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Second-Order Magnetic Perturbations in Nuclear Quadrupole Spectra and the "Pseudo-Quadrupole" Effect in Diatomic Molecules

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IN the evaluation of nuclear quadrupole interactions from the observed molecular beam or microwave spectra, it is essential to determine whether the interaction between the nuclear magnetic moment and the fields of the orbital electrons may perturb the energy levels in the same manner as does a nuclear quadrupole moment. Van Vleck[1] has pointed out that such a perturbation may exist in the second-order magnetic interaction. It is the purpose of this note to estimate the importance of this and of several other closely related magnetic effects.

The interaction of the nuclear spin angular momentum and magnetic moment with the orbital electrons and the molecular rotation is properly treated in a representation which is the nuclear analog of Hund's "case *b*." Van Vleck[2] and Hebb[3] have treated the analogous case of the magnetic and rotational interactions of the electron spin in a diatomic molecule, starting from a "case *a*" representation. In the case of the nuclear moment interactions in a $^1\Sigma$ molecule with large rotational quantum numbers, it is simpler to proceed directly from "case *b*." In this representation the nuclear spin precesses about the axis of total angular momentum, and the orbital angular momentum vector precesses rapidly about the inter-nuclear axis. The quadrupole-like energy term, which is independent of rotational effects for large rotational quantum numbers, arises from the interaction of the nuclear magnetic moment and the moments of the rapidly precessing components of orbital angular momentum perpendicular to the molecular (Z) axis. This interaction, of the form $A(i_x l_x + i_y l_y)$ yields in second order (case *b*) an energy term

$$W' = \sum_{\Lambda} A_\Lambda^2 \langle l^2 \rangle_{\text{Av}} i^2 / 4\Delta E_{\Sigma\Lambda}, \qquad (1)$$

for a molecule in a $^1\Sigma$ state. The quantity $i\hbar$ gives the component of nuclear spin angular momentum in the direction of the molecular angular momentum, while $\langle l^2 \rangle_{\text{Av}} \hbar^2$ is the average square of the electronic angular momentum. This energy term has the same dependence on the nuclear spin angular momentum as does the electric quadrupole interaction and contributes additively with the latter term in the total energy expression. The exact evaluation of the coefficient in a particular case requires a knowledge of the molecular wave function. If Van Vleck's "hypothesis of pure precession" is assumed for the precessing orbital momentum, Eq. (1) becomes

$$W' = [(e^2\hbar^2/2m_e M_p c^2) g_N]^2 \times \langle 1/r_e^3 \rangle_{\text{Av}}^2 i^2 L(L+1)/4\Delta E_{\Sigma\pi}, \qquad (2)$$

in which g_N is the nuclear "g factor" and r_e is the distance from the nucleus to a point in the charge distribution of the electrons producing the magnetic interaction. In the cases of H_2 and the alkali molecules, such as Na_2, the combining atoms are in S-states, so that the pure precession hypothesis can hardly be made and the perpendicular components of angular momentum are expected to be small. (Evidence for this fact is given below in the case of H_2.) Insofar as the alkali halides are considered to be composed of S-state ions, the expected perpendicular momentum components will be small. It is well known,[4, 5] however, that the ground states of this class of molecules must include a contribution from a state formed from neutral atoms. The bonding P electron of the halogen atom may be considered to be precessing perpendicular to the molecular axis in these Σ-state molecules. When these considerations, together with the usual expression for $\langle 1/r_e^3 \rangle_{\text{Av}}$ involving the observed atomic fine-

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[1] Private communication to I. I. Rabi.

[2] J. H. Van Vleck, Phys. Rev. **33**, 467 (1929).

[3] M. H. Hebb, Phys. Rev. **49**, 610 (1936).

[4] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940).

