# Rotational transitions in the excitation of electronic states of molecules by electron impact

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An estimate of the probability of rotational transitions in the excitation of electronic states of a molecule by electron impact near threshold is proposed. The zero radius potential (or the separable potential) approximation is initially used in the adiabatic approximation in the molecular rotation. Then additional arguments are presented in favor of the generality of the estimate obtained, which is analogous to the Franck-Condon principle, but pertains to rotational transitions. In particular, for the excitation of the $^3\Pi_u^-$ state of the $H_2$ and $D_2$ molecules, when a change of the rotational quantum number of the molecule must be even in accordance to the rigorous selection rules, the rotational momentum of the molecule practically cannot change at incident electron energies which are not too great. This makes it possible to explain the experimental data on the population of the rotational sublevels of excited electron-vibrational states of molecules in a low-pressure gas discharge plasma and to base the method of determining the gas temperature of this plasma on measurements of the relative distribution of the intensities in the rotational structure of the molecular bands.

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1. Collisions of molecules with electrons are one of the most important processes producing excited molecules in a plasma. In general, the electronic, vibrational, and rotational states of the molecule are changed in such collisions. In the Born-Oppenheimer approximation these processes are separated because of the difference of their characteristic times. The electron excitation is usually calculated for specific nuclei, and the corresponding cross sections can also be found experimentally by the emission method, for example.[1] A change of the vibrational state occurs in accordance with the well known Franck-Condon principle which has been experimentally verified; in addition, at the present time the Franck-Condon factors for the case of hydrogen have been calculated very accurately.[2] As to the change of the rotational momentum occuring in the electron excitation process, however, the experimental determination of the probability for this process has encountered great difficulties.

The general (kinematic) problems in the theoretical description of these rotational transitions have been dealt with by Rubin[3] within the framework of the adiabatic approximation (see below), but as far as we know no specific calculations have been carried out.

In the present study we derive a simple yet fairly general estimate of the probability for rotational transitions in the excitation of electron-vibrational states as a function of the change of the rotational angular momentum $\Delta J$. Such an estimate is also needed from the purely practical point of view of, use in low-pressure plasmas, of the technique for finding the gas temperature from the measured relative distributions of the intensity in the rotational structure of the electron-vibrational bands of diatomic molecules.[4] The important yet insufficiently well-founded premise of the method is the negligibly small probability of a change in the angular momentum in electron excitation of the molecules.

We shall restrict ourselves to the case where the incident electron energy does not too greatly exceed the excitation threshold of the electronic state. In a low-temperature plasma these electrons give the dominant contribution to the excitation frequency because of the sharp drop of the electron energy distribution function at high energies. The effect is enhanced for triplet states, whose excitation functions have a maximum near threshold (see Ref. 1, for example).

2. According to classical mechanics, the maximum angular momentum which can be transferred to a scatterer of dimension $R$ is[5]

$$\Delta J \leqslant k_i R, \tag{1}$$

where $k_i$ is the initial momentum of the relative motion (atomic units are used). Table I gives the values of $k_i R$ for the scattering of electrons of energy corresponding to the excitation thresholds of various electronic states of a number of molecules, calculated according to Herzberg's data.[6] From this table it is seen that the estimate (1) is not a sufficient reason for neglecting transitions with $\Delta J \neq 0$ in studying the electron excitation of molecules in a plasma.

Relation (1) corresponds to the elastic reflection of the incident particle. If it is assumed that after the scattering the electron momentum is small (the energy goes to excite an electronic state), then our estimate becomes

$$\Delta J \leqslant {}^1/_2 k_i R.$$

Below we shall show that even this estimate is still too rough.

3. In a quantum description the adiabatic approxima-

TABLE I.

| Molecule | Electronic state | $k_i R$ | Molecule | Electronic state | $k_i R$ |
|---|---|---|---|---|---|
| $H_2$, $D_2$ | $d^3\Pi_u$ | 1.4 | $N_2$ | $B^3\Pi_g$ | 1.7 |
| $Cl_2$ | $A^3\Pi_{0u}+$ | 1.5 | | $a^1\Pi_g$ | 1.8 |
| CO | $A\Pi$ | 1.6 | | $C^3\Pi_u$ | 1.9 |
| $I_2$ | $B^3\Pi_{0u}+$ | 1.9 | | | |

tion can be used to calculate the rotational transition probabilities. This approximation is based on the assumption that the deflection angle of the molecule during the collision with the incident electron is small; in view of the short time in which the interaction occurs, this often is also called the sudden approximation.

