A RIGID ROTOR IN A BIHARMONIC RESONANT FIELD

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This paper presents results of experiments on irradiation of airmolecules with second-harmonic radiation from a Nd–YAG laser operating simultaneously at the two wavelengths of the two longitudinal modes. About 750 lines in the emission spectrum of excited molecules in the region 0.198 to 0.394 μm *were recorded. These lines are due to transitions between excited electron states of* N_2 *molecules as well as of the molecular ions* N_2^+ *and* O_2^+ *and the ionized atoms* N^+ *and* O^+*. In this paper it is shown that the effect can only be observed in the case of irradiation by a biharmonic field of a medium which contain molecules with rotational energy levels, where the difference between the energies of the biharmonic pump waves is in resonance with the energy of the rotational states of the molecules of the medium.*

Interpretation of the experimental results is based on a qualitative analysis of the differential equations of motion. On the basis of our analysis we conclude that there exists a stationary point of "center" type and a limit cycle with "screwing" trajectories on it (independent of their initial conditions). As a consequence, a rigid rotor placed in a biharmonic resonant (at the difference frequency) field can be considered as a synenergistic system.

EXPERIMENT,[1,2,3] AND THE IDEA OF ITS INTERPRETATION

A biharmonic field with the wavelengths $\lambda_1 = 0.5275$ μm and $\lambda_2 = 0.5277$ μm (the second harmonic of a pulsed Nd–YAG laser with selection of two longitudinal modes and pulse duration of nearly 25 nsec) focused in air initiates a great variety of frequencies as shown in Fig. 1: 750 lines were found within the limits of the recording range from 0.198 to 0.394 μm. This effect occurs only under the following conditions: a biharmonic field and a molecular medium with rotational states (the effect disappears when one of the frequencies is removed or when the molecular gas is replaced by an atomic one). The field frequency difference turns out to be between the rotational numbers $j = 1$ and $j = 2$ of the O_2 and N_2 molecules, dramatic importance for the interpretation.

Figure 1 testifies to the extremely "broadband" character of the excitation, and shows lines of the excited electron states of N_2 molecules, N_2^+ and O_2^+ ions, and the ionized atoms N^+ and O^+ (charged particles are directly recorded during special experiments). All the frequencies of these formations within the interval 0.198–0.394 μm are included here.

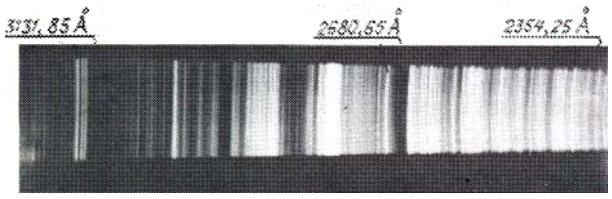

FIG. 1. Spectrum of the excited electron states of N_2 *molecules,* N_2^+ *and* O_2^+ *ions and the ionized atoms* N^+ *and* O^+*. The recording range extends from within 0.198* μm *to 0.394* μm *(The most striking part of this range is shown).*

These events, however, occur with an extremely low threshold when the field intensity in the focusis approximately equal to 10^4–10^5 V/cm. For example, 10-photon absorption of optical-frequency radiation is required for ionization of N_2. This is a process the probability of which is insignificant in a field with this intensity. There is one more very essential point — the coherence of the resulting field, i.e., the radiation of all the frequencies which are shown in Fig. 1 is concentrated "foreward" of the direction of propagation of the external wave.

Such a combination forces us either "to play a very clumsy game of patience" with already known nonlinear phenomena (see Ref. 2) or to search for a

version which sufficiently "minimizes" the interpretation of the phenomenon. The starting element of this process is quite similar to ASCS theory[4]: the optical field induces an electron dipole moment (in what follows a will denote the corresponding polarizability), and, continuing to interact with the field, it contributes a potential energy to the rotor (the usual rotational model of a two-atom molecule) $V = -\alpha U^2 \sin\theta \cos\varphi$ (see Ref. 5). The angles θ and φ are shown in Fig. 2. For the biharmonic field

$U = U_1 \exp(-i\omega_1 t) + U_2 \exp(-i\omega_2 t) + \text{c.c.}$,

where t denotes time. Here ω_1 and ω_2 are the frequencies, U_1 and U_2 are the amplitudes of the two components, and both fields are linearly and equally polarized.

It becomes clear that the harmonic with frequency $\omega_1 - \omega_2$ appears in U^2, and can be compensated for by combinations of $\exp[i(\pm\varphi(t) \pm \theta(t))]$ in the equations of motion that are explicitly present in the expression for V. If one of the values $\pm(\omega_1 - \omega_2)t \pm \varphi(t) \pm \theta(t)$ is approximately equal to zero, then the rotation energy at once becomes proportional to t with all the "cumulative" consequences.

