Λ-doubling and parity-nonconservation effects in spectra of diatomic molecules

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Parity nonconservation effects due to mixing of Λ-doublet component mixing by weak interaction in diatomic molecules are considered. An experiment is proposed on Raman scattering by the $^2\Pi_{1/2}$ state of the molecule; the experiment should result, at the Raman frequencies, either in circular polarization of the scattered light or in a dependence of the scattered-light intensity on the sign of the circular polarization of the incident light. The relative magnitude of these effects is $\sim 10^{-6}$ for CuO, CuS, and CuSe molecules, provided that the bandwidth of the radiation source (laser) does not exceed 1 MHz.

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1. INTRODUCTION

Attempts to observe effects of electron-nuclear weak interaction of neutral currents in atomic experiments on bismuth vapor[1] have not led so far to an unequivocal confirmation of the theoretical predictions discussed in a large number of papers (see, e.g., the review of Moskalev *et al.*[2]). It follows therefore that all other possibilities of measuring or estimating the constants of the weak neutral currents are presently of primary interest. In particular, it was suggested[3] to use for this purpose electronic transitions in diatomic molecules. Among the possibilities considered in Ref. 3 was also Λ doubling.1) In the present paper we propose a new type of experiment for the observation of effects of parity nonconservation–Raman scattering (or resonant fluorescence) by closely lying levels of opposite parity. In contrast to the corresponding atomic experiments, we propose here to use allowed magnetic transitions, work with which is preferable from an experimental point of view.

Finally, it should be noted that the question of the mixing of the sublevels by a weak interaction is by itself not a trivial one, and was not investigated to a sufficient degree in Refs. 3 and 4; this question is discussed in detail in the present paper.

Let us recall briefly, to simplify the exposition that follows, the origin of Λ doubling in molecular spectra.[5-7] In the present paper we confine to heteroatomic molecules. If we disregard the electron spin, then the only quantum number that characterizes the motion of the electrons when the nuclei are immobile is the projection Λ of the electron orbital momentum on the internuclear axis. The electron Hamiltonian at fixed nuclei is invariant to reflection in a plane passing through the axis, and this reflection reverses the sign of Λ. This leads to double degeneracy of all the levels with $\Lambda \neq 0$ with respect to the sign of Λ. When spin is taken into account, a distinction must be made between the types of states in accord with Hund's rules. In states of type (a), the energy of the spin-axis interaction exceeds the energy of rotation of the molecule as a unit, so that a meaningful quantum number is the projection Σ of the spin on the axis, as well as the magnetic quantum number $\Omega = \Lambda + \Sigma$. When the rotation is taken into account, the quantum number J appears and characterizes the total angular momentum of the molecule ($J \geqslant |\Omega|$). In states of type (b) the situation is reversed, so that the quantum number Σ is meaningless, but the number K, which characterizes the total orbital angular momentum of the molecule ($K \geqslant |\Lambda|$), becomes significant. In both cases, the quantum number S, which characterizes the electron spin, is important. Thus, in a state of type (a) we use wave functions with a set of quantum numbers $\psi(nv\Lambda\Sigma\Omega SJM)$, where M is the projection of the total angular momentum on an arbitrary direction, v is the vibrational quantum number, and n stands for all the other quantum numbers; in a state of type (b) we use the wave functions $\psi(nv\Lambda SKJM)$. In a state of type (a) the degeneracy mentioned above occurs in fact when the signs of Λ and Σ (and consequently also of Ω) are reversed simultaneously.

We consider now symmetry operations that include transformations of the nuclear coordinates. The Hamiltonian of the entire molecule as a whole is invariant to the operator P of inversion of the coordinates of the electrons and nuclei. It follows therefore that all the states must be even (positive, in accord with the present terminology) or odd (negative). Inversion of P reverses the signs of the quantum numbers Λ and (as projections of the axial vectors on the axis, which itself reverses direction upon inversion), therefore the wave functions of the positive and negative states of type (a) will be the linear combinations

$$\psi^{\pm}(nv\Lambda\Sigma\Omega SJM) = 2^{-1/2}(\psi(nv\Lambda\Sigma\Omega SJM) \pm \psi(nv\bar{\Lambda}\bar{\Sigma}\bar{\Omega}SJM)), \tag{1}$$

where $\bar{\Lambda} \equiv -\Lambda$ etc. We can write down analogously the wave functions for the case (b). The ± sign in the left-hand side, which designates the parity of the state, is not uniquely connected with the ± sign in the right-hand side, since the inversion operation is accompanied also by multiplication of the wave function by $(-1)^K$. In the case (a), the quantum number K does not have the meaning of angular momentum, but determines the parity of the state. The quantity K can be determined by going over in the limit to the case (b), since the parity of the state is not altered by such a transition.

