Excitation of electron-vibrational-rotational levels of hydrogen molecules by electron impact in a nonequilibrium gas-discharge plasma

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The excitation of the K' rotational levels of $H_2(d\,^3\Pi, I\,^1\Pi)$ by direct electron impact in a transition from the electronic ground state is investigated in a hydrogen discharge cooled in liquid nitrogen under conditions when the lowest rotational levels K_0 of both modifications are populated in the ground state $(X\,^1\Sigma)$ of the H_2 molecule. The possibility is demonstrated of changing appreciably the angular momentum of the molecule in such a process. The experimental data are used to determine the electronic partial cross sections for the excitation of the rotational $(d\,^3\Pi)$ levels of H_2. An excitation probability matrix is formulated in the adiabatic approximation and describes satisfactorily the experimental data. The radiative lifetimes of the various rotational levels of $H_2(I\,^1\Pi)$ and the relative probabilities of the $I\,^1\Pi \to B\,^1\Sigma$ rotational transitions are determined. The rotational excitation of the molecules by electron impact is more intense in the transition to the $I\,^1\Pi$ state than to the $d\,^3\Pi$ state.

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I. INTRODUCTION

The question of the change of the rotational angular momentum when the electron shell of a molecule is excited by electron impact has been long discussed in the literature, principally in connection with the probelm of spectroscopic measurements of the temperature of the neutral component of a plasma,[1-3] but is also of independent interest. The initial premise used in the method of relative intensities in the rotational structure of the electronic molecular spectrum is usually the assumption of the "copying" properties of the direct electron impact, i.e., that the angular momentum is preserved in the excitation; this, however, is physically unfounded.

Attempts to investigate this question quantitatively were made in recent years. Thus, general formulas were obtained in the adiabatic approximation for the cross sections of the excitation of electronic states, with allowance for the dependence on the rotational quantum numbers.[4] The formulas contain coefficients whose calculation calls for the solution of the problem of electron scattering by a molecule with fixed nuclei. In view of the lack of sufficiently simple and reliable methods of solving this problem, no numerical results are given in Ref. 4.

The difficulty in experimentally determining the angular-momentum change probabilities lie in the fact that the initial (ground or metastable) electronic states of the molecules are usually populated by a large number of rotational levels. It was therefore proposed in Ref. 2 to use as the object of the investigation the hydrogen molecule in the plasma of a low-pressure glow discharge cooled with liquid nitrogen. The large value of the rotational constant and the presence of weakly interacting ortho- and para- modifications makes it possible to realize in experiment a situation wherein one rotational level $K_0 = 1$ is populated in practice in the ground electronic state $X^1\Sigma$ of ortho-hydrogen. The relative values of the rates $a_{1K'}$ of excitation from this level to the K' levels of upper state depleted by radiative decay are obtained simply from measurements of the relative intensities $I^{\text{rel}}_{K'K''}$

$$a_{1K'}=\text{const}\cdot I^{\text{rel}}_{K'K''}(\tau_{K'}A_{K'K''}\nu_{K'K''})^{-1}. \tag{1}$$

Here $\tau_{K'}$ is the radiative lifetime of the K' level, $A_{K'K''}$ is the Einstein coefficient of the $K' \to K''$ transition. Investigations of the spectra of Fulcher α system $(d^3\pi \to a^3\Sigma)$ transition have shown that appreciable angular momenta can be transferred to the molecule by direct electronic excitation of the $d^3\pi$ state.

An attempt to estimate theoretically the cross sections of the rotational transitions following excitation of the electronic states of the molecules by electron impact, with the zero-radius potential model as the basis, was made in Refs. 5–7. The gist of the result obtained in Ref. 6 is that the only possible changes of the rotational quantum number are $\Delta K = 0$ and ± 1, but the transitions with $\Delta K = 0$ predominate. This conclusion is taken to be quite general in character. In Refs. 5 and 7 they obtained in the adiabatic approximation the cross sections $\sigma_{K_0K'}$ of the electron-vibrational-rotational transition

$$^1\Sigma(v_0, K_0) \to {}^1\Pi(v', K').$$

In the opinion of the authors of Refs. 5–7, these results do not agree well enough with the data of Ref. 3, and the interpretation offered in Ref. 3 for the experimental results was therefore doubted.

