

POSSIBILITY OF ACTIVATING SPIN-ORBITAL INTERACTION IN A MOLECULE IN AN OPTICAL BIHARMONIC FIELD

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The solution to the problem on activation of the electronic spin-orbital interaction in a molecule being in the ground rovibronic state by an external field opens a new possibilities to control the physicochemical properties of a gaseous medium and a radiation scattered by it, as well as improves the efficiency of the medium diagnostics and separation of isotopes, plasma formation and stability. Direct way to solve this problem is associated with the change of relationship between the magnitudes of nuclear (\mathbf{R}) and electronic (\mathbf{l}, \mathbf{s}) angular momenta of a molecule when composing them, for example, with the total spin of photons (\mathbf{J}_ϕ) of the exciting field into the total mechanical angular momentum $\mathbf{F}' = \mathbf{J}' + \mathbf{J}_\phi = \mathbf{R} + \mathbf{l} + \mathbf{s} + \mathbf{J}_\phi$ (neglecting the nuclear spin \mathbf{I}) due to parametric resonances (see below).

The possibility of directly solving the problem follows from the physical symmetry. For the upper states of a molecule, the magnitude of angular momenta of electrons and photons that excite molecules is small ($|\mathbf{F}'| = |\mathbf{J}' + \mathbf{J}_\phi| \approx |\mathbf{J}'| \gg |\mathbf{s}|, |\mathbf{J}_\phi|, \hbar$) and their quantum fluctuations have no significant effect on the process of light absorption and emission; \hbar is the Planck constant. If the molecule starts from the lower rotational state ($|J=1, M\rangle$ and $|\mathbf{J}'| \approx \hbar$ is the photon angular momentum) and is deexcited into the lowest state ($|J=0, M=0\rangle$ at nonstationary (being a superposition of M -sublevels) overtone (degenerate in projections of angular momentum \mathbf{J}') state $|J, M\rangle$, then significance of quantum fluctuations of angular momenta $\mathbf{s}, \mathbf{J}_\phi$ increases so one can make use of this fact; J and M are rotational and magnetic quantum numbers.

The purpose of this work is to study the possibility of activating the electronic spin-orbital interaction in a diatomic molecule and its transition from the ground rovibronic state to a metastable spin- supermultiplet state under exposure to a field of optical biharmonic

$$E(t) = E_1 \exp[i(\omega_1 t + \psi_1)] + E_2 \exp[i(\omega_2 t + \psi_2)] \equiv \\ \equiv A'' \left(\frac{E_1}{E_2}, \frac{\Delta\omega}{2}, \frac{\Delta\psi}{2}, t \right) \exp \left[i\Phi'' \left(\frac{E_1}{E_2}, \omega_s, \psi_s, t \right) \right]; \quad (1)$$

$$H(t) = H_1 \exp[i(\omega_1 t + \psi_1)] + H_2 \exp[i(\omega_2 t + \psi_2)] \equiv \\ \equiv A' \left(\frac{H_1}{H_2}, \frac{\Delta\omega}{2}, \frac{\Delta\psi}{2}, t \right) \exp \left[i\Phi' \left(\frac{H_1}{H_2}, \omega_s, \psi_s, t \right) \right], \quad (2)$$

whose strengths E_1, E_2 and H_1, H_2 have linear polarization; and the half-difference, $\Delta\omega/2 = (\omega_1 - \omega_2)/2$, and the half-sum, $\omega_s = (\omega_1 + \omega_2)/2$ of the optical frequencies ω_1 and ω_2 are within the "collisional-field" resonances with the ground rotational state $|J=1, M\rangle$ as the initial one and the overtone $|J, M\rangle$ state of the molecule without field; $\Delta\psi/2, \psi_s, \psi_1$ and ψ_2 are half-difference, half-sum and the initial phases of waves of the biharmonic. Angular speeds of rotation of a diatomic molecule as a whole in the $|J=1, M\rangle$ and $|J, M\rangle$ are $\omega_0 = 2B_0$ and $\omega_j = 2B_0 J(J+1)/2$, respectively; $B_0 = \hbar/(4\pi I_b)$ and I_b are the initial ($t < 0$) rotational constant and moment of inertia of the molecule.