2. LEVEL SPLITTING IN Λ DOUBLING

Λ doubling in spectra of diatomic molecules takes place when account is taken of the perturbations that lift

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the degeneracy of the electronic state with respect to the signs of the projections of the angular momenta. We consider first the Λ doubling for molecular states corresponding to Hund's type (a). The Λ doubling appears for such states when account is taken of two perturbations: the spin-orbit interaction H_p, and the interaction of the electron motion with the rotation H_{er}.[5,6] The corresponding effective operators are of the form[6]

$$H_{so}=\xi_{so}\mathbf{LS}, \tag{2}$$

$$H_{er}=\xi_{or}\mathbf{JL}+\xi_{sr}\mathbf{JS}, \tag{3}$$

where L and S are the electron orbital and spin angular momenta. The correct linear wave-function combinations that diagonalize the effective perturbation operator are precisely the functions (1).

The energy-level splitting is determined by the matrix element that connects the states $\langle\Lambda\Sigma\Omega$ and $\overline{\Lambda\Sigma\Omega}\rangle$. Such a connection can be obtained only in perturbation theory of higher-order in the operators H_{so} and H_{er}. The operator S_{so}, is seen from (2), changes Λ and Σ by unity and leaves Ω unchanged, while the operator H_{er} either changes Ω or Λ by unity with Σ unchanged, or else changes Ω and Σ with Λ unchanged. The spin-orbit interaction constant A in states of type (a) is larger than the rotational constant B, therefore in those cases when it is possible it is necessary to use primarily the operator H_{so}. However, the operator H_{so} by itself can result in splitting only at $\Omega=0$. The energy denominators for different intermediate states are of different order of magnitude: if the value of $|\Lambda|$ in the intermediate state coincides with the initial value, then the denominator is determined by the multiplet splitting and is of the order of A^{-1}, while in the opposite case the denominator is determined by the distance between the different electronic terms and is of the order of ω^{-1}, where ω is the transition frequency. The matrix elements H_{sr} do not depend on J, i.e., $H_{so}\approx A$, and the dependence of the matrix elements H_{er} on J is determined by the formula[6]

$$\langle\Lambda\Sigma\Omega J|H_{er}|\Lambda'\Sigma'\Omega-1J\rangle\approx B[(J+\Omega)(J+1-\Omega)]^{1/2}. \tag{4}$$

Using the rules presented above, we can easily estimate the splitting of the Λ sublevels for any state. For example, for the states $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$ we obtain the following change of matrix elements[2)]

$$\Delta E(^2\Pi_{1/2})=\left\langle 1\frac{\bar{1}}{2}\frac{1}{2}\right|H_{so}\left|0\frac{1}{2}\frac{1}{2}\right\rangle\frac{1}{\omega}\times\left\langle 0\frac{1}{2}\frac{1}{2}\right|H_{er}\left|\bar{1}\frac{1}{2}\frac{\bar{1}}{2}\right\rangle, \tag{5}$$

$$\Delta E(^2\Pi_{3/2})=\left\langle 1\frac{1}{2}\frac{3}{2}\right|H_{er}\left|1\frac{\bar{1}}{2}\frac{1}{2}\right\rangle\times\frac{1}{A}\left\langle 1\frac{\bar{1}}{2}\frac{1}{2}\right|H_{er}\left|0\frac{\bar{1}}{2}\frac{\bar{1}}{2}\right\rangle\frac{1}{\omega}\left\langle 0\frac{\bar{1}}{2}\frac{\bar{1}}{2}\right|H_{er}\left|\bar{1}\frac{\bar{1}}{2}\frac{\bar{3}}{2}\right\rangle. \tag{6}$$

Substituting here the estimate (4) for the matrix elements H_{el}, we can separate the J-dependences in the expressions for ΔE. The final expressions for a number of states are given in Table I. These expressions contain also indeterminate factors of the order of unity, due to the matrix elements H_{so} and H_{er} as well as to the summation over the intermediate states. Some of these factors were calculated by Mulliken.[7]

$$\Delta E(\Pi)\approx(B^2/\omega)K(K+1),$$

$$\Delta E(\Delta)\approx B(B/\omega)^3(K-1)K(K+1)(K+2),$$

TABLE I.

State	Splitting
$^2\Pi_{1/2}$	$B(A/\omega)(J+1/2)$
$^2\Pi_{3/2}$	$B(B/A)(B/\omega)(J-1/2)(J+1/2)(J+3/2)$
$^3\Pi_0$	$A(A/\omega)$
$^3\Pi_1$	$B(B/\omega)J(J+1)$
$^3\Pi_2$	$B(B/\omega)(B/A)^2(J-1)J(J+1)(J+2)$
$^3\Delta_1$	$B(B/\omega)(A/\omega)^2J(J+1)$
$^3\Delta_2$	$B(B/\omega)^3(J-1)J(J+1)(J+2)$
$^3\Delta_3$	$B(B/\omega)^3(B/A)^2(J-2)(J-1)J(J+1)(J+2)(J+3)$

For sufficiently large values of J, such that the inequality $BJ(J+1)>A$ is satisfied, all the states go over into the type (b). In this case ΔE is independent of S and is obtained for each level with specified Λ from that expression in Table I which corresponds to $\Sigma=0$, by replacing J with K, i.e., which coincides with expressions given in the book of Landau and Lifshitz[6] for the singlet Π and Δ states.

