

## A MECHANISM FOR ROTATIONAL EXCITATION OF MOLECULES

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Received August 21, 1989*

*A mechanism for pumping energy from a biharmonic optical radiation field to the rotational excitation of a symmetric molecule is suggested. It is shown that a biharmonic field with difference frequency equal to four times the molecular rotational constant  $Be$  "triggers" the initial ( $J = 1 \rightarrow J = 2$ ) direct rotational transition and synthesizes an intramolecular field at the sequence of resonant frequencies  $\Omega_J = 4Be(1 + J/2)$ , where  $J = 1, 2, 3, \dots$ . Simultaneous forcing of the molecule by fields of these two types is accompanied by co-phased energy transfer from the biharmonic field to successively higher rotational states of the molecule. The threshold and limiting values of the rotational excitation are determined. The estimates made agree well with the published experimental data.*

Reference 1 discusses the effect of "rotational sublimation" of the linear molecules  $N_2$  and  $O_2$  by a biharmonic radiation field whose difference frequency,  $\Omega_b = \omega_1 - \omega$ , is almost in resonance with the frequency  $\Omega_0 = 4Be$  of the rotational transition ( $J = 1 - J = 2$ ) from the ground vibrational state of  $N_2$ . In Ref. 2 a mechanism for such a sublimation was examined, based on a qualitative analysis of the differential equations of motion of a rigid rotator. It was treated as a synergistic system in a state of resonance with the difference frequency of the biharmonic field. It was demonstrated that. Independent of the initial state of such a rotator, there exists a stationary point and a limit cycle to which the classic trajectories of motion converge.

In the present paper a quantum-mechanical variant of rotational sublimation of molecules from the level  $J = 1$  is proposed. The algorithm of energy pumping from a biharmonic radiation field into the rotational motion of molecules prescribes the resonant (with the difference frequency) "two-dimensional" rotational Raman scattering.

Let us consider rotational Raman scattering (RS) by a symmetric linear molecule. If the amplitude of the single-frequency (one-dimensional) external field has a time dependence of the form

$$V(t) = E_0 \cos \omega t, \quad (1)$$

then the second-order term in the expansion of the induced dipole moment of the rotating molecule leads to rotational Raman transitions of the molecule. The spectrum of rotational RS for a medium consisting of symmetric molecules consists of two series of lines:

the lines of the  $R$ -branch:  $\Delta J = \pm 1, \Delta K = 0, J = 1, 2, 3, \dots$

$$\begin{aligned} \omega - \omega_{s,J}^R &= 2Be(J+1) = \Omega_{J,s}^R \\ \omega - \omega_{a,J}^R &= -2Be(J+1) = -\Omega_{J,a}^R \end{aligned} \quad (2)$$

and the lines of  $S$ -branch:  $\Delta J = \pm 2, \Delta K = 0, J = 0, 1, 2, \dots$

$$\begin{aligned} \omega - \omega_{s,J}^S &= 4Be(J+3/2) = \Omega_{J,s}^S \\ \omega - \omega_{a,J}^S &= -4Be(J+3/2) = -\Omega_{J,a}^S. \end{aligned} \quad (3)$$

Here  $Be, J,$  and  $K$  are, respectively, the rotational constant for the ground vibrational state, and the rotational quantum numbers for the lower level and for the axial motion of molecule, respectively, and  $\omega, \omega_J$  and  $\Omega_J$  are respectively the frequencies of the exciting radiation, the Raman scattering, and the Stokes and anti-Stokes lines of the rotational Raman scattering. The scattered radiation in the molecular medium simultaneously contains as many frequencies as there are energy levels  $E_{J,K} = BeJ(J+1) + AeK^2$  with frequencies  $\Omega_{J,K}^R$  and  $\Omega_{J,K}^S$ , not exceeding  $\omega$  ( $Ae$  is a rotational constant). The frequency difference between the exciting and the scattered radiation, which satisfies selection rules (2) and (3), corresponds to the eigenfrequencies of the rotational motion of the molecules of the medium,  $\Omega_J^R$  and  $\Omega_J^S$ . Every other  $R$ -branch line coincides with an  $S$ -branch line (i.e., they follow at a step of  $4Be$ ). In this case no twisting forces appear in the molecules of the medium, since the processes of excitation (Stokes transitions) and de-excitation (anti-Stokes transitions) of rotational RS are frequency-symmetric and are therefore equally probable.<sup>3</sup>