We present here the results of systematic measurements of the relative populations of the rotational levels of the triplet $d^3\pi$ and singlet $I^1\pi$ states of hydrogen, as well as an analysis of the experimental data within the framework of the adiabatic approximation.[4] The nature of the $I^1\pi$ state called also for an investigation of the dependence of the radiative lifetimes and of the relative probabilities of the radiative transitions on the rotational quantum numbers.

II. EXPERIMENTAL SETUP FOR THE STUDY OF INTENSITIES IN SPECTRA

The emission spectra were investigated in a discharge tube of 20 mm diameter. The positive column was 600 mm long; the electrodes were inserted through lateral stubs. The pressure of the hydrogen or of its mixtures with helium was 0.5–12 Torr; the discharge dc current was 5–50 mA. To obtain high purity, the gas could be pumped through the discharge at low speed (~1 cm/sec). A DFS-8 spectrometer (dispersion 3 Å/mm) with photoelectric registration. To investigate the line shapes and to analyze the possible superpositions, a pressure-scanned Fabry-Perot etalon was used. The gas temperatures, measured with a thermocouple and by determining the Doppler broadening of the lines of molecular hydrogen and helium, was monitored against measurements of the relative intensities in the rotational structure of the bands of the second positive system of N_2, for which small amounts of nitrogen were added to the H_2 and H_2+He in certain experiments. The tube wall temperature could be maintained constant in the range from 77 to 900 K. To eliminate the influence of the radial inhomogeneity of the discharge we used diaphragms to separate a central discharge zone of ~5 mm diameter.

III. EXCITATION OF $H_2(d^3\Pi)$

The spectroscopic constants and the data for the interpretation of the spectrum of the Fulcher α system are given in Refs. 8–13. The states $d^3\pi$ and $a^3\Sigma$ are characterized by a weak spin-orbit interaction, and the triplet structure was not resolved in the experiment. The splitting was much less than the Doppler line width even when the discharge is cooled with liquid nitrogen, and there is no need to introduce the corresponding corrections to the gas temperature determined from the summary contour of the multiplet. In para-hydrogen (total nuclear spin $I=0$) the populations of the rotational levels of the $d^3\pi$ state with even K' were determined from the lines of the Q branch, and the populations of the levels with odd K' were determined from the lines of the P and R branches, and vice versa for the ortho-hydrogen ($I=1$). The state $d^3\pi$ pertains to the case of Hund's coupling b, and the lifetimes $\tau_{K'}$ do not depend on K'.[14]

1. Populations of rotational level of $H_2(d^3\Pi, v'=0)$ in a discharge cooled with liquid nitrogen

We report below the results of measuring the gas temperature by various methods in a discharge in an H_2+He mixture (1:3) at a total pressure 0.5 Torr, a current density 9.5 mA/cm², and with the discharge-tube walls cooled with liquid nitrogen:

Measurement method:	1	2	3′	3″	3‴
T, K:	140±20	160±25	145±20	135±20	140±20

Here 1 denotes measurement with a thermocouple; 2, the method of relative intensities in the rotational structure of electronic transition [using the second positive system of N_2, band (0, 0)]; 3, the method based on measurement of the Doppler line broadening, with the measurements in cases 3′, 3″, and 3‴ made respectively with the lines H_2 ($d^3\pi - a^3\Sigma$) [lines $Q(1)$ and $Q(5)$ of the (0, 0) band], $H_2(I^1\pi - B^1\Sigma)$ [lines $P(2)$, $P(4)$, $Q(2)$, and $Q(4)$ of the (0, 0) band], and He ($\lambda = 4875.62$ Å).

The results of the different methods agree within the limits of error. The most probable temperature is 145 ± 20 K. Similar measurements in a discharge in pure hydrogen yield 130 ± 20 K.

The relative populations of the rotational levels of the state $H2_2(d^3\pi,\ v'=0)$ in a discharge under the same conditions are:

K':	1	2	3	4	5
Ortho-hydrogen:	0.485±0.05	0.373±0.037	0.077±0.015	0.05±0.016	0.011±0.004
Para-hydrogen:	0.692±0.07	0.146±0.016	0.123±0.015	0.018±0.006	0.010±0.005

These data are normalized by the condition that the sum of the populations of all the rotational levels of each modification be equal to 1. To obtain the correct ratios of the populations of the levels of different modifications, the data for ortho hydrogen must be multiplied by 3.8. We note that the values of the relative populations agree, within the limit of errors, with those cited by us earlier,[3] but were obtained with greatly enlarged measurement statistics. The results of measurements with the (2, 2) band, as well as of measurements with pure hydrogen, are close. In all the investigated cases, the reabsorption can be neglected, a fact specially monitored.