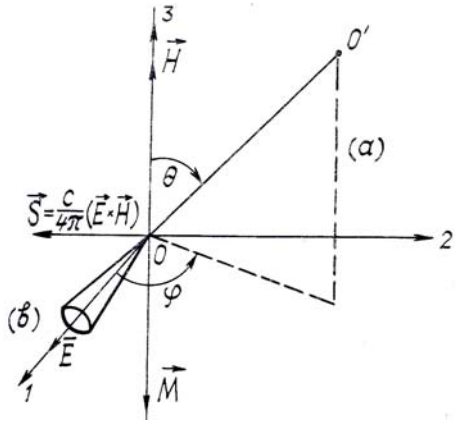

FIG. 2. Rapid rotor states before and after the field is turned on. 00' denotes the rotor axis, (a) is any state of the rotor (before the field is turned on), (b) corresponds to the limit cycle, M denotes the momentum of state (b). The laboratory system (1, 2, 3) is associated with the external field; **E**, **H** *and* **S** *are the intensities of the electric and magnetic fields and Poynting's vector, respectively.*

This picture, of course, is evoked by premises of the very appearance of the phenomenon (see the description of the experiment). It is also clear that the "resonance" must be determined by the condition $\pm(\omega_1 - \omega_2) \pm d\varphi/dt \pm d\theta/dt = 0$ with arbitrary combination of signs. Finally, there is no need to quantize the rotor motion because the rotational spectrum is not yet obligatory.

CLASSICAL ROTATOR WITH POTENTIAL

The Hamiltonian equations of motion

$$\dot\theta = \frac{P_\theta}{I}, \qquad P_\theta = \frac{P_\varphi^2 \cos^2\theta}{I\sin^2\theta} + \alpha U^2 \cos\theta\cos\varphi;$$
$$\dot\varphi = \frac{P_\varphi}{I\sin^2\theta}, \qquad \dot P_\varphi = -\alpha U^2 \sin\theta\sin\varphi \tag{1}$$

with moment of inertia I (P_θ and P_φ are the momenta canonically conjugate to θ and φ) are supplemented by equations the for angular velocity components in a moving coordinate system:

$$\omega_1 = \dot\varphi\sin\theta\sin\varphi + \dot\theta\cos\varphi;$$
$$\omega_2 = \dot\varphi\sin\theta\cos\varphi - \dot\theta\sin\varphi; \tag{2}$$
$$\omega_3 = \dot\varphi\cos\theta + \dot\varphi = 0.$$

As usual, OO' (Fig. 2) denotes the third axis of the moving coordinate system, ψ is the third (besides θ and φ) Euler angle (mathematically, ψ is eliminated by the last equation from Eq. (2)). Until the field is turned,on, the rotor undergoes uniform rotation with frequency ω:

$$\omega_1 = 0, \quad \omega_2 = \dot\theta = \omega, \quad \dot\varphi = 0, \quad \varphi = \text{const}, \tag{3}$$

which determines the initial conditions for Eq. (1). The traditional scheme[6,7] of qualitative analysis of Eq. (1) must be preceded by a remark on the introduction of a stationary point according to the conditions

$$P_\theta = P_\varphi = 0, \quad \dot\varphi = \Omega^{(1)} = \text{const}, \quad \dot\theta = \Omega^{(2)} = \text{const} \tag{4}$$

instead of the usual approach of setting the derivatives with respect to t equal to zero. Actually, when $\dot\theta = \dot\varphi = 0$, Eq. (2) corresponds to the completely nonphysical situation of the stopping of the rotor. Equations (3) testify to its uniform rotation by virtue of the meaning of P_θ and P_φ. The only opportunity to satisfy Eq. (4) (for arbitrary t) is afforded by

$$\theta = \pi/2, \ \varphi = 0. \tag{5}$$

Of course, the obvious reassignments ($\varphi \to \Omega^{(1)} + \varphi(t)$, etc.) underline the mathematical triviality of Eq. (4). However, the values of the constants in Eq. (4) are of decisive importance for the physical validity of the version under discussion. It is an asymptotic trick (neither theory nor "approach") that is the basis here. The initial exact expressions will be

$$\dot\varphi\sin^2\theta = -\int_0^t dt' f(t')\sin\theta(t')\sin\varphi(t'); \tag{6}$$

$$\frac{1}{2}\dot\varphi^2\sin^2\theta\dot\theta + \frac{1}{2}\dot\theta^2 - \frac{1}{2}\omega^2 = \int_0^t dt' f(t')(\dot\theta\cos\theta\cos\varphi - \dot\varphi\sin\theta\sin\varphi) \tag{7}$$

where $f(t) = (\alpha/I)U^2(t)$. Equation (6), which represents the integral of the equations of motion [Eqs. (1)] must be written first in the Lagrangian form:

$$\ddot{\theta} = \dot{\varphi}^2 \sin\theta\cos\theta + f\cos\theta\varphi,$$

$$\ddot{\varphi}\sin^2\theta = -2\dot{\varphi}\dot{\theta}\sin\theta\cos\theta - f\sin\theta\sin\varphi.$$

Equation (7) describes the energy conservation, law (obtained by integrating $(1/I)dH/dt$, where the energy

$$H = V + (1/2)(\dot{\varphi}^2\sin^2\theta + \dot{\theta}^2) = V + (1/2)(\omega_1^2 + \omega_2^2),$$

taking into account initial conditions (3).