In the case of a biharmonic (two-dimensional) pump wave

$$V(t) = E_0 (\cos \omega_1 t + \cos \omega t) = 2E_0 \cos \frac{\omega_1 - \omega}{2} t \cdot \cos \frac{\omega_1 + \omega}{2} t, \quad (4)$$

the second-order term in the expansion of the induced polarization of the medium leads to the generation of

radiation fields at both the difference ( $\omega_1 - \omega$ ) and the sum ( $\omega_1 + \omega$ ) frequencies and to the appearance of *S*- and *R*-branches of rotational RS for each of the components  $\omega_1$  and  $\omega$ . The relative distribution of lines from the *S*- and *R*-branches for  $\omega_1$  and  $\omega$  depends on the degree of detuning  $\omega_1 - \omega$ . When this detuning is equal to

$$\omega_1 - \omega = 4Be = \Omega_0 = \frac{2\pi}{T_0}, \quad (5)$$

(so that for any *J* the frequencies of the *R*-branches and of the direct rotational transition differ by half of that value  $\Omega_0/2$ ), superposition of the two RS spectra leads to an asymmetry in the Stokes-anti-Stokes processes. This can be easily seen if one notes that the relative distribution of the absolute frequency values for the *S*-branch of the two-dimensional RS is described by the expressions

$$\begin{aligned} \omega - \omega_{s,J}^S &= \Omega_0 (J + 3/2), & \omega - \omega_{a,J}^S &= -\Omega_0 (J + 3/2), \\ \omega_1 - \omega_{s,J+1}^S &= \Omega_0 (J + 5/2), & \omega_1 - \omega_{a,J-1}^S &= -\Omega_0 (J + 1/2), \end{aligned} \quad (6)$$

and for the *R*-branch by the expressions:

$$\begin{aligned} \omega - \omega_{s,J}^R &= \frac{\Omega_0}{2} (J + 1), & \omega - \omega_{a,J}^R &= -\frac{\Omega_0}{2} (J + 1), \\ \omega_1 - \omega_{s,J+2}^R &= \frac{\Omega_0}{2} (J + 3), & \omega_1 - \omega_{a,J-2}^R &= -\frac{\Omega_0}{2} (J - 1). \end{aligned} \quad (7)$$

The two-dimensional RS frequencies are equal to the half-sums of the frequencies of two one-dimensional RS (6, 7):

$$\frac{\omega_1 + \omega}{2} - \frac{\omega_{s,J+1}^S + \omega_{s,J}^S}{2} = 2\Omega_0 (1 + J/2), \quad J = 0, 1, 2... \quad (8)$$

$$\frac{\omega_1 + \omega}{2} - \frac{\omega_{s,J+2}^R + \omega_{s,J}^R}{2} = \Omega_0 (1 + J/2), \quad J = 1, 2, 3... \quad (9)$$

$$\frac{\omega_1 + \omega}{2} - \frac{\omega_{a,J+1}^S + \omega_{a,J}^S}{2} = -\Omega_0 (1 + J), \quad J = 0, 1, 2... \quad (10)$$

$$\frac{\omega_1 + \omega}{2} - \frac{\omega_{a,J-2}^R + \omega_{a,J}^R}{2} = -\Omega_0 J/2, \quad J = 1, 2, 3... \quad (11)$$

