# *P*-odd effects in polyatomic molecules

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We consider the corrections that must be introduced in the hyperfine structure of stereoisomers to account for a parity-nonconserving interaction. We show that experiments of the magnetic-resonance type are usually accurate enough to determine one of the heretofore-unmeasured constants of the *P*-odd interaction. Experiments on the observation of the linear Stark effect in stereoisomers can yield independent estimates of the *P*, *T*-odd interactions, with the degree of accuracy attainable at the present time.

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## §1. INTRODUCTION

Investigations of *P*-odd effects in atoms have so far led to the determination of one of the constants of the interaction due to weak neutral currents.[1] *P*-odd effects were discussed also in diatomic molecules[2-4] (optical rotation, circular polarization of resonant fluorescence) and in polyatomic molecules[5-9] (energy difference of stereoisomers).

The experiments aimed at observing *P*, *T*-odd effects in atomic physics have led so far only to an upper bound of the *P*, *T*-odd interaction constant.[1] Labzovskiĭ, Sushkov, and Flambaum[2,3] have suggested experiments on diatomic molecules, capable of increasing the measurement accuracy of one of the constants.

We consider in this paper the difference between the hyperfine structure (hfs) and the Zeeman structure of the levels of right-hand and left-hand molecules, due to *P*-odd interactions, as well as the Stark structure due to *P*, *T*-odd interactions. An investigation of these effects can yield, in principle, information on the heretofore unknown constants of the *P*- and *P*, *T*-odd interactions. We write the effective potentials of the *P*- and *P*, *T*-odd interactions of an electron with a nucleus in the form (we use the units $\hbar = e = 1$ throughout)[1]

$$V_P=V_P^1+V_P^2+V_P^3=\frac{G\alpha^2}{2\sqrt{2}m}\{(Zg_1\mathbf{s}+g_2\mathbf{I})[\mathbf{p},\times\delta(\mathbf{r}-\mathbf{R})]_+ + ig_3[\mathbf{s}\times\mathbf{I}][\mathbf{p}\times\delta(\mathbf{r}-\mathbf{R})]_-\}, \tag{1}$$

$$V_{PT}=V_{PT}^1+V_{PT}^2+V_{PT}^3=\frac{G\alpha^2}{2\sqrt{2}m}\{i(Zh_1\mathbf{s}+h_2\mathbf{I})[\mathbf{p},\delta(\mathbf{r}-\mathbf{R})]_- + h_3[\mathbf{s}\times\mathbf{I}][\mathbf{p}\times\delta(\mathbf{r}-\mathbf{R})]_+\},$$

where $m$, **s**, **p**, and **r** are the mass, spin, momentum and the coordinate of the electron, $Z$, **I**, and **R** are the charge, spin, and coordinate of the nucleus, $G$ is the Fermi constant, $\alpha$ is the fine-structure constant, and $g_i$ and $h_i$ are the constants of the *P*- and *P*, *T*-odd interactions. In the cited atomic experiments they measured the constant $g_1$.

Some of the following sections of the article are not connected directly with parity-nonconservation effects, but their results are used in §§5, 6 to estimate these effects.

## §2. STEREOISOMERS

Linear and planar polyatomic molecules offer no apparent advantages whatever over diatomic molecules in the search for effects of parity nonconservation. We confine ourselves therefore to nonplanar molecules.

The potential-energy surface for a polyatomic molecule can have several minima. If the barriers between them are high, the molecule can stay a long time in one of the minima. Molecules located in different minima can be regarded as different modifications of the material.

If the molecule has no mirror symmetry elements, there exist two potential minima that go over into each other under the inversion operation. These two molecule configurations are arbitrarily called right- and left-hand, and the molecule itself is called a stereoisomer.

The states $\psi_{R,L}$ of right- and left-hand molecules have no definite parity; the inversion operation transform the stereoisomers into each other:

$$P\psi_{R,L}=\psi_{L,R}. \tag{2}$$

Thus, stereoisomers can differ in those physical properties for which the difference between the right and left is important. In particular, they interact differently with right- and left-polarized light, and this leads to optical rotation.

If the Hamiltonian of the system commutes with the inversion operator, the stationary states $\psi_\pm$ with energy $E_\pm$ have a definite parity and are linear combinations of $\psi_{R,L}$:

$$\psi_\pm=(\psi_R\pm\psi_L)/\sqrt{2}. \tag{3}$$

For most molecules, the quantity $\Delta E = |E_- - E_+|$ (the inversion splitting) is very small. The time of transition between the states $R$ and $L$ is $\tau \sim 1/\Delta E$. If the time of the experiment $t \ll \tau$, the states $R$ and $L$ can be regarded as stationary.

On the other hand, if the Hamiltonian contains terms that do not commute with the inversion operator, the stationary states differ from $\psi_\pm$ and correspond to the energy values

$$E_{1,2}=(E_R+E_L)/2\pm[(E_R-E_L)^2/4+|\varepsilon|^2]^{1/2}, \tag{4}$$

$$E_{R,L}=\langle R, L|H|R, L\rangle, \quad \varepsilon=\langle R|H|L\rangle.$$

The positions of the potential minima for two mirror configurations of a molecule can be different also in the presence of mirror symmetry elements. This calls for

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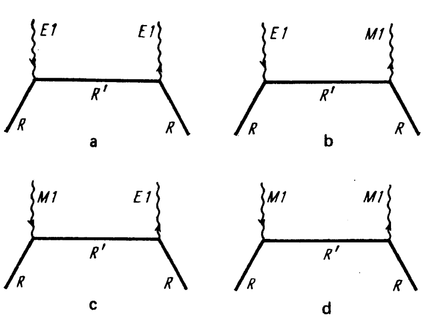

FIG. 1. Feynman diagrams showing scattering of light by a molecule. A solid line means a molecule, a wavy line a photon (electric or magnetic), an arrow indicates absorption or emission. The letters $R$ and $R'$ denote the ground and excited electronic states of the molecule.

the presence of identical nuclei. An example is the pyramidal molecule $XY_3$. But the state $R$ of such a molecule can be changed to the state $L$ not only by inversion, but also by permutation of the identical nuclei, accompanied by rotation. From this follows, by virtue of the indistinguishability principle, that all the physical properties of such molecules are identical in the right- and left-hand modifications. In contrast to true stereoisomers, such molecules are called pseudo-stereoisomers.