2. Partial cross sections of excitation

At low temperatures, the population of the ortho-hydrogen rotational level $d^3\pi$, K' (the vibrational quantum numbers that are not indicated are equal to zero) is proportional to the excitation rate $a_{1K'}$, i.e., to the excitation cross section $\sigma_{1K'}$ averaged over the electron velocities v_e:

$$a_{1K'} \sim \langle v_e \sigma_{1K'} \rangle / \langle v_e \rangle, \tag{2}$$

accurate to a factor independent of the rotational numbers.

The measurements make it possible to obtain the set $a_{1K'}$. To determine $a_{K_0K'}$ at $K_0 \neq 1$, additional considerations are needed. In Ref. 3, the very simple assumptions were made that $a_{K_0K'}$ is "symmetrical" and "similar" with respect to $\Delta K = K' - K_0$. These assumptions are not sufficiently well founded (as is correctly noted in Ref. 7), but even in this approximation the $a_{K_0K'}$ matrix makes it possible to calculate, in satisfactory agreement with experiment, the populations of the $d^3\pi$ and K' levels of ortho- and para-hydrogen at higher gas temperatures.[3] However, as follows from the adiabatic-approximation formulas,[4] with increasing temperature the molecule distribution over the rotational levels in the excited state become less sensitive to the concrete choice of the dependences of the cross sections on the rotational quantum numbers, if the sum

$$(2K'+1)^{-1} \sum_{K_0} (2K_0+1) a_{K_0K'}$$

does not depend on K' (the quantity $a_{K_0K'}$ of Ref. 3 satisfies this condition approximately).

To describe the dependences of the cross sections on the rotational numbers K_0 and K' we use the adiabatic-approximation formulas.[4] Excitation of the $d^3\pi$ term from the $X^1\Sigma$ state is accompanied by a change of the spin of the molecules, and occurs therefore only as a result of exchange scattering. Summing the corresponding expression for the cross section in Ref. 4 over the components of the fine structure (which is not resolved in the experiment), we obtain

$$\sigma_{v_0K_0v'K'}=q_{v_0v'}\sum_r S_r(2K'+1)\begin{pmatrix}K_0 & r & K'\\ \Lambda_0 & \Lambda'-\Lambda_0 & -\Lambda'\end{pmatrix}^2. \tag{3}$$

Here $q_{v_0v'}$ is the Franck-Condon factor, S_r are quantities that characterize the scattering of an electron by a molecule with fixed nuclei, and Λ_0 and Λ' are the projections of the angular momentum of the electrons on the the axis of the molecule in the initial and final electronic states, respectively (in our case $\Lambda_0=0$ and $\Lambda'=1$). A similar formula for a singlet-singlet transition is given in Ref. 5. The sum rules for the j-symbols[15] and the Franck-Condon factors[1] yield for the total excitation cross section σ of the electronic state:

$$\sigma=\sum_{v'K'}\sigma_{v_0K_0v'K'}=\sum_r S_r.$$

The total cross section does not depend on v_0 or K_0, and is determined only by the coefficients S_r, which we shall therefore call the electronic partial cross sections. For transitions from Σ states, the S_r are proportional to $\sigma_{v_00v'r}$. Averaging (3) over the electron velocities, we obtain an analogous relation for the excitation rates. We denote the quanties $\langle v_e S_r\rangle/\langle v_e\rangle$ by $\bar{S}_r$.