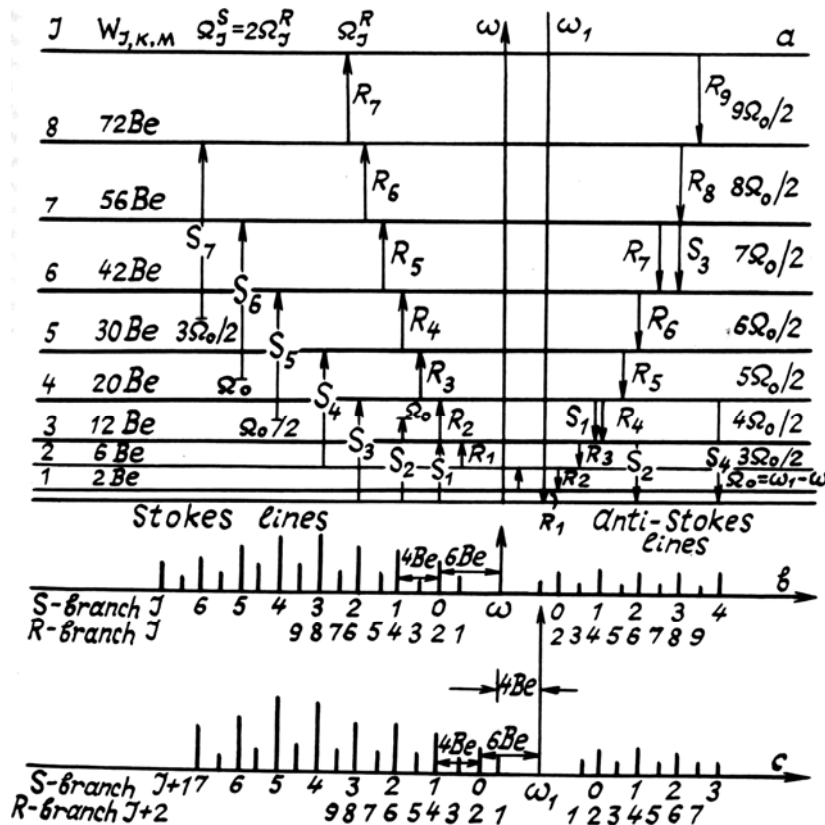


FIG. 1. Rotational spectrum of RS for a symmetric linear molecule: sum-difference frequencies of the *S*- and *R*-branches for two-dimensional RS (a); *S*- and *R*-branch Frequencies for rotational RS during excitation at the frequency  $\omega$  (b); *S*- and *R*-branch frequencies for rotational RS excitation at the frequency (c).

The frequencies (9) of the exciting part of the two-dimensional RS for  $J = 1, 2, 3, \dots$  form a regular resonance sequence, which starts from the difference frequency  $\Omega_0$ . This sequence also includes the first undertones of components (5) and (8). Frequencies (11) of the relaxing (de-exciting) part of the field also fall into a regular resonance sequence, however with totally different absolute values: frequencies (10) fall out of the relaxing sequence (see Fig. 1).

It is important that under condition (5) the intramolecular field formed by the two-dimensional RS at the eigenfrequencies (8)–(11) does not lead to the Raman transitions (2) and (3). Indeed, at the frequencies  $\Omega_{J=1, 2, \dots} = \Omega_0(1 + J/2)$  (9) the intramolecular field is resonant with the molecular transitions, however only with those that start from the lower level  $J+1$ , not from  $J$  as selection rules (2) require; formation of the fields (9) outruns the action of the selection rules for the RS transitions. This condition, together with the asymmetry of the Stokes-anti-Stokes resonant frequencies (5) for two-dimensional RS with regularization of its exciting part, provides a basis to assume that twisting forces may be generated in molecules. To determine the condition for the coordination of such forces, let us consider in more detail the dynamics of the rotational excitation of molecules from the rotational state  $J = 1$  by the biharmonic field (4).

