1 | $1.2688$ $\pm 0.0001$ |

the contribution of *one* bonding electron to the molecular field gradient at the Cl nucleus:

$$q_{zz}(Cl, bond) = \int \Psi_{HgCl}{}^2 r_{Cl}{}^{-5}(3z_{Cl}{}^2 - r_{Cl}{}^2)dV. \quad (3)$$

Here $r_{Cl}$, $z_{Cl}$ are the coordinates of one bonding electron with respect to the Cl nucleus as origin. Approximately, we obtain from (1) and (3)

$$q_{zz}(Cl, bond) \approx b^2 \int (p_z)_{Cl}{}^2 r_{Cl}{}^{-5}(3z_{Cl}{}^2 - r_{Cl}{}^2)dV \quad (4)$$
$$= b^2 q_{zz}(Cl, p_z),$$

where $q_{zz}(Cl, p_z)$ stands for the field gradient caused by an atomic $p$ electron in the substate $m_l = 0$ and with decoupled electron spin. Now we have still to relate the contribution of *one* bonding electron, $q_{zz}(Cl, bond)$, to the total molecular field gradient:

$$q_{zz}(Cl, molecule) = 2q_{zz}(Cl, bond) - 2q_{zz}(Cl, p_z). \quad (5)$$

The factor two of the first term on the right arises because there are two bonding electrons. The last term is a result of the four nonbonding $p$ electrons on the Cl atom. By combining Eqs. (4) and (5) we get

$$eQq_{zz}(Cl^{35}, molecule)/eQq_{zz}(Cl^{35}, p_z) = 2(b^2 - 1). \quad (6)$$

With the molecular $Cl^{35}$ coupling observed here, $-44$ Mc/sec, and the atomic beam value of $-110$ Mc/sec, Eq. (6) yields $b^2 = 0.8$. Effects of possible $sp$ hybridization of the Cl orbitals have been neglected here in view of the rather approximate nature of the whole analysis. Also any reduction of the molecular field gradient against that in the neutral Cl atom, because of an excess negative charge on the Cl atom, has been considered negligible.

Now we shall relate the field gradient per unbalanced $p$ electron in the $6s6p$ configuration of neutral Hg, for which optical hfs data are available, with that in the $HgCl_2$ molecule. The contribution of one electron in the one $Hg-Cl$ bond is given by

$$q_{zz}(Hg, bond) = \int \Psi_{HgCl}{}^2 r_{Hg}{}^{-5}(3z_{Hg}{}^2 - r_{Hg}{}^2)dV. \quad (7)$$

This yields, approximately,

$$q_{zz}(\text{Hg, bond}) \approx (a^2/2)q_{zz}(\text{Hg, } p_z). \qquad (8)$$

The meaning of the symbols corresponds to the meaning of those used in the Cl formulas. The molecular field gradient is simply four times as large since there are two electrons in each of the two bonds and no non-bonding electrons on the Hg atom,

$$q_{zz}(\text{Hg, molecule}) = 2a^2 q_{zz}(\text{Hg, } p_z). \qquad (9)$$

With the value of $b^2$, 0.8, obtained from the Cl coupling, the normalization $a^2 + b^2 = 1$ gives $a^2 = 0.2$. This value of $a^2$ suggests that the bonding creates an electronic charge deficit of $1.2e$ on the Hg atom, so that it is essentially ionized to $\text{Hg}^+$. In terms of the valence bond resonance concepts, the contributing structures

TABLE II. Values for quadrupole coupling and quadrupole moment of $\text{Hg}^{201}$.

| Experimental method | State of $6s6p$ configuration of Hg atom | Measured[a] coupling $eQq_{zz}$ Mc/sec | Coupling per un-balanced $p$-electron $eQq_{zz}(p_z)$ Mc/sec | Quadrupole moment $Q$ $10^{-24}$ cm$^2$ |
|---|---|---|---|---|
| Optical atomic hfs | $^3P_2$ | 390 | 780 | 0.5 |
|  | $^1P_1$ | 168 | 312 | 0.2 |
| Nuclear quadrupole resonance | bonded in HgCl$_2$ | 720 | 1000 | 0.6 |

[a] The optical hfs values given in this column are the $B$ values of references 12 and 15 converted with the help of the formula given in footnote 14. While these couplings depend upon the term for which they are obtained, the $eQq_{zz}(p_z)$ values calculated from them should be the same; this, however, is not the case.

would be

| Cl⁻Hg⁺—Cl | 40 percent |
|---|---|
| Cl—Hg⁺Cl⁻ | 40 percent |
| Cl⁻Hg⁺⁺Cl⁻ | 20 percent. |