First the scattering amplitude $F(\mathbf{k}_i, \mathbf{k}_f, \mathbf{R})$ for atomic nuclei at rest is somehow found; here $\mathbf{k}_i$ and $\mathbf{k}_f$ are the electron momenta before and after scattering and the vector $\mathbf{R}$ characterizes the orientation of the molecule (the vector joining the nuclei can be used as $\mathbf{R}$). Then the amplitudes for transitions between initial $m$, $J$ and final $m', J'$ rotational states of the molecule are calculated according to the formula

$$F_{mJ\to m'J'}(\mathbf{k}_i, \mathbf{k}_f) = \int d\Omega_{\mathbf{R}} Y_{mJ}\left(\frac{\mathbf{R}}{R}\right) F(\mathbf{k}_i, \mathbf{k}_f, \mathbf{R}) Y^{*}_{m'J'}\left(\frac{\mathbf{R}}{R}\right), \tag{2}$$

The main condition for the adiabatic approximation to be applicable is of the form $\Delta E/E \ll 1$, where $\Delta E$ is the energy of the rotational transition and $E$ is the smallest of the incident particle energies before and after the collision. Therefore, the adiabatic approximation is inapplicable only in a very narrow range near threshold.

Let us first of all consider the case where the scattering amplitude $F(\mathbf{k}_i, \mathbf{k}_f, \mathbf{R})$ is calculated in the zero radius potential or the separable potential approximation. If the molecule is simulated by two identical spin centers a distance $R$ from each other, the differential cross section for scattering with the transition $J \to J'$ in the adiabatic approximation is of the form

$$\begin{gathered}\sigma_{J\to J'}(\mathbf{k}_i, \mathbf{k}_f) = \frac{k_f}{k_i}(2J'+1) \sum_{\text{even}, l} \begin{pmatrix} l & J & J' \\ 0 & 0 & 0 \end{pmatrix}^2 (2l+1) \\ \times \left\{ |\Phi^{(+)} - \Phi^{(-)}|^2 j_l^2\left(|\mathbf{k}_i + \mathbf{k}_f| \frac{R}{2}\right) + |\Phi^{(+)} + \Phi^{(-)}|^2 j_l^2\left(|\mathbf{k}_i - \mathbf{k}_f| \frac{R}{2}\right) \right. \\ + 2\,\mathrm{Re}[(\Phi^{(+)} + \Phi^{(-)})(\Phi^{(+)} - \Phi^{(-)})^*] j_l\left(|\mathbf{k}_i + \mathbf{k}_f| \frac{R}{2}\right) \\ \left. \times j_l\left(|\mathbf{k}_i - \mathbf{k}_f| \frac{R}{2}\right) P_l\left(\frac{\mathbf{k}_i + \mathbf{k}_f}{|\mathbf{k}_i + \mathbf{k}_f|} \cdot \frac{\mathbf{k}_i - \mathbf{k}_f}{|\mathbf{k}_i - \mathbf{k}_f|}\right) \right\},\end{gathered} \tag{3}$$

where the $j_l(x)$ are the spherical Bessel functions. The cross section (3) has been averaged over the projections of the rotational angular momentum in the initial state and summed over the projections in the final state.