3. MIXING OF Λ SUBLEVELS BY A WEAK INTERACTION

The effective neutral-current weak interaction operator for electron-nuclear interactions takes in atomic units $\hbar=e=1$ the form[2]

$$V^{eN}=\frac{G}{2^{1/2}m}\sum_i^{N_e}\sum_a\{(f_{1a}\sigma_i+f_{2a}\mathbf{I}_a)\times[\mathbf{p}_i\times\delta^{(3)}(\mathbf{r}_i-\mathbf{R}_a)]_+-if_{2a}[\sigma_i\mathbf{I}_a][\mathbf{p}_i\delta^{(3)}(\mathbf{r}_i-\mathbf{R}_a)_-\}, \tag{7}$$

where i is the number of the electron, a is the number of the nucleus, σ_i are the electron spins (Pauli matrices), I_a are the spins of the nuclei, $\mathbf{p}_i\equiv-\nabla_i[\ldots]_\mp$ denotes a commutator or an anticommutator, G is the Fermi weak-interaction constant and is equal to $G\approx10^{-5}(m/m_p)^2$, m_p is the proton mass, m is the electron mass, and N_e is the number of electrons in the molecule. The electron-nuclear interaction constants $f_{sa}(Z_aN_a)$ ($s=1,2$; Z_a, N_a are the numbers of the protons and the neutrons in the nucleus) depend on the choice of the weak-interaction model. In the Weinberg-Salam model we have $f_{1a}\sim Z_a, f_{2a}\sim1$ (Ref. 2).

The off-diagonal matrix elements of the weak-interaction operator between the states $\psi^\pm$ is equal to

$$\langle\psi^+|V|\psi^-\rangle=1/2\{\langle\Lambda|V|\Lambda\rangle-\langle\bar{\Lambda}|V|\bar{\Lambda}\rangle+\langle\bar{\Lambda}|V|\Lambda\rangle-\langle\Lambda|V|\bar{\Lambda}\rangle\} \tag{8}$$

(we leave out the remaining quantum numbers for brevity; $\bar{\Lambda}$ denotes then $\overline{\Lambda\Sigma\Omega}$). Since the operator V is odd in P, and the projections of Λ, Σ, and Ω reverse sign upon inversion, we get

$$\langle\bar{\Lambda}|V|\bar{\Lambda}\rangle=-\langle\Lambda|V|\Lambda\rangle, \tag{9}$$

$$\langle\bar{\Lambda}|V|\Lambda\rangle=-\langle\Lambda|V|\bar{\Lambda}\rangle, \tag{10}$$

$$\langle\psi^+|V|\psi^-\rangle=\langle\Lambda|V|\Lambda\rangle-\langle\Lambda|V|\bar{\Lambda}\rangle. \tag{11}$$

The matrix element $\langle\Lambda|V|\Lambda\rangle$, however, turns out to be equal to zero. The reason is that the matrix elements of the operator V are always pure imaginary (see, e.g., Ref. 2). But $\langle\Lambda|V|\Lambda\rangle$ is a diagonal matrix element of a Hermitian operator and must be real, for which it follows[3)] that $\langle\Lambda|V|\Lambda\rangle=0$. The last equality remains in force also when account is taken of different corrections to the wave functions in the brackets, for example when account is taken of the spin-orbit interaction.

Thus,

$$\langle\psi^+|V|\psi^-\rangle=-\langle\Lambda|V|\bar{\Lambda}\rangle \tag{12}$$

and, as can be easily verified,

$$\langle\psi^-|V|\psi^+\rangle=-\langle\psi^+|V|\psi^-\rangle. \tag{13}$$

The matrix element $\langle\Lambda|V|\bar{\Lambda}\rangle$ is in general not equal to zero, but it vanishes in all cases when $\Lambda, \Sigma, \Omega \geqslant 1$, for in that case the operator does not connect the states $\Lambda\Sigma\Omega$ with the states $\bar{\Lambda}\bar{\Sigma}\bar{\Omega}$. Consequently, to obtain a nonzero effect, we must take into account the corrections to the wave functions, e.g., we must set up the same chain of operators as for the splitting of the Λ sublevels, but one of the operators, H_{so} or H_{er}, must be replaced by the operator V. Naturally, the effect will be maximal when H_{er} is replaced by V. Since H_{er} changes the value of Ω, such a replacement can be attained only with the aid of those terms of the operator V which contain a dependence on the nuclear spin.[4] Thus, in the corresponding experiments we can determine only the constant f_2.