Assume that the populations of the rotational levels in the ground state have Boltzmann distributions with temperature T (with exception of the slowly relaxing ratio of the ortho- and para-hydrogen concentrations), and that the $d^3\pi$ state is excited by direct electron impact (see below). Then

$$\begin{aligned}n_{K'I}&=g_I\sum_{K_0(I)}(2K_0+1)\exp\left\{-\frac{F_0(K_0)hc}{kT}\right\}a_{K_0K'}\\ &=\sum_r\bar{S}_r\sum_{K_0(I)}g_I(2K_0+1)q_{v_0v'}\exp\left\{-\frac{F_0(K_0)hc}{kT}\right\}\begin{pmatrix}K_0 & r & K'\\ 0 & 1 & -1\end{pmatrix}^2.\end{aligned} \tag{4}$$

Here I is the nuclear spin of the molecule, $n_{K',I}$ is the population of the $d^3\pi$ level with quantum numbers K' and I. The quantity g_I is connected with the total density N_I of the molecules of the corresponding modification in the ground state:

$$N_I=g_I\sum_{K_0(I)}(2K_0+1)\exp\left\{-\frac{F_0(K_0)hc}{kT}\right\}. \tag{5}$$

By writing the summation index in the form $K_0(I)$ we emphasize that in the molecule ground state the rotational levels alternate and pertain to different modifications; $F_0(K_0)$ is the value of the rotational term. The relative quantities $\bar{S}_r$ are determined by minimizing the quantity

$$M=\sum_{K',I}\left(\frac{C_I}{g_I}\right)^2\left(1-\frac{n_{K',I}}{n^e_{K',I}}\right)^2, \tag{6}$$

where $n^e_{K',I}$ are the measurement results, and $n_{K',I}$ is given by expression (3). Since we are determining relative quantities, we put $g_0=1$ and assume the quantity $x=g_0/g_1=1/g_1$ to be unknown together with $\bar{S}_r$. The coefficients C_I are introduced to be able to vary the "contribution" made to the minimized sum by the different hydrogen modifications so as to check on the agreement between the values of $\bar{S}_r$ determined for ortho- and para-hydrogen. We actually used two choices of C_I: either $C_0=C_1=1$, or $C_I=g_I$ (in the latter case the calculation is performed with several iterations, since x is not known beforehand). With respect to $\bar{S}_r$ and x, the search for the minimum of M reduces to a solution of a system of linear equations. The calculation is carried out with a computer using data for four levels ($K'=1$ to 4) of both modifications. The number of coefficients $\bar{S}_r$ was varied ($r_{\max}=3$ to 5) to monitor the stability of the results. The values of $\bar{S}_r$ calculated for the $X^1\Sigma\rightarrow d^3\pi$ transitions are:

r:	1	2	3	4
$\bar{S}_r$:	1.0	0.16	0.13	0.018.

They are normalized by the condition $\bar{S}_r=1$. For $r=2$ and 3, the accuracy is 30–40%, whereas $\bar{S}_4$ should be regarded as an estimate with a possible error by a factor 2 or 3. Calculation of the populations of all the rotational levels of ortho- and para-hydrogen at higher gas temperature with the aid of the values of $\bar{S}_r$ turns out to be in good agreement with experiment.

3. Possible causes of errors and analysis of the initial premises

The values of the random errors were given above (see the data for the populations of the ortho- and para-hydrogen levels). We discuss now possible systematic errors, due mainly to two circumstances: the use for the measurements of so complicated an object as a gas discharge, and the difference between the real molecule and the employed theoretical model.

$\bar{S}_r$ is determined by assuming a Boltzmann distribution of the molecules over the rotational levels in the ground state which in principle may be violated as a result of collisions with the electrons.[7] The levels $d^3\pi$ ($K\leqslant 4$) should be excited mainly in collisions of electrons with molecules in two rotational states of both modifications in $X^1\Sigma$ ($K_0=0.2$ and $K_0=1.3$ for para- and ortho-hydrogen, respectively). To estimate the "overpopulation" of the ground-state levels in comparison with the thermal population, we use the data on the cross sections of the pure rotational transition produced by electron impact,[16] and on the rates of rotational relaxation in hydrogen.[17] Even neglecting impacts of the second kind with the electrons and with the atoms, as well as deactivation on the walls, we have arrived at the conclusion that the change of the effective temperature determined from the populations of the levels $K_0=1$ and $K_0=3$ does not exceed 15–20% of the gas temperature under the most unfavorable experimental conditions. The temperature determined from the minimum-M condition practically coincides with that measured in experiment, thus additionally supporting the assumption made.