Expression (3) was obtained from the amplitude of the excitation for specific nuclei of an electronic state of a molecule for the $\Sigma_g - \Sigma_g'$ transition in the zero radius potential and separable potential approximation. The form of this amplitude is similar to the elastic scattering amplitude of an electron in the $^3\Sigma_u^+$ state of the hydrogen molecule, which is given by Demkov and Ostrovskiĭ,[7,8] for example, and has been used to calculate the cross sections for rotational transitions not accompanied by electron excitation (see Refs. 7 and 9). In the zero radius potential approximation the coefficients $\Phi^{(\pm)}$ are expressed in terms of the matrix of the parameters $\alpha$ describing the inelastic scattering by each of the potential centers making up the molecule:

$$\Phi^{(\pm)} = \frac{\alpha_{21}}{(\alpha_{11} + ik_1 \pm R^{-1}\exp(ik_1R))(\alpha_{22} + ik_2 \pm R^{-1}\exp(ik_2R)) - \alpha_{12}\alpha_{21}}.$$

In the following we shall only need the fact that the coefficients $\Phi^{(\pm)}$ depend only on the energy and not on $\mathbf{R}/R$ or $J$ and $J'$.

We can obtain the total scattering cross sections by integrating (3) over the scattering angles $\theta$ (the angle between $\mathbf{k}_i$ and $\mathbf{k}_f$):

$$\begin{gathered}\sigma_{J\to J'} = \frac{k_f}{k_i} \cdot 16\pi(2J'+1) \sum_{l=0}^{\infty} \sum_{L=|l-J|}^{l+J} \sum_{\bar{l}=|L-J'|}^{L+J'} (2L+1) \\ \times \left\{ j_{2l}^2\left(\frac{k_fR}{2}\right) j_{2\bar{l}}^2\left(\frac{k_iR}{2}\right) |\Phi^{(+)}|^2 \begin{pmatrix} J & 2\bar{l} & L \\ 0 & 0 & 0 \end{pmatrix}^2 \right. \\ \times \begin{pmatrix} J' & 2l & L \\ 0 & 0 & 0 \end{pmatrix}^2 (4l+1)(4\bar{l}+1) + j_{2l+1}^2\left(\frac{k_fR}{2}\right) j_{2\bar{l}+1}^2\left(\frac{k_iR}{2}\right) \\ \left. \times |\Phi^{(-)}|^2 \begin{pmatrix} J & 2\bar{l}+1 & L \\ 0 & 0 & 0 \end{pmatrix}^2 \begin{pmatrix} J' & 2l+1 & L \\ 0 & 0 & 0 \end{pmatrix}^2 (4l+3)(4\bar{l}+3) \right\}.\end{gathered} \tag{4}$$

Let us study the behavior of the total scattering cross section (4) for an incident electron energy somewhat larger than the excitation threshold of the electronic state of the molecule. Then $k_fR$ is a small parameter in the problem and we can use the small-argument Bessel function expansion[10]

$$j_l\left(\frac{k_fR}{2}\right) \sim \left(\frac{k_fR}{4}\right)^l \frac{\sqrt{\pi}}{2\Gamma(l+3/2)}[1 + O((k_fR)^2)]. \tag{5}$$

The largest contribution to the cross section comes from the term with $l = 0$. According to the properties of the $3j$ symbols we have

$$\sigma_{J\to J'} \sim 16\pi \frac{k_f}{k_i} \sum_{\text{even } \bar{l}} j_{\bar{l}}^2\left(\frac{k_iR}{2}\right) |\Phi^{(+)}|^2 \begin{pmatrix} J & J' & \bar{l} \\ 0 & 0 & 0 \end{pmatrix}^2 (2\bar{l}+1)(2J'+1). \tag{6}$$

In the case where $k_iR$ can also be considered a small parameter, it is easy to obtain the following estimate for the total cross section using formula (5):

$$\begin{gathered}\sigma_{J\to J+\Delta J} \sim 16\pi \left(\frac{k_fR}{2}\right)\left(\frac{k_iR}{2}\right)^{|2\Delta J|-1} \frac{|\Phi^{(+)}|^2 D}{[(|2\Delta J|+1)!!]^2} (|2\Delta J|+1), \\ \Delta J = J' - J,\end{gathered} \tag{7}$$

where

$$D = \begin{pmatrix} J & J+\Delta J & |\Delta J| \\ 0 & 0 & 0 \end{pmatrix}^2 (2J + 2\Delta J + 1) \tag{7'}$$

becomes unity for $J = 0$ and does not exceed this value for all the remaining $J$. Since we shall primarily be interested in the upper estimate of the cross section $\sigma_{J\to J+\Delta J}$, we shall henceforth take $D = 1$.