The key idea of the working hypothesis consists in creation, by a process of a molecule excitation in the field of optical biharmonic (1) and (2), of such amplitude-phase matching between the dynamics of the three rotational states $|J=1, M\rangle, |J=0, M=0\rangle$, and $|J, M\rangle$ at any time t , at which the multiple splitting of M -sublevels of their overtone state $|J, M\rangle$ occurs and will be accumulated, during a certain time interval T_d , up to the value multiple to the rotational constant of the molecule, B_0 , without the field.

The realization of this idea is based on the coherent excitation of the ensemble of molecules through the channel

$$|J=1, M=0\rangle \rightarrow |J=0, M=0\rangle \rightarrow |J, M\rangle \quad (3)$$

during a half-period

$$T_d = 1/(2\omega_0) = 1/(4B_0) = K'T_j/2c \quad (4)$$

of their rotation in the state $|J=1, M=0\rangle$ by amplitude-phase modulations² of the biharmonic resulting strength (BRS) under conditions of "local" synchronism, independent of the medium pressure $K' = \Sigma k, k=0, 1, 2, \dots$ $J; T_j = 1/\omega_j$.

It is assumed that the local synchronism of BRS (1) and (2) with the molecule rotational states $|J, M\rangle$ and $|J=1, M\rangle$ in the field at dynamic carrier frequency

$$\omega(t) = d\Phi''(t)/dt = d\Phi'(t)/dt = \omega_s + \Omega(t)$$

at the moment $t'_k = kT_j/2$ and its "deviation" $\Omega(t)$, asymmetric in time, at the neighboring moments $t'_k = (k + 1/2)T_j/2$ is provided by the square Stark and Zeeman oscillations of the positions of the lowest $|0, 0\rangle$

and overtone $|J, M\rangle$ rotational states. As a consequence, the electronic orbits shift about the molecule internuclear axis R' that results in amplification of orbital and spin currents in the molecule with corresponding activation of the electronic spin-orbital interaction in it.

To be more precise, under conditions of local synchronism between the slow and fast parts of the Hamiltonian of interaction between the molecule and the field (1) and (2), the parametric connection occurs; at the same time, between molecules of the medium and waves of the optical biharmonic the amplitude-phase parametric resonance (APPR) is formed. At APPR the components of BRS (1) and (2) regularly affect, at the moment t'_k, t''_k the initial amplitude and phase of the process of molecular excitation through the channel (3) and quench the signals of rotational Raman scattering at each quarter-period $T_j/4$ of the half-period T_d (4), but the resonance transfer of energy and moment of momentum from the biharmonic to molecules is activated with the accumulation of the multiplet splitting into M -sublevels of the state $|J, M\rangle$. In particular, the amplitude modulations $A''(t)$ of the electric BRS (1) at a frequency $\Delta\omega/2$ dephase the rotation of medium molecules in the initial state $|J=1, M\rangle$ by Stark oscillation of the position of the lowest state $|0, 0\rangle$ between the neighboring moments t'_k and split the overtone state $|J, M\rangle$ into $\pm M$ levels by a Stark field, whereas phase modulations $\Phi''(t)$ at a carrier frequency, equal to the frequency of the overtone $|J, M\rangle$ state,

$$\omega(t''_k) = \omega_j, \quad (5)$$

corrects the rate of dephasing and the direction of Stark field motion at the moments t''_k (k is even). Phase modulations $\Phi'(t)$ of the magnetic BRS (2) at the frequency (5) induce, at the moments t''_k (k is odd), the dynamic memory between the low- and high- excited M -sublevels of the overtone state $|J, M\rangle$, while the asymmetric deviation $\Omega(t)$ of the carrier frequency $\omega(t)$ at the neighboring moments t'_k corrects the values of this multiplet splitting occurring due to amplitude-phase modulations: $A'(t), A''(t)$ and $\Phi'(t), \Phi''(t)$.

According to the hypothesis, the probability of the Raman transition (3) including, as usually,³ the dynamic and angular multipliers should be considered at the interval (4) taking into account not only the angular momenta of the molecule $\mathbf{J}' = \mathbf{R} + \mathbf{I} + \mathbf{s}$, but also the total spin \mathbf{J}_ϕ of photons of the exciting field $\mathbf{F}' = \mathbf{J}' + \mathbf{J}_\phi$. The dipole moment of the transition (3) due to electronic-nuclear motion of the molecule must precess and nutate about the direction of the moment \mathbf{J}' while the vector \mathbf{J}' must turn by the angle d : $\mathbf{J}' \rightarrow \mathbf{F}'$ at the time (4). At the same time the connection between the rotational momentum \mathbf{R} of the molecule with the i th internuclear axis R' must dynamically decrease at each $T_j/4$ by compensating for \mathbf{R} by the total spin \mathbf{J}_ϕ of photons of the

