Possible P,T-odd effects in NMR spectroscopy of molecules

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The methods of NMR spectroscopy might be useful for an experimental search of P- and T-odd effects in molecules. The accuracy of such measurements is estimated. The existing upper limit on the electric dipole moment of the proton might be reduced by two orders of magnitude by taking this approach.

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The most stringent limit on the electric dipole moment of the proton (and thus on the constant of the P,T-odd electron-nucleus interaction) was established in an experiment by Hinds and Sandars[1] by a magnetic-resonance method with a molecular beam of TlF molecules. In this letter we show that this limit could in principle be lowered even further by making use of the high-precision methods[2] for measuring NMR shifts.

The effective P,T-odd interaction of electrons with a nucleus can be described as follows[3] in a system of units with $\hbar = e = 1$:

$$V_{P,T} = V_{P,T}^{(1)} + V_{P,T}^{(2)} = \frac{i\,a^2}{m^3}\,(\,Zg_1\,S + g_2 I\,)\,[\,P,\delta\,(\,r - R\,)\,], \tag{1}$$

where m, S, P, and r are the mass, spin, momentum, and coordinate of the electron in the molecule; Z, I, and R are the charge, spin, and coordinate of the nucleus; α is the fine-structure constant; $g_{1,2}$ are the constants of the P,T-odd interaction of neutral currents; and the square brackets denote the commutator.

Nuclear-magnetic-resonance methods can be used to determine the constant g_2; a limit on this constant is simultaneously a limit on the electric dipole moment of the nucleus, d_n

$$g_2 \longleftrightarrow \frac{\alpha m^2}{M}\,d_n\,, \tag{2}$$

where M is the mass of the nucleus (see the discussion in Ref. 3 of a corresponding relationship between the constant g_1 and the electric dipole moment of the electron).

Since the matrix elements $\langle V_{P,T} \rangle$ increase rapidly with increasing Z ($\langle V_{P,T}^{(2)} \rangle \sim Z^2$), we would like to use molecules containing a heavy nucleus. The magnetic hyperfine structure of the levels in such molecules is determined by the intereaction $V_{hf} = A\mu_e\mu_n$ (μ_e and μ_n are the magnetic moments of the electron and the nucleus). Admittedly, we have $\langle \mu_e \rangle = 0$ for a singlet, nondegenerate state (which the ground state of the molecule usually is). Under these conditions the hyperfine structure is usually determined by the electric quadrupole moment of the heavy nucleus. If $I = 1/$

2, on the other hand, there is no quadrupole interaction, and the hyperfine structure is determined by the corrections to V_{hf} which incorporate an admixture of excited electronic states due to an interaction of the electron motion with the rotation, $V_{er} = BJL$ (L is the orbital angular momentum of the electrons in the molecule, J is the total rotational angular momentum of the molecule, and B is the rotational constant):

$$\Delta E_{hf} = 2 \, \text{Re} \, \sum_i \frac{<0 \, | \, V_{hf} \, | \, i><i \, | \, V_{er} \, | \, 0>}{E_0 - E_i} , \qquad (3)$$

where $|0\rangle$, $|i\rangle$, E_0, and E_i are the wave functions and energies of the ground and electronically excited states of the molecule, respectively. In order of magnitude, we would have $\Delta E_{hf} \sim 10^5$ Hz in heavy molecules.

In an external magnetic field H the Zeeman level splitting ΔE_H of the heavy molecule is determined primarily by the interaction $V_H = -\mu_e H$. With $H \sim 10^3$ G we find $\Delta E_H \sim 10^6$ G. In such a field, therefore, the hyperfine structure of the molecule is disrupted because the hyperfine interaction is slight,[3] and the moments μ_e and μ_n are independently quantized along the field direction: $\Delta E_H \sim \mu_n H M_I$, where M_I is the projection of the nuclear spin.

If the molecule is also in an external electric field E, we find, using the interaction $V_{P,T}^{(2)}$, a shift of the magnetic-resonance frequency[3]:

$$\Delta E_E = 2 \, \text{Re} \, \sum_{r'} \frac{<r \, | \, V_{P,T}^{(2)} \, | \, r'><r' \, | \, V_E \, | \, r>}{E_r - E_{r'}} , \qquad (4)$$

where $V_E = -dE$, the operator d represents the electric dipole moment of the molecule, and $|r\rangle$, $|r'\rangle$, E_r, and $E_{r'}$ are the wave functions and energies of the rotational states. In a strong magnetic field we would have $\langle V_{P,T} \rangle \langle V_E \rangle \sim M_I f(M^2)$, where M is the projection of the total angular momentum J, and f is some function.

For diatomic molecules in the Σ state the parity of a rotational sublevel is determined by its quantum number J. The summation in (4) is over the states whose parity is opposite that of the states $|r\rangle$.

For polyatomic molecules which are stereoisomers, the states which occur are usually not the states $|\pm\rangle$ but the right-handed (or left-handed) states $|R, L\rangle$. The summation in (4) is over the rotational states having the same helicity R, L as that of the state $|r\rangle$, i.e., simply over the states of the right-handed (or left-handed) molecule. Here $\langle R \, | V_{P,T} | R \rangle = -\langle L \, | V_{P,T} | L \rangle$ and $\langle R \, | V_E | R \rangle = -\langle L \, | V_E | L \rangle$, so that the sign of the correction is the same for the R and L molecules.

The primary distinction between this proposed NMR experiment in the liquid phase and the corresponding experiment in a molecular beam[1] is that in the latter case a definite rotational level can be isolated, while in the former case a signal is received simultaneously from all the levels which are populated at the given temperature. In the case of a diatomic molecule we would have $E_{\text{rot}} = BJ(J+1)$, and at the temperature $T = 100$ K with $B \sim 1$ cm^{-1} (a typical value for heavy molecules) the levels with $J \lesssim 10$ would be populated.

For diatomic molecules we can single out a dependence of the matrix elements on the rotational quantum numbers.[4] Using (4) we can write the resultant frequency shift for a liquid-phase experiment in the form

$$\Delta E_E = 2\frac{\Delta E^{\,\circ}_E}{Z_\circ} \sum_{J,M} \sum_{J',M'}$$

$$\frac{(2J+1)\ (2J'+1)}{J'(J'+1)-J(J+1)}\begin{pmatrix} J' & 1 & J \\ -M & q & M \end{pmatrix}^2 \begin{pmatrix} J' & 1 & J \\ 0 & 0 & 0 \end{pmatrix}^2 e^{-\frac{BJ(J+1)}{kT}}, \tag{5}$$

where Z_0 is the partition function of $-BJ(J+1)/kT$,

$$Z_\circ = \sum_J (2J+1)\,e^{\,\prime} \tag{6}$$

and $\Delta E^{\,\circ}_E$ is the frequency shift in the lower rotational level for the beam experiment. The expression in the summation in (5), except for the temperature factor, is antisymmetric with respect to the interchange $JM \leftrightarrow J'M'$. This circumstance means that the various terms of the sum cancel out to a progressively greater degree as the temperature is increased (i.e., as the temperature factor approaches unity). Expanding the sum in (5) in J' and M', and substituting in the values of the $3j$ symbols, we find

$$\Delta E_E = \frac{\Delta E^{\circ}_E}{Z_\circ}\sum_{JM}\frac{1}{(2J+1)}\left(e^{-\frac{BJ(J+1)}{kT}} - e^{-\frac{B(J+1)(J+2)}{kT}} \right)$$

$$= \frac{\Delta E^{\circ}_E}{Z_\circ}\left(\sum_{J=0}^{\infty} e^{-\frac{BJ(J+1)}{kT}} - \sum_{J=1}^{\infty} e^{-\frac{BJ(J+1)}{kT}} \right) = \frac{\Delta E^{\circ}_E}{Z_\circ}. \tag{7}$$

The partition function Z_0 can be evaluated by replacing the exponential population distribution by a square distribution, for which $Z_0 = (J_{\max}+1)^2$. Taking this approach, we find the estimate

$$\Delta E_E \sim \frac{\Delta E^{\,\circ}_E}{J^2_{\max}} \sim 10^{-2}\,\Delta E^{\circ}_E, \ (T \sim 100\ \text{K}). \tag{8}$$

Corresponding estimates can be found for polyatomic molecules. In the case of a spherical top we should replace $\begin{pmatrix} J' & 1 & J \\ 0 & 0 & 0 \end{pmatrix}$ in (5) by $\begin{pmatrix} J' & 1 & J \\ -k' & q' & k \end{pmatrix}$, where k is the projection of the angular momentum J on some internal direction, and we should sum over k and k'. The remainder of sum (5) is proportional to

$$\sum_{M}^{J_{max}} \sum_{k}^{J_{max}} \frac{1}{J_{max}} \sim J_{max}.$$

In expression (6) for Z_0 we must now replace the factor $(2J+1)$ by $(2J+1)^2$, so that we have Z_0 in the approximation of a square distribution. As a result, we find the same estimate, (8). The symmetric-top molecule is an intermediate case between that of a linear molecule and a spherical top, so that estimate (8) should also be valid in this case.

For experiments in the liquid phase there is accordingly a suppression factor $\sim 10^{-2}$ at $T \sim 100$ K. Since $BJ_{max}^2 \cong kT$, this factor is inversely proportional to the temperature. This factor can also be reduced by choosing a molecule with a larger value of B, but then strong external electric fields would be needed to compensate for the rotational denominator in (4) (without this compensation, an additional small factor would arise in the expression for ΔE_E). In the case $B \sim 1$ cm^{-1} we would need a field $E \sim 10^4$ V/cm^3.

The positions and shifts of NMR lines can be measured by high-precision NMR methods within $\sim 10^{-4}$–10^{-5} Hz in a time[2] ~ 100 s. By making use of the correlation between the shift of the resonant frequency and the switching of the electric field one could improve the accuracy even further, by increasing the measurement time (accumulation time), without running into the danger of long-term instabilities of the resonant levels, a residual nonuniformity of the magnetic field, etc.

In summary, since the measurement accuracy in the experiment of Ref. 1 was 8×10^{-2} Hz, this proposed experiment can be expected to improve the upper limit on the electric dipole moment of the nucleus (in the case of a nucleus having a single valence proton, this would also be an estimate of the electric dipole moment of the proton, d_p) by a factor of about 100, to $d_e/e \sim 10^{-22}$ cm.

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