Formula (3), derived for a homonuclear molecule, gives a nonzero cross section only for transitions with even change of $J$. Study of the more general case of a heteronuclear molecule (which we shall not do here because of the complexity of the calculations) leads to the same estimate (7), which is therefore valid for both even and odd $\Delta J$. It is significant that the dependence included in $\Phi^{(+)}$ on the specifics of the electron transition and the dependence on $\Delta J$ can be factorized. In the case where the collision is not accompanied by a change of the electronic state of the molecule there is, in general, no such factorization.

4. It is not difficult to see that the estimates (7) are governed by interference. The dependence on $\mathbf{R}$ enters into the scattering amplitude $F(\mathbf{k}_i, \mathbf{k}_f, \mathbf{R})$ in the zero radius potential approximation via exponentials of the form[7]

$$\exp\left[i(\mathbf{k}_i \pm \mathbf{k}_f)\frac{\mathbf{R}}{2}\right]. \tag{8}$$

They correspond to the phase difference in the scattering on two potential centers located a distance $R$ from each other. The spherical Bessel functions appear as a result of the expansion (8) in partial waves. It is clear that the appearance of the exponentials (8) has a more general significance than the model used. For example, they must appear in the Born approximation for scattering by an anisotropic potential or in the impulse approximation. In general, the dependence of the scattering amplitude on the orientation of the potential is characterized by a factor of the type (8), where $|\mathbf{R}|$ obviously has the sense of the difference between the largest and smallest characteristic dimensions of the scatterer, which can be either a heteronuclear or a monatomic molecule. In the case of a diatomic molecule it can be assumed that $R$ is of the order of the internuclear spacing.

The inclusion of the phase modulation of the scattered waves is important in these considerations. The effect of neglecting the amplitude modulation would apparently be felt primarily in the case of molecules with a large dipole moment. Also, it is usually important to take into account the polarization forces near threshold, where the adiabatic approximation is no longer applicable. The R-independent part of the scattering amplitude does not contribute to the cross section for rotational transitions, but affects the value of the cross section for $\Delta J=0$. It can be expected that this leads to a still larger increase of the cross section $\sigma_{\Delta J=0}$ than follows from the estimate (7).

The applicability of (7) is primarily related to the possibility of keeping only the first terms in the expansion of the corresponding Bessel function, that is, under the conditions

$$\frac{4}{3}\left(\frac{k_fR}{4}\right)^2 \ll 1, \quad \frac{2}{(\Delta J+{}^3/_2)}\left(\frac{k_iR}{4}\right)^2 \ll 1. \tag{9}$$

Near the excitation threshold the second of conditions (9) is important. The data in Table I show that for the molecules of greatest interest this inequality and, therefore, the estimate (7) are satisfied.

5. In Fig. 1 we give the ratio of the cross sections for rotational transitions $\sigma_{J-J+\Delta J}/\sigma_{J-J}$ as a function of $\Delta J$, calculated for different values of the parameter $k_iR$ in formula (7) with $D=1$. It is seen that the cross section falls off very rapidly with increasing $\Delta J$, even when $k_iR$ is relatively large. In particular, the use of the estimate (7) for the molecules listed in Table I shows that the following inequalities are satisfied in a low-temperature plasma:

$$\sigma_{J\to J} \gg \sigma_{J\to J\pm2}, \quad \sigma_{J\to J\pm1} \gg \sigma_{J\to J\pm3}. \tag{9'}$$

In this sense we can speak of the validity of the following approximate selection rules:

$$\Delta J=0, \ \pm1. \tag{10}$$

In homonuclear molecules an odd or even change of the rotational angular momentum can be strictly forbidden by the properties of symmetry to interchange of the nuclei (which corresponds to the well known dropout of every other the rotational level for homonuclear molecules in certain cases). The approximate selection rules are then respectively

$$\Delta J=0 \tag{10'}$$

or

$$\Delta J=\pm1, \tag{10''}$$

depending on the type of electron transition (see, for example, the following discussion for the $d^3\Pi_u$ states of $H_2$).