We shall consider hereafter only true stereoisomers, since the $P$- and $P, T$-odd effects connected with the difference between the physical properties of the $R$ and $L$ modifications and discussed in the sections that follow do not exist for pseudo-stereoisomers (see the end of § 6).

## §3. OPTICAL ROTATION

We describe briefly the optical-activity phenomenon in the language of Feynman diagrams. Light scattering, without change of frequency, from a molecule in a state $R$ is described by the diagrams shown in Fig. 1. It is necessary to add to them four more diagrams in which the absorbed and emitted photons are interchanged. Diagram a determines the usual light-scattering tensor. Diagrams b and c make a nonzero contribution only because the states $R$ and $L$ have no definite parity. These diagrams lead to optical rotation. The contribution of diagram d is small, since the amplitude of the magnetic transition is smaller by a factor $\alpha$ than that of the electric and adds a correction to the scattering tensor.

The contribution of diagrams b and c to the scattering amplitude is

$$A=\omega\sum_{R'}\omega_{RR'}\left\{\frac{\langle R|\mathbf{d}_e\mathbf{e}_i|R'\rangle\langle R'|\boldsymbol{\mu}_e[\mathbf{e}_f\times{}^{*}\mathbf{n}_f]|R\rangle}{\omega_{RR'}-\omega}\right.$$
$$-\frac{\langle R|\boldsymbol{\mu}_e[\mathbf{e}_i\times\mathbf{n}_i]|R'\rangle\langle R'|\mathbf{d}_e\mathbf{e}_f^{*}|R\rangle}{\omega_{RR'}-\omega}+\frac{\langle R|\mathbf{d}_e\mathbf{e}_i^{*}|R'\rangle\langle R'|\boldsymbol{\mu}_e[\mathbf{e}_f\times\mathbf{n}_f]|R\rangle}{\omega_{RR'}+\omega}$$
$$\left.-\frac{\langle R|\boldsymbol{\mu}_e[\mathbf{e}_i\times{}^{*}\mathbf{n}_i]|R'\rangle\langle R'|\mathbf{d}_e\mathbf{e}_f|R\rangle}{\omega_{RR'}+\omega}\right\}, \tag{5}$$

where $\omega_{RR'}=E_R-E_{R'}$ is the frequency of the transition between the ground and excited states of the isomer, $\omega$ is the frequency of the incident radiation, $\mathbf{d}_e$ and $\mu_e$ are the operators of the electric and magnetic dipole moments of the electrons, $\mathbf{e}$ and $\mathbf{n}$ are the polarization and propagation-direction vectors of the photon, and the labels $i$ and $f$ mark the initial and final states of the photon.

We average the amplitude $A$ over the molecule orientations. To this end, we use the relation[1]

$$\overline{(\langle R|\mathbf{d}_e|R'\rangle)_i(\langle R'|\boldsymbol{\mu}_e|R\rangle)_k}=\langle R\|\mathbf{d}_e\|R'\rangle\langle R'\|\boldsymbol{\mu}_c\|R\rangle\delta_{ik}/3, \tag{6}$$

where the superior bar denotes averaging, and the symbols $i$ and $k$ number the components of the vector in the laboratory frame, while $\langle R\|\ldots\|R'\rangle$ is the matrix element (ME) in the reference frame rigidly connected with the molecule. Reducing (5) to a common denominator, using (6) and the relation

$$n=(\pi\rho/\omega)\bar{A}(0), \tag{7}$$

where $n$ is the refractive index, $\rho$ is the density of the medium, and $\bar{A}(0)$ is the averaged forward-scattering amplitude, putting $\mathbf{e}_i=\mathbf{e}_f=\mathbf{e}$ and $\mathbf{n}_i=\mathbf{n}_f=\mathbf{n}$, and taking finally into account the photon-spin definition $\mathbf{s}=i\mathbf{e}\times\mathbf{e}^*$, we arrive at the expression

$$\operatorname{Re} n=\frac{\pi\rho\omega}{3}\mathbf{sn}\sum\frac{\operatorname{Im}(\langle R\|\mathbf{d}_e\|R'\rangle\langle R'\|\boldsymbol{\mu}_e\|R\rangle)}{\omega_{RR'}{}^2-\omega^2}. \tag{8}$$

The refractive index is thus the same for right- and left-polarized photons ($\mathbf{s}\cdot\mathbf{n}=\pm1$) and, when account is taken of the relation

$$\varphi=\frac{1}{2c}\omega l\operatorname{Re}(n^+-n^-), \tag{9}$$

where $\varphi$ is the rotation angle of the polarization plane and $l$ is the thickness of the absorbing layer, Eq. (8) yields for the optical activity an expression that coincides with that of Ref. 10.