Then, substituting Eq. (5) into the left-hand sides of Eqs. (6) and (7), we obtain $\dot{\varphi} = -\int_0^t dt' f(t')\sin\theta(t')\sin\varphi(t')$. Next, let us replace the second term in Eq. (7) by $\dot{\varphi}^2$. Here, taking Eq. (3) into account, it is possible to appeal to the mean value theorem. The expression which results is interpreted as an integral equation for θ, and the nonzero initial condition (see Eqs. (3)) enables us to solve it by means of an iterative procedure. Naturally, we will restrict ourselves to the first step (in the integral $\dot{\theta} \to \omega$). Finally, we obtain

$$\dot{\theta}^2 = \omega^2 + \dot{\varphi}^2 + 2\omega\int_0^t dt' f(t')\cos\theta(t')\sin\varphi(t').$$

This expression gives rise to a suspicion bordering on a confidence that $|\dot{\varphi}| - |\dot{\theta}| = |\Omega^{(1)}| - |\Omega^{(2)}| = O(\omega)$. It is also clear that the formal expression at $t \to \infty$ corresponds to the stationary point (5) and that Eqs. (4) mean that "$\theta \simeq \Omega^{(2)}(t)$ and $\varphi \simeq \Omega^{(1)}(t)$ at large t".

Coming back to the explanation of the resonance (see the end of Sect. 1), we see that the resonance condition becomes

$$|(\omega_1 - \omega_2) - \omega| \ll \omega, |\omega_1 - \omega_2|. \qquad (8)$$

The rule of asymptotic estimates of the Fourier-type integrals[8] (i.e. the possibility of treating the integrand functions just at large t) and Abel's theorem[9] formalize the calculation of the limit at $t \to \infty$. There appears a series of δ-functions of which naturally only that one which corresponds to a resonance of the type given by Eq. (8) will remain.

This situation requires a heuristic step, which being the substitution of the function σ for the resonance width γ given by Eq. (8). This procedure, of course, excludes indeterminate values of $\Omega^{(1)}$ and $\Omega^{(2)}$ from the integrals, but it raises the problem of γ. Its physical content is to remove the singularity from the energy conservation law (corresponding to Eq. (7)). "Noise" is necessary as "a retarding factor" for a finite energy to appear under the resonance conditions. This situation is typical in synergetics.[7] With the latter we have, in fact, determined the conditions of existence of the stationary point.

The analysis carried out according to these "rules of the game" yields

$$\Omega^{(1)} < 0, \quad \Omega^{(2)} < 0, \quad \Omega^{(1)} - \Omega^{(2)} > 0, \quad \Omega^{(1)} = -\frac{ab}{I\gamma}\cos\beta,$$

$$\Omega^{(2)} = \Omega^{(1)} - \omega, \qquad (9)$$

where the complex number $U_1^* U_2$ is equal to $b\exp(i\beta)$. Now it is possible to elucidate the character of the stationary point in Eq. (5). The dependence of f on t introduces some atypicality; therefore it is better to use the Lagrangian form, which yields $\ddot{x} = -(\Omega^{(1)2} + f)x$, $\ddot{\varphi} = 2\Omega^{(1)}\Omega^{(2)}x - f\varphi$ in the vicinity of the stationary point (5) ($x = \theta - \pi/2$). Going over to the integral equations, we see the asymptotic smallness of the integral terms, and there then remain only "vibrational" expressions, which indicates that Eq. (5) represents a point of "center" type.

Moreover, there exists a limit cycle with "screwing" trajectories on it independent of their initial conditions, and the proof of this fact coincides with the example from Ref. 6. From the geometric point of view the limit cycle shown in Fig. 2b represents rotation at the frequencies $\Omega^{(1)}$ and $\Omega^{(2)}$ given by Eq. (9) around the cone whose vertex angle is $O(I\gamma^2/\alpha\beta)$. Any rotor, independent of its initial state (before the field is turned on, see Fig. 2a), will be in the position shown in Fig. 2b.