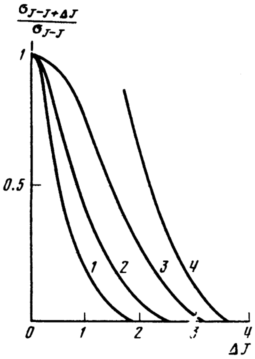

FIG. 1. Ratio of the cross sections for rotational transitions $\sigma_{J\to J+\Delta J}/\sigma_{J\to J}$ as a function of $\Delta J$ for $D=1$. The numbers on the curves indicate the value of $k_iR$.

6. Direct verification of the model proposed here for calculating the probability of rotational transitions in the electronic excitation of molecules is not possible, since the necessary experimental data are not available.

It is possible, however, to find an indirect confirmation of our result ($\Delta J=0$) by analyzing the experimental data on the relative distribution of the populations of different electron-vibrational states of the molecules in low-pressure hydrogen and deuterium plasmas, when the radiative decay probability $\nu_{\text{rad}}$ is much larger than the rates of collisions of excited molecules with electrons $\nu_{eg^*}$ and with unexcited molecules $\nu_{gg^*}$. The point is that as a direct consequence of the selection rule (10′), the excitation temperatures of the different electron-vibrational states $T^{mv}_{\text{rot}}$ are related in a low-pressure plasma to the rotational temperature of the ground state $T^{n0}_{\text{rot}}$ (which is usually equal to the gas temperature $T_g$) in the following manner[4]:

$$T^{mv}_{rot}=\frac{B_{mv}}{B_{n0}}T^{n0}_{rot}=\frac{B_{mv}}{B_{n0}}T_g, \tag{11}$$

where $B_{mv}$ and $B_{n0}$ are the rotational constants of the excited and ground states, respectively. Therefore, the ratio of the rotational temperatures of different electron-vibrational states must equal the ratio of the rotational constants of these states. Relation (11) means that the relative populations of the rotational sublevels do not change during an electron transition in the molecule.

In the following we shall use the data on the population of the $d^3\Pi_u^-$ state in $H_2$ and $D_2$. Since the triplet splitting is small this state is equivalent to the $^1\Pi_u^-$ state, so that the quantum number $J$ introduced above has the sense of the rotational quantum number with the spin neglected and is usually denoted by $N$. In the $d^3\Pi_u^-$ state of hydrogen the levels of parahydrogen correspond to even $N$ and the levels of orthohydrogen correspond to odd $N$. In the ground $X^1\Sigma_g^+$ state of $H_2$ there is the same sequence of levels with different symmetry.

TABLE II.

| $v$ | $B_{mv}/B_{m1}$ | $T_{rot}^{mv}/T_{rot}^{m1}$ | | |
|---|---|---|---|---|
| | | Ref. 11 | Ref. 12 | Ref. 13 |
| 0 | 1.06 | 1.3±0.3 | 1.04±0.02 | 1.10±0.07 |
| 1 | 1.00 | 1.0 | 1.00 | 1.00 |
| 2 | 0.95 | 0.95±0.2 | 0.95±0.06 | 0.73±0.08 |
| 3 | 0.89 | – | 0.85±0.09 | 0.64±0.06 |
| 4 | 0.84 | — | 0.80±0.02 | – |

Since the probability of a transition between the ortho- and para- variants is extremely small, $X^1\Sigma_g^+ - d^3\Pi_u^-$ transitions can take place only with even $\Delta N$ and according to (10′) transitions with $\Delta N = 0$ dominate in the population of the $d^3\Pi_u^-$ state. A similar argument demonstrates that for the $X^1\Sigma_g^+ - d^3\Pi_u^+$ transition $\Delta N$ must be odd and the approximate selection rule is $\Delta N = \pm 1$. All of these conclusions are valid for the $D_2$ molecule.

In Table II we give the ratios of the rotational temperatures of different vibrational levels of the $d^3\Pi_u^-$ electronic state of the $H_2$ molecule in a low-pressure plasma ($\nu_{rad} > \nu_{eg}*, \nu_{gg}*$), calculated by us using the data of Refs. 11–13. It is clear that relation (11) is satisfied experimentally.