Given condition (5), at the instant  $t_0 = 0$  at which the biharmonic pumping is turned on. In addition to the electric dipole moment at the optical frequencies a forerunning (intramolecular) field is induced at the eigenfrequency  $\Omega_{J=1} = 3\Omega_0/2$  (9). Simultaneously, an external (irradiating) field is formed in the medium:

$$E_s(t) = E_{s0} \cos \frac{2\pi}{T_0} t \quad (12)$$

of difference frequency  $\Omega_0 = \omega_1 - \omega$ , which is resonant with the starting rotational transition  $J = 1 \rightarrow J = 2$ , and also a field at the sum frequency  $\omega_1 + \omega$ . Here  $E_{s0}$  is the starting amplitude of the exciting field, controlled by the molecular polarizability  $\Delta\alpha$  of the molecule and by the amplitudes of the biharmonic pumping (4). The component  $\Omega_{J=1}$  of the intramolecular field is formed a time  $T_0/3$  earlier than the component  $\Omega_0$ ; however, the transition corresponding to this frequency  $J = 2 \rightarrow J = 3$  can only start a time  $\Delta t_1$  later, at the instant  $t_2$  when the transition  $J = 1 \rightarrow J = 2$ , which started at  $t_1 = T_0$  ends. By the time  $t_2$  ( $J = 2$ ) the two-dimensional RS forms another forerunning field  $\Omega_{J=2} = 4\Omega_0/2$  (9), resonant with the transition  $J = 3 \rightarrow J = 4$  in the same molecule.

If the phase incursions of the forcing fields at the frequencies  $\Omega_0$  and  $\Omega_{J=1}$  are equal at  $t_2$ , and those of fields  $\Omega_{J=2}$ ,  $\Omega_{J=3}$  – at  $t_3$  (so that the phases of the probability amplitudes of the states  $E_{J=1}$ ,  $E_{J=2}$  and  $E_{J=3}$  are assigned with a certain level of accuracy, then the probabilities of such states will interfere during the simultaneous excitation of the molecular transitions  $J = 1 \rightarrow J = 2$  and  $J = 2 \rightarrow J = 3$ , causing the molecule to transition to the state  $E_{J=3}$  (Ref. 4). If

$\Delta t_n \ll T_0 \ll \tau_p$ , the molecule will reach the rotational state  $J_N = nN$  due to such co-phased excitation transfers, as described by the respective orders of perturbation theory. Here  $\tau_p$  is the duration of the pump pulse (4), and  $n = T_0/T_n$  and  $N = \tau_p/T_0$  are the number of transitions per sublimation period and number of sublimation periods, respectively. For co-phased excitation transfer it is necessary for the phase incursions of the exciting

$$\Delta\Phi_{JN} = \frac{2\pi}{T_0} (\Delta t_1 + \dots + \Delta t_n) N + \Delta_N (\Delta t_1 + \dots + \Delta t_n) N \quad (13)$$

and the forerunning

$$\Delta\Phi_{JN} = \frac{3}{2} \frac{2\pi}{T_0} \left[ \frac{T_0}{3} + (\Delta t_1 + \dots + \Delta t_n) N \right] \quad (14)$$

fields to be equal by the end of each period  $N$ . Here  $\Delta_N$  is the frequency difference between the fields, providing for in-phase excitation of the molecular states during the  $N$ -th period. It follows from the phase equalities (13) and (14), taking into account that  $\Delta t_1 + \dots + \Delta t_n = T_0$ , that

$$\Delta_N = \Omega_0/2 + \Omega_0/2N, \quad (15)$$

Forces twisting the molecule may be coordinated under this condition.