It should also be added that the chain of operators must be made up, if possible, in such a way that the matrix element V connects the Σ and Π states. More accurately speaking, the electron configurations for the states in the operator brackets of the matrix element V should be such that the latter reduce to a single-electron matrix element of the type $\langle\sigma|V_1|\pi\rangle$, where V_1 is the single-electron operator corresponding to V, while σ and π are the single-electron states. The single-electron wave functions for all states, with the exception of the σ states, vanish on the axis of the molecule. Since the operator V_1 contains δ functions of the type $\delta^{(3)}(\mathbf{r}_i-\mathbf{R}_a)$, the only nonvanishing matrix elements V_1 will be those between the σ and π states, in analogy with the fact that in atoms only the V_1 matrix elements between the s and p states differ from zero. From this point of view for example, suitable states for mixing are $^2\Pi$ and $^2\Sigma$, since the corresponding configurations contain one valence electron each in the states π and σ.

Let us examine in greater detail the matrix element $\langle\Lambda'\Sigma'\Omega'|V|\Lambda\Sigma\Omega\rangle$. In the operator (7) we take into account only the terms that depend on the nuclear spins. Then V^{eN} can be written in the form

$$V=\sum_{i=1}^{N_e}\sum_{a=1,2}\mathbf{I}_a\mathbf{u}_{ia},\quad \mathbf{u}_{ia}=\mathbf{a}_{ia}+[\boldsymbol{\sigma}_i\times\mathbf{b}_{ia}],$$

$$\mathbf{a}_{ia}=\frac{Gf_{2a}}{2^{3/2}m}[\mathbf{p}_i\times\delta^{(3)}(\mathbf{r}_i-\mathbf{R}_a)]_+,$$

$$\mathbf{b}_{ia}=\frac{iGf_{2a}}{2^{3/2}m}[\mathbf{p}_i\times\delta^{(3)}(\mathbf{r}_i-\mathbf{R}_a)]_-.$$

To calculate the matrix element V it is necessary to introduce, besides the wave function $\psi(nv\Lambda\Sigma\Omega SJM)$, the spin wave functions of the nuclei η_{Ia} or I_a, and add up the angular momenta. The matrix element will then depend on the values of F_a of the assembly angular momenta $\mathbf{F}_a=\mathbf{J}+\mathbf{I}_a$. The result, averaged over the projections of the nuclear spins, is

$$\begin{aligned}&\langle n'v'\Lambda'\Sigma'\Omega'S'JI_1I_2F_1F_2|V|nv\Lambda\Sigma\Omega SJI_1I_2F_1F_2\rangle\\&=\sum_i\sum_{a=1,2}(-1)^{I_a+J+F_a}\begin{Bmatrix}I_a & I_a & 1\\ J & J & F_a\end{Bmatrix}[I_a(I_a+1)(2I_a+1)]^{1/2}\\&\quad\times\langle n'v'\Lambda'\Sigma'\Omega'S'J\|u_{ia}\|nv\Lambda\Sigma\Omega SJ\rangle.\end{aligned} \tag{14}$$

We can use next the expressions for the reduced matrix element of the electron vector, expressed in the laboratory frame with electron wave functions written in a coordinate system that rotates together with the nuclei (Ref. 6, formula 110.6). This yields

$$\begin{aligned}&\langle n'v'\Lambda'\Omega'S'J\|u_{ia}\|nv\Lambda\Sigma\Omega SJ\rangle\\&=(-1)^{J-\Omega'}(2J+1)\begin{pmatrix}J & 1 & J\\ -\Omega' & \Omega'-\Omega & \Omega\end{pmatrix}\Big\{\langle n'v'\Lambda'|a_{ia(\Omega'-\Omega)}|nv\Lambda\rangle\delta_{SS'}\delta_{\Sigma\Sigma'}\\&\quad-(-1)^{\Omega-\Omega'}i6^{1/2}\begin{pmatrix}1 & 1 & 1\\ \Lambda'-\Lambda & \Sigma'-\Sigma & \Omega-\Omega'\end{pmatrix}\langle S'\Sigma'|\sigma_{\Sigma'-\Sigma}|S\Sigma\rangle\\&\quad\times\langle n'v'\Lambda'|b_{ia(\Lambda'-\Lambda)}|nv\Lambda\rangle\Big\}.\end{aligned} \tag{15}$$

We now apply the obtained formulas to the state $^2\Pi_{1/2}$. In this case the matrix element of the effective operator w that mixes the states $\psi^\pm$ in accordance with (5) and (12), takes the form

$$\begin{aligned}&\langle+|w|-\rangle=-\langle nv\Lambda\Sigma\Omega SJ|H_{so}|n'v'\Lambda'\Sigma'\Omega SJ\rangle\\&\times\omega^{-1}\langle n'v'\Lambda'\Sigma'\Omega SJI_1I_2F_1F_2|V|nv\bar{\Lambda}\bar{\Sigma}\bar{\Omega}SJI_1I_2F_1F_2\rangle,\end{aligned} \tag{16}$$