In Ref. 4 simultaneous measurements of $T_{rot}^{mv}$ and $T_g$ were carried out in the plasma of an arc discharge at low pressure ($P = 8$ Torr) in a $D_2$–Ne mixture. The rotational temperatures of the vibrational levels with $v = 0, 1, 2, 3$ belonging to the $d^3\Pi_u^-$ state of the $D_2$ molecule were determined by measuring the intensities of the lines in the $Q$ branches of the diagonal Fulcher bands. The temperature ratio $T_{rot}^{mv}/T_{rot}^{m1}$ for different values of the discharge currents $i$, averaged over all conditions of the quantity $\langle T_{rot}^{mv}\rangle/\langle T_{rot}^{m1}\rangle$, and the ratios of the corresponding rotational constants for deuterium are given in Table III. We see that within the measurement accuracy relation (11) is satisfied in this case, too.

Under these same conditions the gas temperature was determined from the Doppler broadening of the spectral lines of neon. These measurements also make it possible to verify the validity of (11) for deuterium. In Fig. 2 the temperature $T_g$ measured directly is compared with the temperature $T_{rot}^{mv}B_{n0}/B_{mv}$ determined according to the different bands of the Fulcher system. We see that there is good agreement between the values of the gas temperature determined by the two independent methods.

Simple estimates indicate that a distribution in the rotational levels similar to the Boltzmann distribution with effective temperature $T_{rot}^{m0}B_{mv}/B_{n0}$ can also appear when $\sigma_{J-J+2}$ differs from zero if the temperature is high ($kT \gg B_{n0}$). The experimental data that we used[11-13] were obtained for $kT_g/B = 5$–8. It is possible in principle to reverse the problem and try to obtain an upper bound of the ratio $\sigma_{J-J+2}/\sigma_{J-J}$, for which the relative populations of the rotational levels still do not differ from the Boltzmann populations within the experimental error. The solution to this problem requires an independent investigation.

TABLE III.

| $v$ | $T_{rot}^{mv}/T_{rot}^{m1}$ | | | | | $\left\langle \frac{T_{rot}^{mv}}{T_{rot}^{m1}} \right\rangle$ | $\frac{B_{mv}}{B_{m1}}$ |
|---|---|---|---|---|---|---|---|
| | $i$=0.02 | 0.05 | 0.1 | 0.2 | 0.5 A | | |
| 0 | 1.07 | 1.04 | 1.15 | 1.04 | 1.12 | 1.08±0.05 | 1.04 |
| 1 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 2 | 0.90 | 0.87 | 0.91 | 0.91 | 0.91 | 0.90±0.02 | 0.96 |
| 3 | 0.83 | 0.83 | 0.84 | 0.86 | 0.89 | 0.85±0.02 | 0.92 |

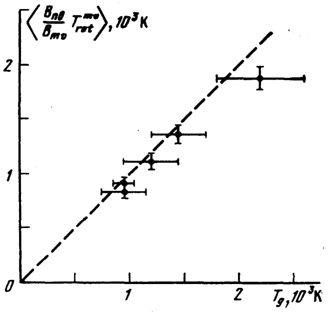

FIG. 2. Comparison of the temperature $T_{rot}^{mv}B_{n0}/B_{mv}$ found from the different bands of the Fulcher system with the temperature $T_g$ measured directly.

7. In spite of its simplicity, the proposed estimate of the rotational transition probability is of a fairly general nature and is valid not only for diatomic, but also for polyatomic molecules. Our result is an analog of the Franck-Condon principle for rotational transitions and was derived using similar, although somewhat less general, assumptions. In particular, for incident electron energies which are not too high transitions without a change of the rotational angular momentum of the molecule are dominant.

The estimates carried out here explain the available experimental data on the distribution of the population of the rotational sublevels of excited electron-vibrational states of molecules in a low-pressure gas-discharge plasma. The technique of determining the gas temperature of a molecular plasma at low pressure from measurements of the relative distribution of the intensity in the rotational structure of the molecular bands is thereby justified.