Since the fine structure doublet separation of the $6p$ electron of HgII ($\text{Hg}^+$) is considerably larger than that in the $6s6p$ configuration of neutral HgI, we have to correct for this positive charge. It is $\Delta\nu(6p, \text{HgII}) = 9322$ cm$^{-1}$, whereas $\Delta\nu(6p, \text{HgI})$, after correction for spin-orbit interaction of unlike electrons, is 5622 cm$^{-1}$.[12] Therefore, we assume a fractional increase of $(9322/5622) - 1 = 0.66$ per positive elementary charge on the Hg atom. Applying this correction, we obtain

$q_{zz}(\text{Hg, molecule})$

$$= (2a^2[1 + 0.66 \times 4(0.5 - a^2)])q_{zz}(\text{HgI, } p_z)$$

$$= 0.72 q_{zz}(\text{Hg, } p_z). \qquad (10)$$

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[12] H. Schuler and T. Schmidt, Z. Physik **99**, 285 (1936).

[Note that $q_{zz}(\text{Hg, molecule})$ is not particularly sensitive to variation of $a^2$.] With the measured $\text{Hg}^{201}$ coupling in HgCl$_2$, $eQq_{zz}(\text{Hg}^{201}$, molecule$) = 720$ Mc/sec, Eq. (10) yields for the atomic coupling constant per $p$ electron in the $6s6p$ configuration of HgI,

$$eQ^{201}q_{zz}(\text{HgI, } p_z) = 1000 \text{ Mc/sec.}$$

This is expected to be equal to the quadrupole coupling measured for the $^3P_2$ state of the $6s6p$ configuration which is independent of the type of coupling between the two electrons.[13] The value $B = 0.27 \times 10^{-3}$ cm$^{-1}$ for the quadrupole hfs parameter obtained from optical hfs measurements then is equivalent[14] to

$$eQ^{201}q_{zz}(\text{HgI, } p_z) = 780 \text{ Mc/sec.}$$

This value, when $q_{zz}(\text{HgI, } p_z)$ is calculated from the doublet separation and small relativistic corrections are applied, leads[12] to

$$Q(\text{Hg}^{201}) = 0.5 \times 10^{-24} \text{ cm}^2,$$

whereas our results indicate that

$$Q(\text{Hg}^{201}) = 0.6 \times 10^{-24} \text{ cm}^2.$$

Recently the optical hfs of the $^1P_1$ term also has been investigated.[15] Its analysis is somewhat more complicated because the type of coupling between the two electrons enters into it. The calculations give

$$Q(\text{Hg}^{201}) = 0.2 \times 10^{-24} \text{ cm}^2.$$

Our result favors the value obtained from the $^3P_2$ term. The difference between the optical value of 0.5 and our value of 0.6, however, cannot be considered significant. The various results are summarized in Table II.

Murakawa and Suwa report significant differences between the ratios of the magnetic hfs parameters $A$ of the $\text{Hg}^{199}$ and $\text{Hg}^{201}$ isotopes depending upon the term for which they are measured. Since only the magnetic moment of the $\text{Hg}^{199}$ isotope is known from nuclear magnetic resonance measurements, an experiment is under way to determine the $\text{Hg}^{201}$ magnetic moment from the Zeeman effect of the nuclear quadrupole resonance line.

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[13] H. Kopfermann, *Kernmomente* (Akademische Verlagsgesellschaft, Leipzig, 1940), Sec. 13.

[14] The hfs parameter $B$ and the atomic quadrupole coupling constant for the aligned state $m_J = J$ are related in this way:

$$eQq_{zz}(m_J = J) = (8/3)B \cdot I(2I-1) \cdot J(2J-1).$$

In the discussion of $p$ bonds, it is convenient to use the atomic coupling for a $p$ electron with decoupled electron spin in the substate $m_l = 0$ instead of $m_l = 1$ which is double the latter one. Further, it can be shown that the coupling constants for a $p_{\frac{1}{2}}(m_J = J = \frac{3}{2})$ electron and a $p(m_l = l = 1)$ electron with decoupled spin are the same.

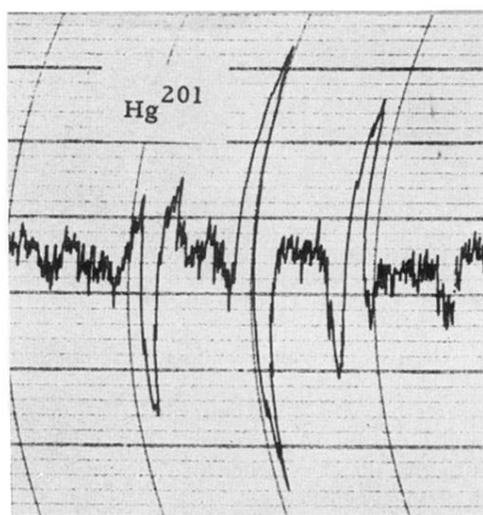[15] K. Murakawa and S. Suwa, J. Phys. Soc. Japan **5**, 429 (1950).

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