where $\Lambda=1, \Lambda'=0, \Sigma=-\frac{1}{2}, \Sigma'=\frac{1}{2}, \Omega=\frac{1}{2}, S=\frac{1}{2}$, i.e., the intermediate states are the $^2\Sigma^\pm$ states. We assume here that the matrix elements of the electron operator H_{so} is diagonal in the quantum numbers v and J. The energy denominator in this case is equal to $\omega=E(^2\Sigma^\pm)-E(^2\Pi_{1/2})$. Substituting expressions (14) and (15) in (16), expanding the expressions for the $3j$ and $6j$ symbols, and using the explicit expressions for the vectors $\mathbf{a}_{ia}$ and $\mathbf{b}_{ia}$, we get

$$\begin{aligned}&\langle n'v'\Lambda'\Sigma'\Omega SJI_1I_2F_1F_2|V|nv\Lambda\Sigma\Omega SJI_1I_2F_1F_2\rangle\\&=\frac{iG}{4m}\frac{J+1/2}{J(J+1)}\sum_{a=1,2}f_{2a}\{F_a(F_a+1)-I_a(I_a+1)-J(J+1)\}\\&\quad\times\langle^2\Sigma^\pm|\sum_i\delta^{(3)}(\mathbf{r}_i-\mathbf{R}_a)\nabla_{i1}|^2\Pi\rangle,\end{aligned} \tag{17}$$

where ∇_{i1} is a cyclic component of the vector ∇_i.

4. RESONANCE FLUORESCENCE

We consider the process of scattering of light by a molecule in the ground state with $\Lambda\neq 0$ (examples of such molecules are given in Sec. 5). We assume here that the frequency of the incident radiation is tuned to resonance with a certain electronic transition in the molecule. An approximate scheme of the levels of interest to us for such a molecule, with allowance for the Λ doubling, is shown in Fig. 1. The Feynman diagrams corresponding to the processes that are possible in the case of scattering are shown in Fig. 2. The frequency ω of the incident radiation is assumed to be at resonance with the magnetic transition $1^-\to 2^-$. The electric transition 1^+

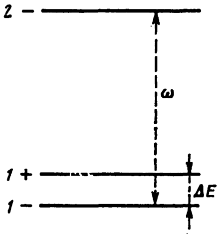

FIG. 1. Approximate arrangement of molecule levels. The numbers denote various electron levels; the ± signs denote positive (negative) levels, ω is the electron-transition frequency, and ΔE is the splitting of the Λ sublevels.

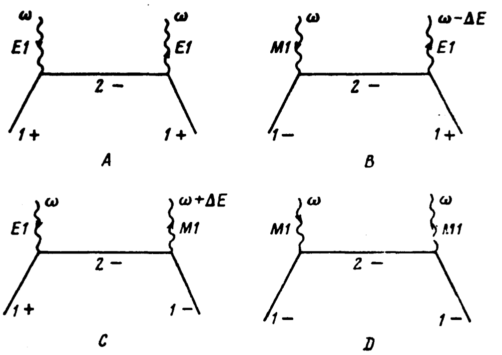

FIG. 2. Feynman diagrams for the light scattering process. The symbols 1± and 2− on the electron (solid) lines indicate the molecular states, and the symbols $E1$ and $M1$ on the photon lines indicate the character of the absorbed and emitted photons (electric or magnetic).

$\rightarrow 2^-$ is also excited, because of the large natural width Γ of the level 2.

We now take into account the mixing of the Λ sublevels by a weak interaction. Instead of one diagram A of Fig. 2, we must now consider the aggregate of diagrams shown in Fig. 3. The amplitude of this process can be written in the form

$$\frac{1}{\Delta E_R}\left\{A_{E1}{}^{i}A_{E1}^{f*}-\frac{\langle+|w|-\rangle}{\Delta E}A_{M1}{}^{i}A_{E1}^{f*}-\frac{\langle-|w|+\rangle}{\Delta E}A_{E1}{}^{i}A_{M1}^{f*}\right\}, \tag{18}$$

where A_{E1}, A_{M1} are the amplitudes for the absorption of the electric and magnetic photons, A_{E1}^*, A_{M1}^* are the corresponding emission amplitudes, the symbols i and f pertain to the initial and final photons, $\Delta E = E_+ - E_-$, ΔE_R is the resonance denominator. Under the condition $\Gamma \gg \Delta E$ this denominator is the same for all diagrams and is equal to Γ. In the calculation of the probability of the process A of Fig. 2 (i.e., when taking the square of the modulus of the amplitude), interference terms appear:

$$w_A{}^{int}=\frac{\langle+|w|-\rangle}{\Delta E_R{}^2\Delta E}w_{E1}^{i}(A_{M1}^{f*}A_{E1}^{f}-A_{E1}^{f*}A_{M1}{}^{f})$$
$$+\frac{\langle+|w|-\rangle}{\Delta E_R{}^2\Delta E}w_{E1}{}^{f}(A_{M1}{}^{i*}A_{E1}{}^{i}-A_{E1}{}^{i*}A_{M1}{}^{i}), \tag{19}$$

where $w_{E1}^{i,f}=|A_{E1}^{i,f}|^2$. We have used here the property $\langle+|w|-\rangle^* = -\langle+|w|-\rangle$, which must hold for the effective operator w just as for V.