## ADDENDUM (14 November 1978)

After this paper was sent to press new experimental data appeared on the relative probability of rotational transitions in the excitation of the $d^3\Pi_u$ state of the hydrogen molecule [D. K. Otorbaev, V. N. Ochkin, S. Yu. Savinov, N. N. Sobolev, and S. N. Tskhaĭ, JETP Letters **28**, 392 (1978); Preprint FIAN No. 161, Moscow, 1978]. In order to compare the data on the rate constants obtained in this study with the above theoretical estimate, it is necessary to average the cross sections of the corresponding transitions [formula (7) of the present article] over the rates using the electron energy distribution function, which was not measured in the cited study. On the other hand, it can be verified that the measurements are in qualitative agreement with our estimate (Fig. 1). The numerical data from the experimental measurements are conveniently written in the following form:

| Band for which measurements were made | 0–0 | 2–2 | 3–3 |
|---|---|---|---|
| $\sigma_{1\to3}/\sigma_{1\to1}$: | 0.18 | 0.12 | 0.096 |
| $\sigma_{1\to4}/\sigma_{1\to2}$: | 0.16 | 0.12 | 0.086 |

It is seen from these data that, in agreement with formula (9′), the experiment indicates that in the excitation of the $d^3\Pi_u$ states the following approximate selection rules hold fairly well: $\Delta N = 0$ for the $d^3\Pi_u^-$ state and $\Delta N = \pm 1$ for the $d^3\Pi_u^+$ state. A critical discussion of this experiment and further development and refinement of the ideas in the present study are contained in Refs. 14.

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# Exact theory of resonant third-harmonic generation in gases

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We consider the self-consistent problem of passage of resonant pump and third-harmonic pulses through a gas consisting of four-level atoms (molecules). An exact solution of the problem is obtained, with account taken of all the terms of the expansion of the nonlinear polarization in powers of the field intensities. It is shown that the wave propagation equation coincides in form with the canonical Hamilton equations, so that the mathematical formalism of classical mechanics can be used. The dependence of the conversion efficiency and of the intensity-transfer period on the pump emission parameters is investigated. The case of small detunings from resonance, in which deviations from the ordinary theory are observed, is considered.

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## 1. INTRODUCTION

In the theoretical analysis of third-harmonic (TH) generation the nonlinear polarization of the medium is usually expanded in powers of the field intensities, and only the terms of lowest order, which contribute to this process, are retained (see e.g., Refs. 1 and 2). This approach, however, is no longer correct in the presence of resonances, when all the terms of the expansion must be retained.[3] The ensuing mathematical difficulties are in part unsurmountable and make it necessary nonetheless either to include a small number of expansion terms[3] or to assume that the resonance condition is satisfied for only one of the transition; otherwise, other approximations must be used. In this paper we develop a procedure for solving this problem exactly, by taking the effects of coherent saturation into account.

## 2. POLARIZATION OF A FOUR-LEVEL SYSTEM

Consider the behavior of a four-level system with nondegenerate levels in the field of two linearly polarized pulses with carrier frequencies $\omega$ and $3\omega$. The pulse durations are assumed to be small compared with all the relaxation times of the system. The pulses will be assumed to be adiabatic, to propagate in the same directions, and to be described by the classical intensity vectors

$$\mathbf{E}_1 = E_1(x)\mathbf{e}_1 \exp\{i\omega(x/c-t)\} + \text{c.c.},$$

$$\mathbf{E}_3 = E_3(x)\mathbf{e}_3 \exp\{3i\omega(x/c-t)\} + \text{c.c.}$$

The frequency $\omega$ is assumed close to the system transition frequencies. In the resonance approximation[4] we seek the solution of the Schrödinger equation in the form of the following superposition of unperturbed wave functions $\psi_n$:

$$\Phi = e^{-i\lambda t} \sum_{n=1}^{4} a_n(x)\psi_n \exp\{i(n-1)\omega(x/c-t)\}. \qquad (1)$$

The energy is reckoned from the ground state. Substituting (1) in the Schrödinger equation we obtain a system of equations for the amplitudes $a_n(x)$, which we shall write in matrix form: