Collision-radiative processes and molecular lasers

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The possibility of designing molecular lasers based on collision-radiative transitions $A^* + B = A + B^* + h\nu$ is considered. The probability for such transitions is expressed in terms of the combined polarizability and other known molecular parameters. The shape of the transition line is investigated.

1. In spite of the considerable progress in the development of molecular lasers for the IR band, coherent IR radiation has been obtained only in several regions of the spectrum. The region most thoroughly investigated is that of 10.6 μ, owing to the unique properties of the $CO_2 - N_2$ mixture. Progress to higher regions of the spectrum is hindered by the difficulty in selecting molecular systems in which the electric energy can be effectively converted into coherent-radiation energy (nonelectric lasers have not found wide application so far).

It is known that vibrations of the diatomic molecules N_2, CO, H_2[1], and apparently also D_2 and O_2, are quite effectively excited in discharges. The very same molecules have the maximum excited-state (vibrational) lifetime[2]. Unfortunately, none of them, with the exception of CO, possess a dipole moment, and this prevents lasing from occurring, even if population inversion on these molecules can be obtained. Nonetheless, there is a possibility in principle of directly converting the vibrational energy of such molecules into electromagnetic radiation without prior transfer of this energy to the emitter molecules in collisions. Namely, it is possible in principle to obtain lasing on radiative collision transitions of the type[3]

$$A^* + B \rightleftarrows B^* + A + h\nu.$$

The probability of such transitions in collisions of atoms in a resonant-frequency field was estimated in[3]. A distinguishing feature of molecular systems is the presence of a large number of close-lying levels, and consequently the need for taking quasiresonant transitions into account. On the other hand, as will be shown below, in a number of cases the probability of the vibrational radiation-collision transitions is expressed in terms of parameters that are either known or easy to measure experimentally, making it possible to obtain concrete estimates of the gains attainable with such transitions. These estimates show that to realize molecular IR lasers on collision-radiative transitions, it is necessary to use high pressures (dozens of atmospheres). It is then possible to obtain radiation that is frequency-tunable in an interval on the order of 50–100 cm^{-1} with a center determined by the choice of the partner molecules. The power and efficiency of such lasers can be comparable with the power and efficiency of CO_2 lasers with transverse discharge.

2. It is known that when a molecule is acted upon by alternating electric fields with frequencies ω and ω' such that the difference or sum $\hbar\omega \pm \hbar\omega'$ is equal (almost equal) to the spacing between two energy levels of the molecules, transitions between these two levels can occur with simultaneous emission or absorption of quanta $\hbar\omega$ and $\hbar\omega'$ (Raman scattering, two-photon emission or absorption of light). From the point of view of action on the considered molecules, the causes of the appearance of electrical fields are of no significance. In particular, one of the fields (or both) can be induced by another molecule. From this follows the possibility of simultaneous transitions between the energy levels in different molecules, accompanied by emission or absorption of a quantum with frequency

$$\begin{gathered} \omega = \omega_0 + \Delta, \\ \omega_0 = (\mathscr{E}_{1A} + \mathscr{E}_{1B} - \mathscr{E}_{0A} - \mathscr{E}_{0B}) / \hbar, \quad \Delta \ll \omega, \end{gathered} \tag{1}$$

where $\mathscr{E}_{0A}$, $\mathscr{E}_{0B}$, $\mathscr{E}_{1A}$, and $\mathscr{E}_{1B}$ are the energies of the initial and final states of the molecules A and B, and the cross section of the process is determined in the simplest case by the combination polarizability of one molecule and by the transition dipole moment of the other.