Substituting the expressions for the amplitudes A_{E1}, A_{M1} and averaging over the projections of the angular momenta, in analogy with the procedure used for atoms, we can reduce (19) to the form

$$w_A{}^{int}=-\frac{2i\langle+|w|-\rangle}{\Delta E_R{}^2\Delta E}w_{E1}(w_{E1}w_{M1})^{1/2}(\mathbf{s}_i\mathbf{n}_i+\mathbf{s}_f\mathbf{n}_f), \tag{20}$$

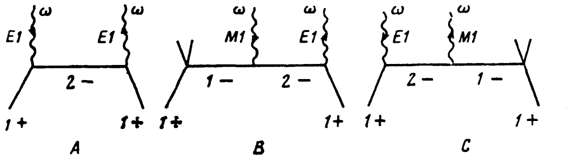

FIG. 3. Feynman diagrams for scattering without change of frequency, with the weak interaction taken into account. The weak interaction is represented by the "fork" on the diagrams.

where $\mathbf{s}$ and $\mathbf{n}$ are the photon spin and propagation direction.

Analogous operators for the processes B and C of Fig. 2 yield

$$w_B{}^{int}=\frac{2i\langle+|w|-\rangle}{\Delta E_R{}^2\Delta E}w_{E1}(w_{E1}w_{M1})^{1/2}\mathbf{s}_i\mathbf{n}_i, \tag{21}$$

$$w_C{}^{int}=\frac{2i\langle+|w|-\rangle}{\Delta E_R{}^2\Delta E}w_{E1}(w_{E1}w_{M1})^{1/2}\mathbf{s}_f\mathbf{n}_f. \tag{22}$$

No account is taken here of the diagrams that contain the magnetic transition twice, such as diagram D of Fig. 2. The presence of $\mathbf{s}_f\cdot\mathbf{n}_f$ in the expression for the total probability of the scattering process means onset of circular polarization of the scattered radiation. The presence of $\mathbf{s}_i\cdot\mathbf{n}_i$ means that the scattering cross section depends on the direction (sign) of the circular polarization of the incident radiation. Both are the result of parity nonconservation.

A possible experiment in which to observe parity nonconservation effects can be imagined as follows. Circularly polarized radiation of a laser is scattered by the molecule ground (or metastable) state in which there is Λ doubling. If the natural width of the level from which the scattering takes place is small or zero (it is for the latter that the ground state is necessary), then the picture shown in Fig. 4 is observed in the scattering. According to theory,[8] the width of the scattering peaks is determined in this situation by the width γ of the laser emission line. It is also necessary to satisfy the inequality $\gamma \ll \Delta E$. Thus, we are dealing with Raman scattering of light by a molecule in the presence of resonance, i.e., with resonance fluorescence.

If the three lines are not optically resolved, the effect is equal to zero, since the interference terms in the combined probability cancel each other, as follows from formulas (20)–(22). The parity-nonconservation effects observed on the central line will be much smaller than on the side lines, for when the interference terms are equal the principal background-producing term in the expression for the probability is much larger on the central line. Thus, the experiment can consist either of measuring the degree of circular polarization of scattered radiation at frequency $\omega + \Delta E$, or of observing the change in the intensity of the scattered radiation of the frequency $\omega - \Delta E$ with changing sign of the circular polarization of the incident radiation.

Both experimental variants were in essence considered already in the first studies of Bouchiat and Bouchiat[9] as applied to atoms. The new element in the experiments proposed is the use of an allowed transi-

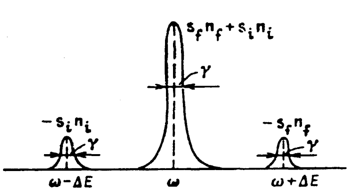

FIG. 4. Schematic dependence of the scattering cross section on the frequency of the incident radiation. The heights of the central and side peaks are not to scale. The figure indicates also the pseudoscalars that characterize the parity nonconservation effects when observed at various frequencies.

tion, the proximity of the levels, and the absence of a natural width (ground state).