The existence of optical rotation calls for

$$\operatorname{Im}(\langle R\|\mathbf{d}_e\|R'\rangle\langle R'\|\boldsymbol{\mu}_e\|R\rangle)\neq0.$$

The electron wave functions in the ME brackets can be regarded as real, since all possible symmetry groups of a nonplanar molecule of the asymmetric-top type have only one-dimensional representations,[11] and all the states are accordingly not degenerate.

The operator $\mu_e$ is equal to

$$\boldsymbol{\mu}_e=\mu_0(\mathbf{L}+2\mathbf{S}), \tag{10}$$

where $\mu_0$ is the Bohr magneton, and $\mathbf{L}$ and $\mathbf{S}$ are the summary orbital and spin momenta of the electrons. Only the operator $\mathbf{L}$ contributes to (8), since the ground state of the molecule is a singlet, and the operators $\mathbf{d}_e$ and $\mu_e$ cannot transform a singlet into a triplet. The ME $\mu_e$ is then pure imaginary, since the operator $L$ is imaginary, while the ME $\mathbf{d}_e$ is real and the entire expression (8) differs from zero.

It is easily seen that for the pseudo-stereoisomer we have

$$\langle a\|\mathbf{d}_e\|a'\rangle\langle a'\|\boldsymbol{\mu}_e\|a\rangle=0, \tag{11}$$

since no state that connects both ME exists. Indeed, the electron wave functions of a pseudo-stereoisomer should have a definite symmetry with respect to some reflection (for an $XYZ_2$ molecule, e.g., with respect to the plane that shares the two $Z$ atoms). The vectors $\mu$ and d, however, behave differently in such a reflection, and it is this which leads to (11). Pseudo-stereoisomers have therefore no optical activity.

## §4. HYPERFINE STRUCTURE

Since weak interactions increase with increasing charge of the nucleus $Z$, we shall consider molecules that contain a heavy nucleus. The magnetic hyperfine interaction operator of such molecules can be approximately written in the form

$$H_{hf}=H_{hf}{}^1+H_{hf}{}^2+H_{hf}{}^3=\frac{\mu_e\mu_n}{r^3}+\frac{\mu_r\mu_n}{R_0{}^3}+\sum_m\frac{\mu_n\mu_m}{R_0{}^3}, \tag{12}$$

where $\mu_e$ is defined by Eq. (10), $\mu_n=\mu_{\text{nuc}}\mathbf{I}$, I is the spin of the heavy nucleus, $\mu_{\text{nuc}}$ is the nuclear magneton, $r$ is the distance from the electron to the heavy nucleus, $R_0$ is the characteristic distance between the nuclei, $B$ is the rotational constant ($\sim m/M$, where $M$ is the reduced mass of the nuclei in the molecule), and $\mu_r$ is the magnetic moment of the rotation of the molecule as a whole:

$$\mu_r=B\mu_0(\mathbf{J}-\mathbf{L}-\mathbf{S}). \tag{13}$$

The summation in (12) is over all the remaining nuclei of the molecule.

If we consider a singlet nondegenerate state of the molecule, then

$$\langle R|\mu_e|R\rangle=0 \tag{14}$$

and consequently the first (leading) term in (12) makes no contribution to the hfs. In this situation the hfs is usually determined by the electric quadrupole moment of the nucleus. If, however, we take a molecule with $I<1$, then there is no quadrupole interaction and the hfs is determined by the terms $H^{2,3}_{\text{hf}}$, as well as by the correction to $H^1_{\text{hf}}$.

Equation (14) is valid so long as no account is taken of the admixture of excited electronic states due to the interaction of the electron motion with the rotation:

$$H_{er}=B\mathbf{J}(\mathbf{L}+\mathbf{S}). \tag{15}$$

The required energy correction is described by the diagram of Fig. 2 (here and elsewhere we do not show the diagrams that differ only in the arrangement of the vertices). It is equal to

$$\Delta E_{hf}{}^1=2\,\mathrm{Re}\sum_{R'}\frac{\langle R|H_{hf}{}^1|R'\rangle\langle R'|H_{er}|R\rangle}{\omega_{RR'}}. \tag{16}$$

The order of magnitude of the correction (16) can be obtained from the estimate

$$1/r^3\sim Z, \tag{17}$$

which is suitable for the outer electrons of a heavy atom[12] these electrons make the largest contribution to (16). We obtain

$$\Delta E_{hf}{}^1\sim Z\mu_0\mu_{\text{nuc}}B\sim 10^5\ \text{Hz}. \tag{18}$$

An estimate of the contributions of the operators $H^{2,3}_{\text{hf}}$, with allowance for (13), yields

$$\Delta E_{hf}{}^2\sim B\mu_0\mu_{\text{nuc}}, \tag{19}$$

$$\Delta E_{hf}{}^3\sim \mu^2_{\text{nuc}}, \tag{20}$$

which does not exceed (18).

Because of the smallness of the hyperfine interaction (18)–(20) in the molecules considered, the hfs is broken already in an external magnetic field $H\sim10^3$ G, and the angular momenta J and I are quantized independently of the field direction. This is the most important case in practice, since magnetic-resonance-type experiments seem to be the most promising for the observation of parity nonconservation in polyatomic molecules.