Having in mind the use of perturbation theory for the calculation of the probability of such processes, we write down the energy of interaction of the molecules with one another and with an electric field $\mathbf{E} = \tilde{\mathbf{E}} \exp(i\omega t) + \text{c.c.}$, in the dipole approximation,

$$V = -\mathbf{d}_A\mathbf{E} - \mathbf{d}_B\mathbf{E} - \frac{\mathbf{d}_A\mathbf{d}_B - 3(\mathbf{n}\mathbf{d}_A)(\mathbf{n}\mathbf{d}_B)}{R^3}, \tag{2}$$

where $\mathbf{d}_A$ and $\mathbf{d}_B$ are the dipole-moment operators of the molecules A and B, including the moment induced by the field $\mathbf{E}$ and by the field of the partner molecule. We assume for simplicity that the dipole moment of the 0 – 1 transition of the molecule A is equal to zero, so that $\mathbf{d}_A$ is the induced moment:

$$d_{Ai} = \alpha_{ij}(\omega)E_j + \alpha_{ij}(\omega_B)[d_{Bj} - 3n_j\mathbf{n}\mathbf{d}] / R^3, \tag{3}$$

where $\omega_B = (\mathscr{E}_{1B} - \mathscr{E}_{0B})/\hbar$, $\alpha(\omega)$ is the operator of the polarizability tensor of molecule A. The contribution of the induced moment to $\mathbf{d}_B$ vanishes in the employed approximation, and after substituting (3) in (2), we obtain

$$V = -\alpha_{ij}E_iD_j; \quad D_j = [d_j - 3n_j\mathbf{n}\mathbf{d}] / R^3(t), \tag{4}$$

where

$$\mathbf{d} = \mathbf{d}_B, \quad \alpha_{ij} = \alpha_{ij}(\omega) + \alpha_{ij}(\omega_B).$$

Substituting (4) in the well-known form of perturbation theory[4], we obtain the probability $W_{v,b}(\omega)$ of the transition $A(0)B(0) \to A(1)B(1)$ in a field $\mathbf{E}$ when molecules collide with relative velocity v and impact parameter b:

$$W_{v,b}(\omega) = \frac{|\tilde{E}|^2}{\hbar^2} \left| \int_{-\infty}^{\infty} \alpha_{ij}e_iD_j \exp(i\Delta t)\, dt \right|^2. \tag{5}$$

In (5), $\mathbf{e} = \tilde{\mathbf{E}}/E$, and α_{ij} and d_i stand for the matrix elements $(\alpha_{ij})_{01}$ and $(d_i)_{01}$.

Replacing $|\tilde{E}|^2$ in (5) by $2\pi\hbar\omega\rho(\omega)d\omega$ ($\rho(\omega)$ is the density of the field modes), and averaging over all the directions of the vector $\mathbf{e}$, we obtain the probability of the spontaneous emission of a quantum $\hbar\omega$ in the interval $d\omega$ and of the transition $A(0)B(0) \to A(1)B(1)$ (or the inverse transition if $\mathscr{E}_{A(1)}+\mathscr{E}_{B(1)}>\mathscr{E}_{A(0)}+\mathscr{E}_{B(0)}$) in such a collision:

$$W^{\text{сп}}_{v,b}(\omega)\,d\omega=\frac{2\pi\omega}{3\hbar}\rho(\omega)\,d\omega\,\alpha_{ij}\alpha_{jk}^{*}\int\limits_{-\infty}^{\infty}dt\int\limits_{-\infty}^{\infty}dt'\,D_i(t)D_k(t')\exp[i\Delta(t-t')].\tag{6}$$

Averaging (6) over the magnetic quantum number of the molecule B, i.e., making the substitution $d_i d_k^* \to \frac{1}{3}|d|^2\delta_{ik}$, we obtain

$$\overline{W^{\text{sp}}_{v,b}}(\omega)\,d\omega=\frac{4\pi\omega}{9\hbar}\rho(\omega)\,d\omega\,|d|^2\alpha_{ij}\alpha_{jk}^{*}\times\int\limits_{-\infty}^{\infty}dt\int\limits_{-\infty}^{\infty}dt'\exp[i\Delta(t-t')]\frac{\gamma_{il}(t)\gamma_{lk}(t')}{R^3_{v,b}(t)R^3_{v,b}(t')},\tag{7}$$

$$\gamma_{il}(t)=\delta_{il}-3n_i(t)n_l(t),\quad \gamma_{lk}(t')=\delta_{lk}-3n_l(t')n_k(t').$$

3. It will be convenient in what follows to use the transition probability per unit time or the Einstein coefficient. We define the Einstein coefficient for the considered transition in the following manner:

$$A_{\text{sp}}=\int\limits_0^{\infty}2\pi b\,db\int\limits_0^{\infty}vf(v)\,dv\int\limits_0^{\infty}\overline{W^{\text{sp}}_{v,b}}(\omega)\,d\omega,\tag{8}$$

where f(v) is the distribution function, normalized to unity, with respect to the relative molecule velocities.