5. ESTIMATES OF THE MAGNITUDE OF THE EFFECTS

The degree of parity nonconservation in the considered processes is determined by the ratio of w^{int} to the probability w^0 of the process without allowance for weak interaction. Inasmuch as for both side lines on Fig. 4 this quantity is equal to $w^0 = w_{E1}w_{M1}$, we obtain for the degree parity nonconservation P

$$P = \frac{2i\langle + |w| - \rangle}{\Delta E}\left(\frac{w_{E1}}{w_{M1}}\right)^{1/2}. \tag{23}$$

According to (16) and (17), as well as Table I, for the state $^2\Pi_{1/2}$ the ratio $2i\langle + |w| - \rangle/\Delta E$ is equal to

$$\frac{2i\langle + |w| - \rangle}{\Delta E} = \frac{G}{2Bm}\sum_a f_{2a}\frac{F_a(F_a+1) - I_a(I_a+1) - J(J+1)}{J(J+1)}$$
$$\times \langle ^2\Sigma^\pm | \sum_i \delta^{(3)}(\mathbf{r}_i - \mathbf{R}_a)\nabla_{i1}|^2\Pi\rangle,$$

where B is the rotational constant for the molecule. It is seen that this ratio does not increase with increasing J. For the matrix element

$$\langle ^2\Sigma^\pm | \sum_i \delta^{(3)}(\mathbf{r}_i - \mathbf{R}_a)\nabla_{i1}|^2\Pi\rangle$$

we use the atomic estimate[2]

$$\langle ^2\Sigma^\pm | \sum_i \delta^{(3)}(\mathbf{r}_i - \mathbf{R}_a)\nabla_{i1}|^2\Pi\rangle \approx \frac{1}{4\pi}m^3(\alpha Z_a)^2 \tag{24}$$

(in the atomic units $\hbar = e = 1$), where α is the fine-structure constant.

For the value of the probability ratios we also use the atomic estimate (see the discussion in Ref. 3)

$$(w_{E1}/w_{M1})^{1/2} \approx 1/\alpha Z_{\text{eff}}, \tag{25}$$

where Z_{eff} is the effective charge of the nucleus. We shall assume $Z_{\text{eff}} \sim 1$, inasmuch as an important role in the calculation of the matrix elements of the transitions is played by the regions of space that are far from the nuclei. Using (23)–(25), we obtain the following final estimate for P:

$$P = \frac{\alpha}{8\pi B[\text{cm}^{-1}]}\left(\frac{m}{m_p}\right)^2 \sum_a f_{2a}Z_a^2 \frac{F_a(F_a+1) - I_a(I_a+1) - J(J+1)}{J(J+1)}. \tag{26}$$

Formula (26) presupposes that the hyperfine splitting is larger than the distance between the Λ sublevels ΔE, and we are dealing with a definite hyperfine component of the Λ sublevel.

The molecules that are suitable for our purposes, their parameters, and the resultant values of ΔE and P are listed in Table II. The lowest rotational state $J = \frac{1}{2}$ and the hyperfine-structure components F_n that make the largest contribution to (26) are considered throughout.

TABLE II.

Molecule	Transition	Z_1, Z_2	$I_1(F_1)$, $I_2(F_2)$	B, cm^{-1}	$\Delta E\cdot 10^2$, cm^{-1}	P	λ, Å	Reference
CuO	$A^2\Sigma^+ \rightleftarrows X^2\Pi_{1/2}$	29.8	$^3/_2$ (1), 0 ($^1/_2$)	0.42	1.0	$0.6\cdot 10^{-6} f_2$	6100	[10]
CuS	$A^2\Sigma^+ \rightleftarrows X^2\Pi_{1/2}$	29.16	$^3/_2$ (1), 0 ($^1/_2$)	0.19	0.46	$1.2\cdot 10^{-6} f_2$	5700	[11]
CuSe	$A^2\Sigma^+ \rightleftarrows X^2\Pi_{1/2}$	29.34	$^3/_2$ (1), $^1/_2$ (0)	0.10	0.35	$4.3\cdot 10^{-6} f_2$	6200	[12]

6. ESTIMATES OF THE INTERFERENCE NOISE

If the laser line width γ is not small enough, then the wing of the strong central line on Fig. 4 can overlap the side lines, thereby effectively decreasing the value of P. Assuming Lorentz line contours, we can write down the condition under which there is no such interference:

$$w_{M1} \gg (\gamma/\Delta E)^2 w_{E1}.$$

From this we obtain condition on the width γ:

$$\gamma \ll \Delta E(w_{M1}/w_{E1})^{1/2} \approx 10^{-2}\Delta E. \tag{27}$$

At $\Delta E \sim 10^{-2}$ cm^{-1} we get $\gamma \lesssim 10^{-4}$ cm^{-1} ~ 1 MHz, which is quite feasible with many laser sources.

We consider now interference produced by a random magnetic field. In a magnetic field, owing to the Zeeman splitting of the levels the probabilities of the transition turned out to be different for left- and right-polarized photons (looking along the magnetic field) and in the absence of weak interactions. The necessary condition for the absence of such interference is that this difference be smaller than the difference due to the weak interactions.