We determine the $R$ labels in (16), assuming the isomer to be an asymmetric top:

$$|R\rangle\equiv|RJM\tau IM_I\rangle, \tag{21}$$

where $\tau$ is the additional quantum number for the rotational functions of the asymmetric top,[11] and $M_I$ is the projection of the spin of the heavy nucleus on the outward direction. Separating in (16) the dependence on the projections of the angular momenta, we obtain

$$\Delta E_{hf}{}^1\sim M_IM. \tag{22}$$

In a magnetic field, the usual Zeeman effect is observed in the molecule. If the hfs is disrupted by the field, the splitting takes place independently with respect to the quantum numbers $M_I$ and $M$. The operator of the interaction with the magnetic field is of the form

$$W_H=W_H{}^1+W_H{}^2+W_H{}^3=\mathbf{H}\Big(\mu_e+\mu_r+\sum_n\mu_n\Big). \tag{23}$$

By virtue of (14), the first term of (23) makes no contribution in first-order perturbation theory and the interaction $H_{er}$ or $H^1_{\text{hf}}$ must be taken into account. The corresponding corrections are described by the diagram of Fig. 3. In a strong magnetic field we obtain the following estimates:

$$\Delta E^1_{H,er}\sim\mu_0BMH, \tag{24}$$

$$\Delta E^1_{H,hf}\sim\mu_0\mu_{\text{nuc}}{}^2ZM_IH. \tag{25}$$

To obtain numerical estimates it must be recognized that $\mu_0H[\text{a.u.}]=10^{-9}H\,[\text{G}]$. In a field $H\sim10^3$ G we have then for a molecule containing a heavy atom$^{2)}$ ($Z\sim100$)

$$\Delta E^1_{H,er}\sim\Delta E^1_{H,hf}\sim10^4\ \text{Hz}. \tag{26}$$

An estimate of the contributions of the operators $W^{2,3}_H$

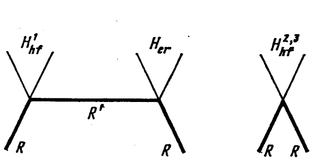

FIG. 2. Hyperfine interaction in a molecule. The V-event denotes various interamolecular interactions.

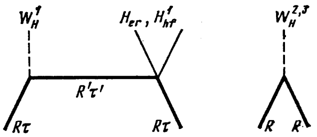

FIG. 3. Interaction of molecule with a magnetic field. The field is represented by the dashed line. The letters $\tau$ and $\tau'$ denote rotational quantum numbers.

yields

$$\Delta E_H{}^2 \sim \mu_0 BMH \sim 10^4 \ \text{Hz}, \tag{27}$$

$$\Delta E_H{}^3 \sim \mu_{\text{nuc}} M_I H \sim 10^6 \ \text{Hz}. \tag{28}$$

The correction (28) exceeds (18), meaning in fact disruption of the hfs. For heavy stereoisomers the main effect is thus connected with the nuclear spin. Expression (25) determines the correction to this effect, while (24) and (27) determine the additional weak Zeeman structure.

To conclude this section, we consider briefly the interaction of the molecule with an electric field E. The interaction operator is

$$W_E = (\mathbf{d}_e + \mathbf{d}_N)\mathbf{E}, \tag{29}$$

where $\mathbf{d}_e$ and $\mathbf{d}_N$ are the operators of the summary electric dipole moments (EDM) of the electrons and nuclei in the molecule.

Since the $P$-odd, $T$-even interaction $V_P$ lifts the energy degeneracy of the $R$ and $L$ states, it follows from the $T$-invariance that the molecule cannot have an EDM in the states $R$ and $L$, and consequently no linear Stark effect can be observed.$^{3)}$ Let us show how this takes place formally.

The equality

$$\langle R|\mathbf{d}|R\rangle = 0 \tag{30}$$

holds for an asymmetric top by virtue of the selection rules with respect to the quantum number $\tau$: a vector cannot have ME that are diagonal in $\tau$ (Refs. 11 and 12; see Appendix 1). This selection rule is not rigorous and is lifted when account is taken of the interaction of the rotation with the electronic motion (this is in fact how the vector $\mu_e$ acquires a nonzero mean value). The latter takes the form

$$H_{vr} = BJL_v, \tag{31}$$

where $\mathbf{L}_v$ is the vibrational angular momentum. However, allowance for the interactions $H_{er}$ and $H_{vr}$ does not lead to a linear Stark effect, inasmuch as in all orders of perturbation theory we obtain pure imaginary expressions that make no contribution to the energy (see Appendix 1). Therefore, without allowance for the $T$-nonconserving interactions, only a quadratic Stark effect is possible in the isomers.

## §5. *P*-ODD INTERACTIONS

We take into account now the correction to the energy on account of the $P$-odd interaction $V_P{}^1$ (1). Since the orbital part of the Hermitian operator $V_P{}^1$ is pure imaginary, its mean value on the nondegenerate orbital functions is zero. In addition, the spin part in the singlet state also vanishes. To obtain a nonzero result we must take into account an interaction that mixes the singlet and triplet states and cancels out the imaginary orbital part of $V_P{}^1$. These conditions, as shown in Appendix 2, are satisfied by the spin-orbit interaction

$$H_{so} \sim (\alpha Z)^2. \tag{32}$$

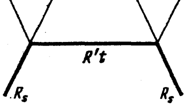

FIG. 4. $V_P^1$ interaction in a molecule. The letters $s$ and $t$ denote the singlet and triplet states.

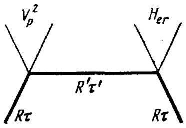

FIG. 5. $V_P^2$ interaction in a molecule.