This quantity has the meaning of the probability of a spontaneous transition per unit time per pair of molecules, and has the dimension sec-cm^3. Since there are $N_{A(0)}N_{B(0)}$ such pairs per unit volume, the gain for the transitions A(0)B(0) → A(1)B(1) is determined by relation (20), where $\overline{F}(\omega)$ should be taken to mean the line shape $F(\omega)$ of a single transition, averaged over all the transitions between the vibrational-rotational sublevels

$$F(\omega)=A(\omega)/A^{\text{sp}},\quad A(\omega)=\int\limits_0^{\infty}2\pi b\,db\int\limits_0^{\infty}vf(v)\,\overline{W^{\text{sp}}_{v,b}}(\omega)\,dv.\tag{9}$$

Integration with respect to the frequency in (8) can be carried out by assuming $\omega\rho(\omega)$ to be constant. Substituting $\overline{W^{\text{sp}}_{v,b}}(\omega)$ from (7) and recognizing that

$$\int\exp[i\Delta(t-t')]\,d\Delta=2\pi\delta(t-t'),$$

we represent the result of the integration in the form

$$A^{\text{sp}}=2\pi C\int\limits_0^{\infty}2\pi b\,db\int\limits_0^{\infty}vf(v)\,dv\int\limits_{-\infty}^{\infty}R^{-6}_{v,b}(t)\,dt,\qquad C=\frac{4\pi}{9}\omega\rho(\omega)|d|^2\operatorname{Sp}(\hat{\alpha}\hat{\alpha}^{*}).\tag{10}$$

We continue the transformation of (10) and (9) for the model of colliding hard spheres, with average diameter R_0. Then

$$\begin{aligned}R_{v,b}(t)&=(b^2+v^2t^2)^{1/2}\quad\text{if}\quad b>R_0,\\ R_{v,b}(t)&=[b^2+(\sqrt{R_0^2-b^2}+|vt|)^2]^{1/2}\quad\text{if}\quad b<R_0.\end{aligned}\tag{11}$$

Substituting (11) in (10) and recognizing that $\int\limits_{0}^{\infty}f(v)dv\equiv1$ we obtain

$$A^{\text{sr}}=4\pi^2C\int\limits_{-\infty}^{\infty}dx\left[\int\limits_0^{R_0}\frac{b\,db}{[R_0^2+2|x|(R_0^2-b^2)^{1/2}+x^2]^3}+\int\limits_{R_0}^{\infty}\frac{b\,db}{(x^2+b^2)^3}\right].\tag{12}$$

Integration with respect to (12) yields $2R_0^{-3/3}$. As a result we get

$$A^{\text{sr}}=\frac{32\pi^3}{27\hbar}\omega\rho(\omega)|d|^2\operatorname{Sp}(\hat{\alpha}\hat{\alpha}^{*})R_0^{-3}=\frac{4}{3}\frac{\omega^3|d|^2}{\hbar c^3}\frac{8\pi}{9}\frac{\operatorname{Sp}(\hat{\alpha}\hat{\alpha}^{*})}{R_0^3}.\tag{13}$$

To obtain the transition probability per unit time, say for the molecule A(0), it is necessary to multiply (13) by the density $N_{B(0)}$ of the molecules B(0). As expected, such a probability coincides exactly with the probability of the spontaneous Raman transition A(0) → A(1) in a field $\tilde{\mathbf{E}}_B\exp(i\omega_B t)$ + c.c. with frequency ω_B and with an amplitude squared

$$|E_B|^2=N_{B(0)}\int dV|D|^2,\tag{14}$$

where the integration is carried out over the entire volume accessible to the molecule B (i.e., over the entire volume after subtracting the spherical volume $(4/3)\pi R_0^3$ with center at the point B = 0). This probability does not depend on the temperature and on the aggregate state of the material (the latter is true if there is no ordering in the arrangement of the molecules). In the case of nonspherical molecules, it apparently suffices to change the integration region in (14) in order to determine the transition probability.