biharmonic in such a way that $|\mathbf{R} - \mathbf{J}_\phi| = 0$ and then $|\mathbf{F}'| = |\mathbf{L} + \mathbf{S}|$; $\mathbf{L} = \Sigma\mathbf{l}$, $\mathbf{S} = \Sigma\mathbf{s}$. In other words, APPR of the molecule and the optical biharmonic "prepares for itself", during the time (4), the symmetry of the tensor of the inertia moment and the rotational polarizability $\alpha_{\text{rot}}(F' = L + S, M)$ of the molecule in the state $|J, M\rangle$ with the lifted degeneration in projections of the angular momentum \mathbf{F}' . Molecules of the medium make, at the same time, the phase transition in the systems "molecule+field" with the properties of hysteresis about the direction of the vector \mathbf{F}' . The gaseous medium of systems "molecule+field" is anisotropic. The systems "molecule+field" formed have the rotational momentum $|\mathbf{R}|$ of the molecule compensated for by the total spin of photons $|\mathbf{J}_\phi|$ and the initial kinetic energy of nuclei rotation compensated for by the sum of K' Stark shifts, $\delta k'$, of the state $|0, 0\rangle$.

The process of interaction of the optical biharmonic and the molecule transformed into the system "molecule+field" for the period (4) qualitatively changes. Every system "molecule+field" of the gaseous medium resonantly transforms, during period T_j of the time interval

$$T_d < t < T_b \ll T_g = (\delta\omega_1 \delta\omega_2)^{-1/2} \quad (6)$$

the set of photons of the biharmonic into the photons of scattered radiation of the frequency (5) with the turn of their plane of polarization by the angle d ; T_b and $\delta\omega_1 \approx \delta\omega_2$ is the time of phase relaxation of the rotational states of the nonperturbed molecule and the spectral width of the biharmonic components. Within the period $T_g(c)$, the systems "molecule+field" of a medium will break down into "e/m background"+molecules in one of the stationary rovibronic states (break down into "e/m background"+ions+electrons) and the gaseous medium will again become isotropic (become the plasma).

The above hypothesis of activation of the electronic spin-orbital interaction in a molecule by a field of optical biharmonic is of a radical character and needs for experimental verification. The indirect evidence supporting the theory was obtained in 1971, when the experiments revealed several weak absorption lines and the anomalously narrow intensity distribution in the water vapor absorption line when exposing the medium to biharmonic radiation of a ruby laser.⁴ Later on analogous result was obtained in the re-emission line of the same molecule when studying the atmospheric air in the dynamic Stark cell of a multimode ICL spectrometer based on a ruby laser.⁵

For direct experimental verification of the hypothesis in addition to the condition (6) and frequencies, $\Delta\omega/2$ and ω_s , one has to choose the ratio and the sum of powers of biharmonic components in such a way, that the sum of square Stark oscillations, asymmetric in each half-period $T_j/2$, of the lowest

rotational state of the molecule for the period (4) would be of the order of $2B_0$.

The valid signal in this case should be at the frequency (5) in the direction (forward/backward) of propagation of the exciting biharmonic.

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REFERENCES

1. M.J. El'yashevich, *Atomic and Molecular Spectroscopy* (Fizmatgiz, Moscow, 1962), 889 pp.

2. E.B. Aleksandrov, *Opt. Spcktrosk.* **14**, No. 3, 436–438 (1963); **19**, No. 3, 452–455 (1965).

3. M.P. Auzin'sh and R.S. Ferber, *Usp. Fiz. Nauk* **160**, No. 10, 73–122 (1990).

4. V.E. Zuev, V.P. Lopasov and M.M. Makogon, *Dokl. Akad. Nauk SSSR*, No. 5, 1041–1043 (1971).

5. V.P. Kochanov, V.P. Lopasov and S.F. Luk'yanenko, *Izv. Akad. Nauk SSSR, ser. Fiz.* **49**, No. 3, 516–520 (1985).

EDITOR'S NOTE

This material is published as a letter to the editor because it is a purely hypothetical statement of the assumed scenario for a molecule in a biharmonic field. The editorial board reserves the right for itself to assess the reliability of this hypothesis once the author will present the detailed argumentation.