The ensuing correction to the energy is described by the diagram of Fig. 4. The matrix element of the weak interaction $V_P$ has different signs for the right- and left-hand isomers

$$\langle R|V_P|R\rangle = -\langle L|V_P|L\rangle. \tag{33}$$

Using the atomic order-of-magnitude estimates[1]

$$V_P{}^1 \sim 10^{-16} Z^3 g_1, \tag{34}$$

$$V_P^{2,3} \sim 10^{-16} Z^2 g_{2,3} \tag{35}$$

and taking (32) into account, we obtain the estimate

$$\Delta E_P{}^1(R, L) \sim \pm 10^{-16} Z^3 (\alpha Z)^2 g_1 \sim g_1 \cdot 10^5 \ \text{Hz}. \tag{36}$$

It is noted in Ref. 8, however, that this estimate is too high by several orders of magnitude, because of some specific cancellations in the ME of the operators $V_P{}^1$ and $H_{so}$. In all the papers cited above they considered only the correction $\Delta E_P{}^1$.

We consider now the interaction $V_P^{2,3}$, which depends on the nuclear spin. The corresponding energy corrections will be determined by the difference between the hfs intervals of the right- and left-hand isomers.

The operator $V_P{}^2$ has no ME that are diagonal in either the electronic or the rotational states (its electronic part is pure imaginary, and is a vector with respect to the rotational variables). It can therefore contribute to the energy only when combined with $H_{er}$ (Fig. 5). Averaging over the rotational variables we find that the contribution of the diagram of Fig. 5 is

$$\Delta E_P{}^2(R, L) \sim \pm 10^{-16} Z^2 B\mathbf{IJ} g_2 \sim g_2 \cdot 10^{-2} \ \text{Hz}. \tag{37}$$

The operator $V_P{}^3$ is likewise a vector with respect to the rotational functions; in addition, it depends on the electron spin. A contribution to the energy arises therefore only in third-order perturbation theory when $H_{so}$ and $H_{er}$ are taken into account (Fig. 6).

We note that the interactions $H_{er}$ and $H_{vr}$ are by them-

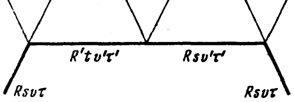

FIG. 6. $V_P^3$ interaction in a molecule. The letter $v$ stands for the vibrational state of the molecule.

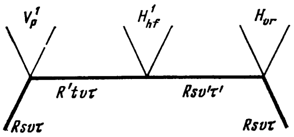

FIG. 7. Contribution of the $V_P^1$ interaction to the hfs of a molecule.

selves of the same order, the addition of $H_{er}$ calls for admixture of an excited electronic state, while $H_{vr}$ calls for a vibrational addition. In the latter case the intermediate energy denominator is smaller by a factor $\sqrt{B}$, i.e., the correction is larger.

For the diagram of Fig. 6 we obtain the estimate

$$\Delta E_P{}^3(R,\ L)\sim\pm10^{-16}Z^2(\alpha Z)^2BIJg_3\sim g_3\cdot10^{-2}\ \text{Hz}. \tag{38}$$

A similar correction to the hfs may result also on account of the potential $V_P{}^1$ with allowance for $H_{hf}{}^1$ and $H_{er}$ (Fig. 7). In the operator $H_{hf}{}^1$ it is necessary to take into account the terms that transform a singlet into a triplet. In order of magnitude we have

$$\Delta E_P{}^1(R,\ L)\sim\pm10^{-16}Z^3\mu_0\mu_{\text{nuc}}ZBIJg_1\sim g_1\cdot10^{-4}\ \text{Hz}. \tag{39}$$

The main contribution to the difference between the hfs of the $R$ and $L$ isomers is thus made by the potentials $V_P{}^{2,3}$.

We proceed now to the $P$-odd corrections in a magnetic field. Besides the corrections (37) and (38), there arise additional corrections proportional to the field intensity. They are shown in Fig. 8. These corrections are estimated at:

$$\Delta E_{P,H}^1(R,L)\sim\pm10^{-16}Z^4\mu_0{}^2\mu_{\text{nuc}}M_IHg_1\sim g_1\cdot10^{-6}\ \text{Hz}, \tag{40}$$

$$\Delta E_{P,H}^2(R,L)\sim\pm10^{-16}Z^2\mu_0M_IHg_2\sim g_2\cdot10^{-3}\ \text{Hz}, \tag{41}$$

$$\Delta E_{P,H}^3(R,L)\sim\pm10^{-16}Z^2(\alpha Z)^2\mu_0M_IHg_3\sim g_3\cdot10^{-3}\ \text{Hz}. \tag{42}$$

## §6. *P, T*-ODD INTERACTIONS

We examine finally the additional effect that arise in an external magnetic field when the interaction $V_{PT}$ is taken into account. (In the absence of an electric field it follows from $T$-invariance that there are no energy corrections linear in $V_{PT}$.) We bear in mind, as before, experiments of the magnetic-resonance type and assume that the hfs is broken by the field.

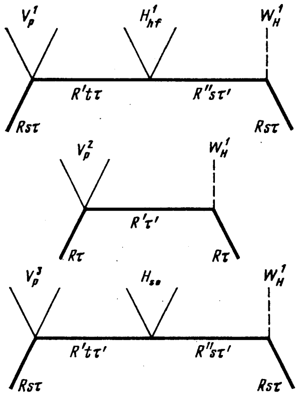

FIG. 8. Contribution of the operators $V_P^1$, $V_P^2$, and $V_P^3$ to the magnetic moment of the nucleus.

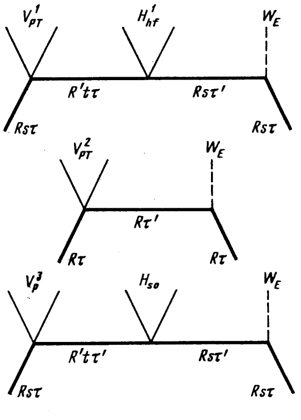

FIG. 9. Contribution of the operators $V_{PT}^1$, $V_{PT}^2$, and $V_{PT}^3$ to the linear Stark effect.