The selection rules for the considered transitions are combinations of the selection rules for the Raman scattering by the molecules A ($\Delta j = 0, \pm 2$) and for the dipole radiative transitions of the molecule B ($\Delta j = \pm 1$). Since the selection rules for the emission and Raman scattering are different, it is clear that in the general case when the molecule A also has a dipole moment there appear transitions with $\Delta j = 0, \pm 2$ of the molecule B and $\Delta j = \pm 1$ of the molecule A, and expression (13) for A^{sp} remains valid if we replace in it $|d|^2\operatorname{Sp}|\hat{\alpha}|^2$ by $\operatorname{Sp}|\alpha_A|^2|d_B|^2+\operatorname{Sp}|\hat{\alpha}_B|^2|d_A|^2$ (no interference effects arise). For simplicity we assume below that the second term of this sum is small.

Expression (13) enables us to estimate the coefficient A^{sp} if we know the combination polarizability $\hat{\alpha}$ of the molecule A (the remaining parameters of this expression are known as a rule). For many molecules, the combination polarizability was measured at optical frequencies[5,6]. If the electron absorption bands are far from these frequencies, as is usually the case, then the dependence of $\hat{\alpha}$ on ω is quite weak. As shown by theoretical estimates, the combination polarizability of such molecules as H_2, N_2, CO, O_2, and D_2 in the IR band should be lower than in the optical band by not more than a factor of 1.5. The exact value of the coefficient A^{sp} can be determined from the intensity of the absorption line at the frequency $(\mathscr{E}_{A(0)}\mathscr{E}_{B(0)}-\mathscr{E}_{A(1)}\mathscr{E}_{B(1)})/\hbar$, where A(1) and B(1) are the ground levels of the molecules A and B, while A(0) and B(0) are the excited levels.

4. The Einstein differential coefficient $A(\omega)$ can be easily calculated at the point $\omega = \omega_0$. Without presenting the intermediate steps, we write down the result of the integration of (9) with respect to the velocities and the impact parameters at $\omega = \omega_0$ ($\Delta = 0$):

$$A(\omega_0)=A^{\text{sp}}F(\omega_0),\qquad F(\omega_0)=\frac{3\ln4}{2\pi}R_0\overline{\left(\frac{1}{v}\right)}=\frac{3\ln4}{2\pi}R_0\left(\frac{2m}{\pi kT}\right)^{1/2}.\tag{15}$$

Here m is the reduced mass $m_Am_B/(m_A+m_B)$. As seen from (15), the value of $F(\omega)$ at the center of the line is approximately equal to R_0/v, i.e., the "interaction time" of the molecules. It is natural to assume also that the half-width of the line is $1/F(\omega_0)$. However, the validity of such an estimate is not obvious beforehand, because the maximum of $F(\omega)$ may not coincide with $F(\omega_0)$. Indeed, the line shape is determined by the square of the Fourier expansion of the function $R^{-3}_{v,b}(t)$ averated over the velocities and the impact parameters (see (7) and (9)). This expansion has two maxima which are symmetrical with respect to the point $\Delta = 0$, and both are shifted towards the point $\Delta = 0$ only when $b/v \to \infty$. It is therefore necessary to investigate the line shape in greater detail.