The first part of Eq. (15) reflects the sublimation threshold condition:  $1/T_n \geq \Omega_0/2$  (the amount by which the transition rate in the external field exceeds the rate of variation of the self-field of the molecule at the rotational ground-state frequency), and the second is related to the limiting number of periods, and, correspondingly, to the maximum value of  $J_N$  during sublimation. Apart from the transition rates  $N$ , the sublimation is limited by the pulse duration  $\tau_p$  and the resonance detuning  $\Delta_1 = \Omega_b - \Omega_0$ . In the first case  $J_N \leq \tau_p/T_n$ , and in the second  $J_N \leq \pi/(T_n\Delta_1)$ .

Thus, coordination of forces twisting the molecule, and co-phased energy pumping from the biharmonic field (4) by means of the mechanism of two-dimensional RS, during which energy is transferred from rapid (at the optical frequencies) motion of the molecule to rotational motion of the molecule, may occur under conditions (5) and (15). Condition (5) provides for resonance between the difference frequency  $\omega_1 - \omega$  and the frequency of the starting rotational transition  $J = 1 \rightarrow J = 2$ ; condition (15) provides for autoresonance of the sequence of frequencies of the forerunning field (9) to the transitions following the starting one; it also sets the limit for rotational excitation of the molecule. If the amplitudes of the exciting fields at the end of each sublimation period are added together in-phase, then the intensity of the combined exciting field may reach the value  $E(t_N) = E_s(t) \cdot J_N$ . Then the energy from the rapid motions of the molecule is pumped into its rotational motion.

Let us determine the possible limits of  $J_N$  and the rotational sublimation energy of  $N_2$ , applying to that

end the initial data and the results of experiment<sup>1</sup>:  
 $E_0 = 10^5$  V/cm;  $\tau_p = 25$  ns;  $\nu_b = \nu_1 - \nu = 2.34 \cdot 10^{11}$  Hz;  
 $Be = 1.99$  cm<sup>-1</sup>;  $\nu_0 = (\Omega_0/2\pi) = 2.397 \cdot 10^{11}$  Hz;  
 $T_0 = 4.18 \cdot 10^{-12}$  s;  $\Delta\alpha = 2.4 \cdot 10^{-24}$  m<sup>3</sup>;  
 $\Delta_1 = 0.057 \cdot 10^{11}$  Hz.

The time of a single molecular transition  $T_n$  (the sublimation rate is  $1/T_n$ ) may be estimated from a condition on the population level of the upper energy level,  $\Omega_p T_n = \pi$ , where  $\Omega_p$  is the oscillation frequency of the population difference during the transition (the Rabi frequency). Using the induced molecular moment for rotational RS

$$D_{\text{ind}} = \frac{1}{3} \Delta\alpha E_0 \frac{3M^2 - J(J+1)}{(2J-1)(2+3)}$$

as the matrix element of the transition,<sup>4</sup> for  $M = J$  we obtain for the first transition ( $J = 1$ )  $T_n \approx 1.04 \cdot 10^{-12}$  s.

Taking into account both of the above limiting factors we find that under experimental conditions<sup>1</sup> the value of  $J_N$  may vary within the bounds  $1.75 \cdot 10^2 \leq J_N < 1.2 \cdot 10^4$ . Assuming that  $J_N \sim 10^3$ , we find that during rotational excitation the molecule may be excited to the rotational state  $E_{J,K} \approx 6 \cdot 10^6$  Hz ( $2 \cdot 10^6$  cm<sup>-1</sup>) and acquire an energy of  $W_{J,K} \approx 8 \cdot 10^{-17}$  J.

These results agree with the available experimental data.<sup>1</sup>

We note in conclusion that the process of energy pumping from a biharmonic field to rotational motion of the molecule is linear and parametric. It is linear since a term in the expansion of "radiation field + molecule" interaction energy, which is quadratic in the field, corresponds to it, and parametric in the sense that the relationship between the oscillators (5) and (9), successively switched on in the system "molecule + biharmonic field" is realized via changing states of the molecule.

The author is grateful to S.D. Tvorogov for helpful discussions of the article.

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