Diagrams with the operator $W_E$ can be easily constructed in analogy with the diagrams of Fig. 8. It must be taken into account here that replacement of $W_H'$ by $W_E$ and at the same time $V_H^1$ by $V_{PT}$ leaves the diagram real. The additional difference is that $W_E$ can have nonzero ME that are diagonal in all but the rotational quantum numbers,[4)] i.e., the electronic denominators are replaced by rotational in the diagrams. The corresponding diagrams are shown in Fig. 9. The same estimates (37) and (38) as for $V_P{}^i$ hold also for the operators $V_{PT}{}^i$, except that the constants $g_i$ must be replaced by $h_i$. We shall assume that $dE\sim B$, where $d$ is the EDM of the molecule when the nuclei are immobile. For heavy nuclei this holds true in fields $E\sim10^4$ V/cm. Then

$$\Delta E_{PT}{}^1\sim10^{-16}Z^3\mu_0\mu_{\text{nuc}}ZB^{-1}dM_IEh_1\sim h_1\ \text{Hz}, \tag{43}$$

$$\Delta E_{PT}{}^2\sim10^{-16}Z^2B^{-1}dM_IEh_2\sim h_2\cdot10^3\ \text{Hz}, \tag{44}$$

$$\Delta E_{PT}{}^3\sim10^{-16}Z^2(\alpha Z)^2B^{-1}dM_IEh_3\sim h_3\cdot10^3\ \text{Hz}. \tag{45}$$

We note that the corrections (43)–(45) are of the same sign for the $R$ and $L$ forms of the molecule, since both $V_{PT}$ and $W_E$ reverse sign on going from the $R$ to the $L$ form.

None of the parity-nonconservation effects listed in §§ 5 and 6 take place for pseudo-stereoisomers. This follows from the already mentioned symmetry properties of the wave functions of the pseudo-stereoisomer relative to a certain reflection. Since the operators $V_P$ and $V_{PT}$ reverse sign under such a reflection, the diagonal ME of these operators (i.e., the contributions to the energy) are equal to zero when account is taken of any of the corrections that do not violate the indicated symmetry.

We note that an incorrect wave function was used in Ref. 14 for the pseudo-stereoisomer, resulting in nonzero diagonal ME of the operators $V_P$ and $V_{PT}$. The results of Ref. 14, which pertain to $P, T$-odd effects, apply in fact to pyramidal molecules that have no identical nuclei (e.g., NHDT). At the same time the $P$-odd effects connected with nondiagonal ME can exist also for pseudo-stereoisomers. In particular, the experiment discussed in Ref. 14, aimed at finding the $P$-odd effect

TABLE I.

|  | Constant |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|
|  | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_4'$ | $C_5$ | $C_6$ | $C_6'$ |
| Equation No. | (28) | (24), (26), (27) | (18), (22) | (44) | (45) | (38) | (41) | (42) |
| Estimate, Hz | $10^6$ | $10^4$ | $10^5$ | $10^3$ | $10^3$ | $10^{-2}$ | $10^{-3}$ | $10^{-3}$ |

of mode splitting of an ammonia maser, is also feasible.

## §7. CONCLUSION

We now gather all the results obtained in §§4–6. They enable us to write down an expression for the hfs energy level of a stereoisomer in magnetic and electric fields. To this end we substitute in (4) the estimates obtained in these sections, assuming that $\varepsilon$ is negligibly small:

$$E_{M_I M}(R, L)=C_1 M_I+C_2 M+C_3 M_I M+(C_4 h_2+C_4' h_3)$$
$$\times \mathbf{eh} M_I \pm [C_5 g_3 M_I M+(C_6 g_2+C_6' g_3) M_I], \quad \mathbf{e}=\mathbf{E}/E, \quad \mathbf{h}=\mathbf{H}/H. \tag{46}$$

The constants $C_i$ are gathered in Table I.

It follows from (46) that the following experiments are feasible. First, the Zeeman structure determined by the numbers $C_1$, $C_2$, and $C_3$ in (46) can be split because of the weak interaction (the term $C_5$). This splitting, $\sim 10^{-2}$ Hz, is observable in principle by contemporary magnetic measurement techniques and can yield information on the constant $g_3$ of the $P$-odd interaction.

Second, the following experimental procedure of observing $P, T$-odd effects is conceivable. We consider magnetic resonance of the nuclear sublevels [the term with the constant $C_1$ in (46)]. The terms with the constants $C_4$ and $C_4'$ also contribute to this resonance and shift the frequency by $\sim 10^3 h_{2,3}$ Hz. When the sign of the electric field is reversed, the resonance frequency changes by double the value of this shift.

Such an experiment can provide estimates of the constants $h_2$ and $h_3$ of the potential $V_{PT}$. Other conditions being equal, this estimate will be no better than the estimate of $h_2$ based on the experiment on the TlF molecule.[15]