To simplify the problem we put $\alpha_{ij} = \alpha\delta_{ij}$ (since the tensor properties of the polarizability determine the selection rules and not the line shape), and approximate the exact line shape (8) by means of the function

$$F_{R_0}(\omega) = \int vf(v)\,\overline{W^{\rm sp}_{v,R_0}}(\omega)\,dv \Big/ \int vf(v)\,dv \int \overline{W^{\rm sp}_{v,R_0}}(\omega)\,d\omega, \tag{16}$$

which represents the "line shape" corresponding to transitions in collisions with impact parameter $b = R_0$. Actually, collisions with impact parameter close to R_0 make the main contribution to the transition probability. At $b > R_0$, the integrated (with respect to frequency) transition probability decreases with increasing b like b^{-5}. At $b = 0$ it is approximately one-third as large as at $b = R_0$. Therefore the function $F_{R_0}(\omega)$ approximates the exact line shape sufficiently well. For example, at the line center, where the accuracy of such an approximation is relatively low, we have $F_{R_0}(\omega_0) \approx 0.85F(\omega_0)$.

$\overline{W^{\rm sp}_{v,b}}(\omega)$ is calculated by integrating (7) with respect to time:

$$\overline{W^{\rm sp}_{v,b}}(\omega) = CG(z)/v^2R_0^4, \quad z = \Delta R_0/v. \tag{17}$$

Here G(z) is expressed as a Bessel function of imaginary argument $K_\mu(z)$:

$$G(z) = \sum_{\mu=-2}^{2} \frac{z^{2\mu}K_\mu^2(z)}{(2-\mu)!\,(2+\mu)!}. \tag{18}$$

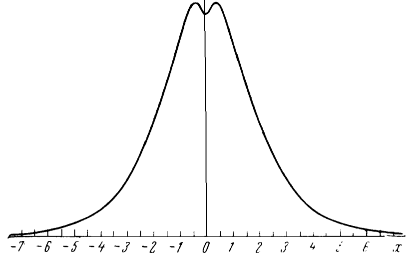
Substituting in (16) the expressions (17) and (18), as well as the Maxwell-Boltzmann distribution with respect to the velocity f(v), we can represent $F_{R_0}(\omega)$ in the form

$$\begin{gathered} F_{R_0}(\omega) = \frac{32}{3\pi^2} R_0 \left(\frac{2m}{\pi kT}\right)^{1/2} \varphi(x), \\ \varphi(x) = \int_0^\infty G(x/u)\exp(-u^2)\,u\,du, \quad x = \Delta R_0/v_0, \quad v_0 = (2kT/m)^{1/2}. \end{gathered} \tag{19}$$

The computer-calculated function $\varphi(x)$ is shown in the figure. As expected, there is a dip at the center of the line, but its depth is small. The width of the function $\varphi(x)$ at the level 1/2 is close to four, i.e., the width $W_{R_0}(\omega)$ is approximately equal to $4v_0/R_0$, which differs little from $1/F(\omega_0)$.

Since the intensity of the $\Delta j = 0$ line in Raman scattering is much higher than that of the $\Delta j = \pm 2$ lines, we can roughly assume that $\mathscr{E}_{A(0)} - \mathscr{E}_{A(1)}$ is fixed. Then the function $F(\omega)$ should be avereged over the vibrational-rotational transitions of the molecule B, i.e., over the vibrational-rotational band of this molecule.

Estimates show that the width of the function is practically always larger than the distance between the lines of the vibrational-rotational spectrum. In different particular cases the averaged line shape $\overline{F}(\omega)$ can be either close to the envelope of the vibrational-rotational band of the molecule B (for example, if B is HCl or HF, and A is a heavy molecule), or else differs little from $F(\omega)$ (if A is a hydrogen or deuterium molecule, and B is a molecule with a large moment of inertia). Intermediate cases are also possible.



The gain on the transitions A(0)B(0) → A(1)B(1) can be expressed in the form

$$K = {}^1\!/_4\lambda^2 A^{\rm sp}\overline{F}(\omega)\,[N_{A(0)}N_{B(0)} - N_{A(1)}N_{B(1)}g_{A(0)}g_{B(0)}/g_{A(1)}g_{B(1)}], \tag{20}$$

where $g_{A(n)}$ and $g_{B(n)}$ are the statistical weights of the levels.