[5] R. W. Mulliken, Phys. Rev. **51**, 310 (1937).

structure separation, are used to evaluate Eq. (2), the values for the F and Br nuclei in fluoride and bromide molecules are $0.045(\Gamma/d)$ mc and $0.008(\Gamma/d)$ mc, respectively. Γ is the fraction of atomic wave function in the ground state and d is the $\Sigma-\Pi$ energy separation in electron volts. From the ratio of the observed electric dipole moments to the product of the electronic charge and the inter-nuclear separation, it may be concluded that the fraction lies between one-tenth and one-half. The energy level difference d is about four volts. Thus the 'pseudo-quadrupole' effect in these molecules is about 0.001 mc. The effect on the alkali nucleus in these molecules is presumably very much smaller because of the $\langle 1/r_e^3\rangle_{\mathrm{Av}}$ factor. In the use of the 'pure precession hypothesis' and in the evaluation of the $\langle 1/r_e^3\rangle_{\mathrm{Av}}$ factor from atomic properties it is probable that the interaction energy has been overestimated.

The interaction with electron spin would lead to energy terms similar to Eq. (1) and those given below. This effect, however, in singlet molecules involves the partial decoupling of the total spin by the nuclear moment and will be very much smaller than the interaction with a precessing p-electron described in this note.

In the second-order treatment of the magnetic interactions there occurs a "cross term" between the magnetic interaction given above and the rotational perturbation which produces "Λ-doubling." This term is of the form

$$W''=\sum_{\Lambda} 2AB\langle l^2\rangle_{\mathrm{Av}} iJ/\Delta E_{\Sigma\Lambda}, \tag{3}$$

in which $B=\hbar^2/2I$. To explain the anomalously wide fluorine resonance line in the spectrum of LiF, Nierenberg and Ramsey[6] introduced a term 13.1×10^{-23} $(\mathbf{I}\cdot\mathbf{J})$ ergs into the molecular Hamiltonian. With an estimated inter-nuclear separation 1.7A and with a value of 0.1 for Γ for LiF, Eq. (3) yields for the coefficient 3.8×10^{-22} ergs when evaluated as described above. The overestimate of the effective coupling by only a factor of three is considered a reasonable support for the foregoing theory. In the case of NaBr a coupling coefficient of 5.5×10^{-23} ergs is estimated.

The "cross term" of the "Λ-doubling" matrix element and the interaction with an external magnetic field yields the expression for the electronic contribution to the magnetic moment produced by rotation.

$$\mu_R=\sum_{\Lambda} 2B\langle l^2\rangle_{\mathrm{Av}}\mu_e J/\Delta E_{\Sigma\Lambda}, \tag{4}$$

in which μ_e is the Bohr magneton. The previous methods of evaluation give $0.008J$ and $0.023J$ for the moments, in nuclear magnetons, of NaBr and LiF, respectively. Thus an average moment of not more than one nuclear magneton is to be expected in a molecular beam experiment with alkali halide molecules.

In the case of H_2 the electronic part of the molecular moment per unit angular momentum is accurately known[7] to be 0.12 nuclear magnetons. From Eq. (4) we may evaluate $\langle l^2\rangle_{\mathrm{Av}}=0.0044/ev$ which is approximately one-tenth to one-thirtieth the values estimated for the alkali halides. From this evaluation and the observed value of 2.5×10^{-22} ergs for the electronic contribution to the $c\mathbf{I}\cdot\mathbf{J}$ term, the value of the magnetic coefficient A is 3.7×10^{-18} ergs. The pseudo-quadrupole effect in HD and D_2 is consequently entirely negligible ($\sim$1 c.p.s.).

The large values of the perpendicular component of angular momentum which seem to be present in alkali halide molecules lead to a large paramagnetic contribution to the temperature-independent part of the magnetic susceptibility. It is even possible that for this class of molecules this term would be weakly paramagnetic.

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[6] W. Nierenberg and N. F. Ramsey (to be published).

[7] N. F. Ramsey, Phys. Rev. **58**, 226 (1940).