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## APPENDIX 1

## MATRIX ELEMENTS OF VECTOR OPERATORS

We consider the properties of the ME of vector operators in the basis $|RJM\tau\rangle$. The asymmetric-top functions are chosen to be linear combinations of the Wigner functions $|JMK\rangle$, which have the correct symmetry:

$$|RJM\tau\rangle \equiv |RJMK\eta\rangle=\frac{1}{\sqrt{2}}(|JMK\rangle+\eta|JM-K\rangle), \tag{A1.1}$$

where $K$ is the projection of the angular momentum on a certain internal direction, and $\eta=\pm 1$. We reduce the ME of the spherical component of the vector $\mathbf{U}$ in the lab to the ME in a rotating frame:

$$\langle J'M'K'\eta'|U_q|JMK\eta\rangle=\frac{1}{2}(-1)^{K'-M'}[(2J'+1)(2J+1)]^{1/2}$$
$$\times\begin{pmatrix} J' 1 J \\ -M' q M\end{pmatrix}\begin{pmatrix} J' 1 J \\ -K' q' K\end{pmatrix}\Big\{\delta_{K,K'}(1-\chi)\langle R'\|U_\zeta\|R\rangle$$
$$-\frac{i}{\sqrt{2}}\delta_{K,K'\pm 1}(1-\chi)\langle R'\|U_\eta\|R\rangle \mp \frac{1}{\sqrt{2}}\delta_{K,K'\pm 1}(1+\chi)\langle R'\|U_\xi\|R\rangle\Big\}, \tag{A1.2}$$
$$\chi=(-1)^{J'+J}\eta\eta',$$

where $\xi$, $\eta$, and $\zeta$ are the principal inertia axes of the molecule.

The electron-vibrational wave functions in the ME $\langle R'\|U_i\|R\rangle$ are nondegenerate and can be regarded as real. Therefore the reality properties of these ME are determined only by the operator. Thus, the ME are real for the real operator **d** and imaginary for the operator **L**. On the other hand, the phase of the initial ME differs, depending on which of the Cartesian component of the vector (relative to the reference frame tied to the molecule) differs from zero. Equation (A1.2) leads to the selection rules for the Cartesian components of the vector **U** in the frame that rotates with the molecule.

For the quantum number $\tau$ one uses frequently the representations of the symmetry group $D_2$ of the rotational Hamiltonian: $A, B_1, B_2, B_3$ [Ref. 12, p. 473 of Russ. orig.]. While these representations do not yield an unambiguous classification of the rotational levels, they do determine selection rules according to which, in this notation, the nonzero matrix elements are

$$\|\langle A\|U_\xi\|B_3\rangle, \quad \langle A\|U_\eta\|B_2\rangle, \quad \langle A\|U_\zeta\|B_1\rangle,$$
$$\langle B_1\|U_\xi\|B_2\rangle, \quad \langle B_1\|U_\eta\|B_3\rangle, \quad \langle B_2\|U_\zeta\|B_3\rangle. \tag{A1.3}$$

Therefore if we have the ME of a scalar product in the form $\mathbf{A}\cdot\mathbf{U}$, where **A** is any external vector relative to the electron-vibrational system in the molecule (e.g., **H**, **E**, **I**), then the selection rules (A1.3) hold for such a scalar product. If the scalar product is written in the laboratory frame, the selection rules hold for the vector **U**. The total angular momentum vector **J** of the molecule behaves like **A**: it is diagonal in $\tau$.

It can thus be stated that, for example, the ME of the operators $H_{\rm hf}{}^1$, $H_{er}$, $W_E$, and $V^{2,3}$ obey the selection rules (A1.3).

In second-order perturbation theory there appear chains of two operators:

$$\langle\tau\|U_i\|\tau'\rangle\langle\tau'\|U_k\|\tau\rangle, \tag{A1.4}$$

and it follows from the selection rules that $i=k$. In third-order perturbation theory we obtain the chain

$$\langle\tau\|U_i\|\tau'\rangle\langle\tau'\|U_k\|\tau''\rangle\langle\tau''\|U_j\|\tau\rangle, \tag{A1.5}$$

for which it follows from the selection rules that all three indices must be different.

In order that the chains (A1.4) and (A1.5) not vanish, it is necessary that all the electron-vibrational ME exist. This is not always the case. If the complete symmetry group is not lower than rotational, then the selection rules with respect to $\tau$ are not lifted when the interactions $H_{er}$ and $H_{vr}$ are taken into account. The symmetry group of the isomer must therefore be either

$C_1$ or $C_2$.

Using the foregoing results, it is easy to verify that allowance for the Coriolis forces does actually not lead to the nonzero matrix element (30). In second-order perturbation theory we have[5)]

$$\langle RJMK\eta|\mathbf{dE}|R'J'M'K'\eta'\rangle\langle R'J'M'K'\eta'|B\mathbf{JL}|RJMK\eta\rangle. \qquad \text{(A1.6)}$$

According to (A1.2) and (A1.4) it reduces to

$$\alpha_1 E\langle R\|d_i\|R'\rangle\langle R'\|L_i\|R\rangle, \qquad \text{(A1.7)}$$

where $\alpha_1$ is a real coefficient that depends on all the rotational quantum numbers. We conclude therefore that the chain (A1.6) is pure imaginary and consequently Eq. (30) is valid in second order.

In third-order perturbation theory we obtain by the same method

$$\alpha_2 E\langle R\|d_i\|R'\rangle\langle R'\|L_k\|R''\rangle\langle R''\|L_j\|R\rangle, \qquad \text{(A1.8)}$$

and it follows from (A1.5) that the indices $i$, $k$, and $j$ should be different. Therefore the coefficient $\alpha_2$ is imaginary, since the $\eta$ component of one of the vectors enters in the chain (A1.8), thereby introducing in the coefficient $\alpha_2$, in accord with (A1.2), an uncompensated $\sqrt{-1}$. The chain (A.18) is consequently imaginary.

It is easily seen that in any order of perturbation theory the result is always imaginary, since either the coefficient $\alpha_i$ is imaginary, or the angular momentum operator $\mathbf{L}$ enters an odd number of times.