An analogous procedure for the equations in Euler form

$$\dot{\omega}_1 = (\cos\theta\cos\varphi\cos\psi - \sin\varphi\sin\psi)f,$$

$$\dot{\omega}_2 = (\cos\theta\sin\varphi\sin\psi + \sin\varphi\cos\psi)f$$

enables us to find the direction **M** (see Fig. 2) in the limit cycle. If we suppose that after the field is turned off the molecule becomes free of an anomalous large **M** by spontaneous emission of radiation, then it will be directed only along **S** (**E** is concentrated along the rotor axis and the final momentum of the molecule is much less than M) because of momentum conservation. In this way we explain the coherence that was discussed in Sect. 1.

In the above analysis the following synergetic aspects are important. First there is the nonlinearity of problem (1) (here specifically the radical difference from the analogous problem of ASCS), which leads to a change (as compared to the linear version) of the role of the external field and acts as a "trigger," mobilizing the internal resources of the nonlinear system (in the linear case this role is played by the main dynamic factor). The problem of resonance appears to be different — see the last paragraph in Section 1 and the discussions of Eqs. (6) and (7) (for example, it obviously differs from the resonance of an oscillator under the influence of an external periodic force).

Finally, the existence of "noise" appears to be a matter of principle. It is a central point for the self-organization of the steady state (b) shown in Fig. 2. Actually, the extremely low threshold of the effect is due to these very factors, i.e., at values of y corresponding to the Doppler effect (see Sect. 3) and fields in the range ~ 10^4–10^5 V/cm the value of Ω from Eqs. (9) is equal to 10^7 cm^{-1} (for N_2 and O_2, and the corresponding rotational energy significantly exceeds not only the electron levels but also the dissociation and ionization levels of nitrogen and oxygen.

RESONANCE (8), ITS WIDTH, AND POPULATION OF STATES

Here other aspects of the physical picture of the phenomenon will be discussed on a strictly qualitative level. The content of Sect. 2 constitutes the main element of the interpretation.

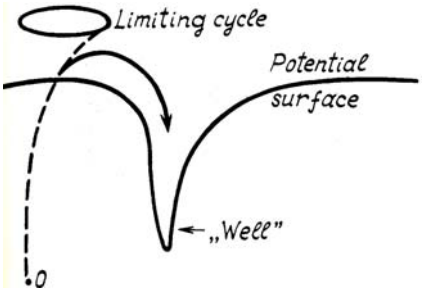

FIG. 3. Rotor motion towards the limit cycle in phase space. The "well" corresponds to a stationary electron-rotational state; – – – schematically represents the rotor trajectory "screwing" into the limit cycle (see Sect. 2); → denotes the motion due to the electron-rotational interaction. The limit cycle energy is estimated at the end of Sect. 2.

The initial appearance of resonance (8) is easily interpreted as occurring during the process of a molecular collision, because a collision is sufficient to induce a transition between rotational states and the classical background of centers of mass continuously "fills" the gaps between the quantum levels. Of necessity, we estimate the probability of the exact fulfillment of conditions (8) in a simplified way. Since we are talking about an individual collision, referring to the theory of spectral line shapes (see, e.g. , Ref. 10), it is possible as a completely acceptable hypothesis to take as the value of γ the Doppler halfwidth (the natural halfwidth is negligible for the rotational frequency).

The next point, to which the diagram in Fig. 3 is related, should explain the picture of the broadband excitation (see Sect. 1). The electron-rotational interaction, which is quite insignificant under normal conditions, will also play a role for very energetic rotation. Of the corresponding terms of the exact Hamiltonian,[11] at the stationary point (S) the term $\hat{\Gamma} = (ih\hat{L}_2 / I)d / d\theta$ can be retained, where $\hat{L}_2$ is the electron momentum operator (for the molecular system). The operator $\hat{\Gamma}$ acts as the cause of the nonradiative transition, causing the rotor to "turn away" from the limit cycle into a "well" (see Fig. 3). It is clear that all the states, whose energy lies below the energy level of the limit cycle, are populated.

There are no difficulties in posing the question of the probability of subsequent spontaneous emission. But this discussion is not likely to be constructive because the behavior of the molecule at very large rotational quantum numbers is not one of the solved problems of molecular spectroscopy. However one detail is worth noting. Granted that in the scheme in Fig. 3 there is not one single conceivable possibility of excitation and "luminescence". But the total probability is proportional to the external field intensity. This calculation is based on the assumption that the rotational wave function is equal to $P_v^{-v}(\cos\theta)\exp(-iv\varphi)$. Here $P_v^{-v}(\cos\theta)$ is the Legendre function, and v corresponds to the rotational energy with frequencies given by Eq. (9). This function reproduces case (b) in Fig. 2 (which enables one to refer to the method of semiclassical representation,[12] while proceeding from the classical description given in Sect. 2 to the modern quantum description), and satisfies the Scrödinger equation of the rigid rotor.

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