We shall carry out the concrete estimates for the gain on the transitions $H_2(v = 1)SF_6(v_3 = 0) \rightarrow H_2(v = 0)SF_6(v_3 = 1)$, where the vibrational quantum number v_3 of the SF_6 molecule pertains to the triply degenerate vibration of frequency 965 cm^{-1}.

According to the published data for hydrogen, $\mathrm{Tr}\,\alpha\alpha^* = 3 \times 1.6 \times 10^{-50}$ cm^6[5], $R_0 \approx 3 \times 10^{-8}$ cm (the arithmetic mean of the kinetic diameters of the molecules H_2 and SF_6), and $|d|^2 \approx 3 \times 1.3 \times 10^{-37}$ cgs esu[6] (the coefficient 3 takes into account the degeneracy of the vibrations). Substituting (13) and (15) in (20) and using these values of the parameters, we obtain for the gain at the frequency $\nu_{H_2} - \nu_{SF_6} \approx 3200$ cm^{-1} at room temperature

$$\begin{gathered} K = 0.6 \cdot 10^{-43} N_{H_2}N_{SF_6}[\exp(-h\nu_{H_2}/kT_{H_2}) \\ - \exp(-h\nu_{SF_6}/kT_{SF_6})]Z_{H_2}^{-1}Z_{SF_6}^{-1}. \end{gathered} \tag{21}$$

The populations of the vibrational levels are expressed here in terms of the vibrational temperatures:

$$N_{H_2(v)} = N_{H_2}Z_{H_2}^{-1}\exp(-vh\nu_{H_2}/kT_{H_2}),$$

$$N_{SF_6(v)} = N_{SF_6}Z_{SF_6}^{-1}\exp(-vh\nu_{SF_6}/kT_{SF_6}),$$

Z_{H_2} and Z_{SF_6} are the vibrational partition functions, which are close to unity if T_{H_2} and T_{SF_6} are not too high.

Let $\exp(-h\nu_{SF_6}/kT_{SF_6}) \ll \exp(-h\nu_{H_2}/kT_{H_2}) \approx 10^{-1}$. Then the gain is $K \approx 10^{-3}$ cm^{-1} at $N_{H_2}N_{SF_6} \approx 1.5 \cdot 10^{41}$, i.e., at $p_{H_2}p_{SF_6} \approx 150$ atm^2. Estimates for the molecular pairs $H_2 - CF_4$ ($\nu_{CF_4} \sim 1265$ cm^{-1}), $D_2 - SF_6$, $D_2 - CF_4$ give results that are close.

For the systems $N_2 - SF_6$, $N_2 - CF_4$, $H_2 - CO_2$, the gain is approximately one-quarter as large (at the same populations).

As seen from the estimates, to develop lasers using the considered transitions in the $H_2 - SF_6$ mixture, for example, it is necessary to excite the vibrational levels of the hydrogen at very high pressures (on the order of several dozen atmospheres). We note that the vibrational relaxation time of the hydrogen can in this case be sufficiently large (in pure hydrogen at room temperature $p\tau \approx 10^{-3}$ sec-atm[7] and we can expect the presence of SF_6 in the mixture not to lead to a sharp decrease of this quantity). Therefore the difficulties in producing electric-discharge lasers on such transitions are determined mainly by the difficulty in realizing a homogeneous discharge at high pressures.

Among the prospective advantages of such lasers are the possibility of obtaining large power, a relatively large frequency tuning range (on the order of 100 cm^{-1}), and also the possibility in principle of obtaining ultrashort pulses by mode locking.

If the molecule B has a constant dipole moment, it is possible in principle to obtain amplification on the transitions A(0)B(0) → A(1)B(0), if inverted population is realized on the levels of the molecule A. Inasmuch as the constant dipole moments can be much higher (by one order of magnitude and more) in comparison with the dipole moment of the vibrational transition, the gain for such transitions can be higher than for the transitions $A(0)B(0) \rightarrow A(1)B(1)$.

We note in conclusion that the foregoing estimates can be readily verified experimentally by using the absorption spectra at the summary frequencies $\omega_A + \omega_B$. Such measurements make it also possible to obtain information on the value of the combination polarizability of molecules in the IR region of the spectrum.

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16