It is convenient to compare the total probabilities (we recall that w_{E1} and w_{M1}, as well as expressions (19)–(22), pertain to the probabilities of decay per unit time). The difference between the total probabilities, which is due to the weak interaction, will obviously be determined by the same relative quantity as for the probabilities per unit time, namely, the quantity P. The total-probability difference due to the magnetic field of intensity $\mathscr{H}$, is written in the form

$$\delta w_{\mathscr{H}} = \frac{\gamma}{2\pi}\int_{\omega-\Delta/2}^{\omega+\Delta/2}\frac{d\omega'}{(\omega-\omega')^2+(\gamma/2)^2}$$
$$-\frac{\gamma}{2\pi}\int_{\omega-\Delta/2+\delta\omega_{\mathscr{H}}}^{\omega+\Delta/2+\delta\omega_{\mathscr{H}}}\frac{d\omega'}{(\omega-\omega')^2+(\gamma/2)^2},$$

where ω is the resonant frequency, Δ is the radiation-receiver bandwidth, and $\delta\omega_{\mathscr{H}}$ is the width of the Zeeman splitting of the levels, for which there is a known relation[13]

$$\delta\omega_{\mathscr{H}}[\text{cm}^{-1}] \approx 10^{-4}\mathscr{H}[\text{G}].$$

It is natural to regard the quantity Δ as equal to the width of the source bandwidth, $\Delta \approx \gamma$. Assuming that the field is weak enough, i.e., $\delta\omega_{\mathscr{H}} \ll \Delta$ (this assumption holds true already at $\mathscr{H} \sim 0.1$ G), calculation of the integral yields

$$\delta w_{\mathscr{H}} \approx -\frac{4}{\pi}\frac{\delta\omega_{\mathscr{H}}}{\Delta}.$$

From this we get the following limitation on the value of:

$$\mathscr{H}[\text{G}] \ll 10^4 P\gamma[\text{cm}^{-1}]. \tag{28}$$

Assuming $P \sim 10^{-6}$, $\gamma \sim 10^{-4}$ cm^{-1}, we obtain the rather stringent condition $\mathscr{H} \lesssim 10^{-6}$ G, satisfication of which is apparently one of the main difficulties in the experiments in question.

Random electric fields also lead to the appearance of interference. The main interference from an electric field (Ref. 14) consists of mixing of the states 1^+ and 1^-, as a result of which the expressions for the probabilities of the processes B and C (Fig. 2) acquire additional terms of the order of $\delta\omega^2 w_{\mathscr{E}1}^2/\Delta E^2$, where $\delta\omega_{\mathscr{E}}$ is the Stark splitting of the levels. These terms make no contribution to the interference term, but they can lower the value of P. To prevent this, it is necessary to satisfy the condition

$$w_{M1} \gtrsim \frac{\delta\omega_{\mathscr{E}}^2}{\Delta E^2} w_{E1}.$$

Using also the known relation for $\delta\omega_{\mathscr{E}}$ (Ref. 13)

$$\delta\omega_{\mathscr{E}}[\mathrm{cm}^{-1}] \approx 10^{-4}\mathscr{E}[\mathrm{V/cm}],$$

we obtain a condition for $\mathscr{E}$:

$$\mathscr{E}[\mathrm{V/cm}] \leqslant 10^2 \Delta E[\mathrm{cm}^{-1}]. \tag{29}$$

From (29) at $\Delta E \sim 10^{-2}\ \mathrm{cm}^{-1}$ we obtain the upper bound $\mathscr{E} \lesssim 1$ V/cm, which seems quite realistic.

In conclusion let us compare the possibilities of molecular experiments with the analogous atomic experiments proposed earlier for the cesium atoms.[9] The order of magnitude of the effect P in both cases is approximately the same (we recall that the value $P \sim 10^{-4}$ was obtained in Ref. 9 under the assumption that $f_1 \sim Z$ in the operator (7), but this assumption has not yet been confirmed by experiment). Molecular experiments provide better statistics, since the principal magnetic transition is allowed and its intensity is approximately 10^4 times larger than the intensity of the forbidden magnetic transition in the Cs atom. The shortcoming of the molecular experiment is the need for resolving closely lying lines within an interval $\sim 10^{-2}\ \mathrm{cm}^{-1}$. This calls for eliminating the Doppler broadening of the lines and consequently for using molecular beams. To be sure, the limitations on the perpendicular components of the velocity in the situation considered by us are not stringent ($v_\perp \lesssim 10^4$ cm/sec) and are apparently attainable in standard experiments with molecular beams.[16]

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[1] The feasibility in principle of using Λ doubling for the investigation of parity-nonconservation effects was first considered by Onishchuk.[4]

[2] In such chains one can encounter a state with $\Lambda = 0$, which always corresponds to a coupling of type b) and for which the quantum numbers Σ and Ω have no meaning. This state, however, can be resolved into states with definite values of Σ and Ω, and when the chains are made up one can use the expansion terms with the required values of Σ and Ω.

[3] This circumstance was not taken into account earlier in Ref. 3, so that the formulas and the estimates given there for effects connected with Λ doubling are incorrect.

[4] This can likewise not be accomplished with the aid of the operator V^{ee} of weak electron-electron interaction; we therefore do not consider V^{ee} in this article.

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