## APPENDIX 2

## SPIN MATRIX ELEMENTS

We shall assume that all the electronic excitations take place in an outer shell that contains two electrons, and will break up all the spin-dependent operators into two parts, a part $W'$ that transforms the singlet $s$ into a triplet $t$ and contains the difference $\mathbf{s}_1 - \mathbf{s}_2$, and a part $W''$ that does not transform $s$ into $t$ and contains the sum $\mathbf{s}_1 + \mathbf{s}_2$.

To obtain the energy correction due to the interaction $V_P{}^1$ we must take into account in second-order perturbation theory the operators $V_P{}^{1\prime}$ and $H_{s0}{}'$. This yields the following chain of spin ME:

$$\sum_t \langle s|(s_1-s_2)_i|t\rangle\langle t|(s_1-s_2)_k|s\rangle=\langle s|(s_1-s_2)_i(s_1-s_2)_k|s\rangle=a\delta_{ik}, \qquad \text{(A2.1)}$$

where the summation is carried out over the components of the triplet. The tensor $\delta$ is a unit tensor that can arise upon averaging a second-rank spin tensor over the singlet state. At $i=k$ the expression in the left-hand side of (A2.1) is real, i.e., the number $a$ is real. Thus, the spin factor in the expression for the entire correction is real, and since the coordinate part of $H_{s0}$ contains the imaginary $i$, addition of the operator $H_{s0}$ cancels out the imaginary character of the operator $V_P{}^1$, as stated in the main text.

In third-order, the only possible chain is

$$\sum_{t,t'} \langle s|(s_1-s_2)_i|t\rangle\langle t|(s_1+s_2)_k|t'\rangle\langle t'|(s_1-s_2)_j|s\rangle$$
$$=\langle s|(s_1-s_2)_i(s_1+s_2)_k(s_1-s_2)_j|s\rangle=ibe_{ikj}, \qquad \text{(A2.2)}$$

where $e$ is a unit antisymmetric tensor. Since now $i\neq k\neq j$, the product of the spin vectors will contain the imaginary $y$ component once, and the entire expression (A2.2) will be pure imaginary.

The reasoning can be continued and it can be shown that a chain will be imaginary if it has an odd number of spin ME, and real with an even number. It follows therefore that by adding to the imaginary spin-independent operator (e.g., $V_P{}^2$) $H_{s0}$ in an arbitrary order of perturbation theory, it is impossible to obtain a real expression. Nor is it possible to obtain a real expression by adding $H_{s0}$ to a real spin-dependent operator (e.g., $V_P{}^2$).

[1] The mean values of two arbitrary vectors **a** and **b** should be expressed in terms of the unit tensor $\delta$: $a_i b_k = c\delta_{ik}$. Assuming $i=k$ and summing over $k$, we arrive at Eq. (6).

[2] In all the estimates that follow we shall assume that $Z\sim 100$ and $H\sim 10^3$ G.

[3] In symmetric tops there exists an additional degeneracy of the rotational states and, consequently, a linear Stark effect is possible,[13] similar to the linear Stark effect in the hydrogen atom.

[4] The same holds for the operator $V_{PT}^2$, since its electronic part is a real $T$-even vector.

[5] For the $H_{vr}$ interaction it is necessary to replace $\mathbf{L}$ by $\mathbf{L}_v$, but this does not affect the reasoning.

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[1] I. B. Khriplovich, Nesokhranenie chetnosti v atomnykh yavleniyakh (Parity Nonconservation in Atomic Phenomena), Nauka, 1981.

[2] L. N. Labzovskiĭ, Zh. Eksp. Teor. Fiz. **73**, 1623 (1977); **75**, 856 (1978) [Sov. Phys. JETP **46**, 853 (1977); **48**, 434 (1978)].

[3] O. P. Sushkov and V. V. Flambaum, *ibid.* **75**, 1208 (1978) [**48**, 608 (1978)].

[4] V. G. Gorshkov, L. N. Labzovskiĭ, and A. N. Moskalev, *ibid.* **76**, 414 (1979) [**49**, 209 (1979)].

[5] G. Marx, Acta Phys. Austr. Suppl. XIII, 569 (1974).

[6] V. S. Letokhov, Phys. Lett. **53A**, 275 (1975).

[7] B. Ya. Zel'dovich, D. B. Saakyan, and I. I. Sobel'man, Pis'ma Zh. Eksp. Teor. Fiz. **25**, 106 (1977) [JETP Lett. **25**, 94 (1977)].

[8] R. A. Hegstrom, D. W. Rein, and P. G. H. Sanders, J. Chem. Phys. **73**, 2329 (1980).

[9] I. B. Khriplovich, Zh. Eksp. Teor. Fiz. **79**, 354 (1980) [Sov. Phys. JETP **52**, 177 (1980)].

[10] W. Kozman, Introduction to Quantum Chemistry [Russian translation], IL, 1960, Chap. 15.

[11] G. Herzberg, Molecular Spectra and Molecular Structure, Vol. 3, Van Nostrand, 1966. [Russian translation Mir, 1969, pp. 111, 106, and 244].

[12] L. D. Landau and E. M. Lifshitz, Quantum Mechanics, Nonrelativistic Theory, Pergamon, 1978, §§72, 103.

[13] C. H. Townes and A. H. Schawlow, Microwave Spectroscopy, McGraw, 1955, §§1,2.

[14] M. G. Kozlov and L. N. Labzovskiĭ, Zh. Eksp. Teor. Fiz. **78**, 437 (1980) [Sov. Phys. JETP **51**, 221 (1980)].

[15] E. A. Hinds, C. E. Loving, and P. G. H. Sanders, Phys. Lett. **62B**, 97 (1976).

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