It is easy to conclude from the balance conditions that if transitions from levels $K_0>1$ predominate in the population of the levels with high K' (ortho-hydrogen), then the dependence of the population $n_{K'}$ on the discharge current is quadratic. Figure 1a shows plots of the intensities of the (0, 0) band as a whole and of the lines

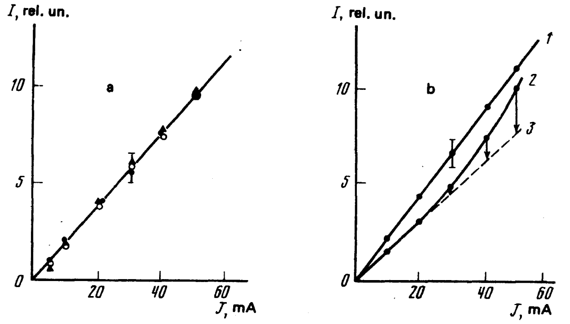

FIG. 1. Line intensities and level populations vs. discharge current in H2 + He mixture (1:3) at a pressure 0.5 Torr (the scales for the different curves are different). a) Discharge tube cooled with liquid nitrogen. Intensities of (0, 0) bands in individual rotation lines. ○—(0, 0) band, •—$Q(3)$, ▲—($Q(5)$. b) Discharge tube cooled with running water: 1) populations of vibrational level of para- H_2 ($d^{3\pi}$, $v'=0$); 2) populations of rotational level of para-H_2 ($d^{3\pi}$, $v'=0$, $K'=4$); 3) calculated population of the level para-H_2 ($D^{3\pi}$, $v'=0$, $K'=4$) with correction for the change of the gas temperature.

$Q(3)$ and $Q(5)$ of the same band against the discharge current (with liquid-nitrogen cooling). The plots are not linear, thus attesting to both direct electron excitation and to a small role of the levels $K_0>1$. This conclusion is independent of the possible axial inhomogeneities of the discharge.[7]

At sufficiently high gas temperatures, account must be taken of the influence of the levels with $K_0>1$. Figure 1b shows plots of the populations of the vibrational level $d^3\pi$ ($v'=0$, $K'=4$) of para-hydrogen on the discharge current in a water-cooled tube. When the current is changed from 10 to 50 mA the gas temperature increases from 290 to 330 K. The population of the $K'=4$ level varies nonlinearly with current. The values of $\overline{S_r}$ (see Table II below) make it possible to calculate the corrections for the population change (they are indicated by the arrows in Fig. 1b). When these corrections are introduced we obtain again a linear dependence. The same holds also for other rotational levels ($K'=1$ to 6). The influence of the levels $K_0>1$ on the population of $d^3\pi$ manifests itself thus in the gas temperature region $T>300$ K, which is certainly higher than the temperature in a discharge cooled with liquid nitrogen.

We note that this "classical" verification of the validity of the concept of direct electronic excitation, based on the linearity of the radiation intensity in the discharge current, is not always sufficient. The current dependences of the intensities in the rotational structure of electronic transitions can be linear also when the corresponding levels are populated with participation of particles in metastable states, excited in turn by direct electron impact. These processes, as shown with N_2 ($C^3\pi$) molecules as the example, can lead to an effective excitation of the rotation.[18] A characteristic sympton of the presence of such a mechanism is anomalous broadening of the spectral lines.[19] Investigations of the shapes of the line contours show that in all cases the rotational components of the $d^3\pi-a^3\Sigma$ transitions are subject to normal Doppler broadening with the gas temperature. Thus, Fig. 2 shows by way of example plots of $\ln(I/I_0)$ against $mc_2(\lambda-\lambda_0)/2k\lambda_0^2$ for a number of transitions in H_2 and He (λ_0 and I_0 are the wavelength and intensity at the line center, and λ and I are the same at an arbitrary point of the contour, m is the emitter mass, k is Boltzmann's constant, and c is the speed of light).

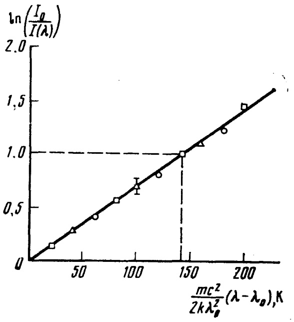

FIG. 2. Normalized Doppler contours of the following lines: △) $Q(5)$ line of (0, 0) band of the hydrogen $d^{3\pi}\to a^3\Sigma$ transition; □) helium $\lambda=5875.62$ Å line; ○) $Q(4)$ line of (0, 0) band of $I^{1\pi}\to B^1\Sigma$ transition of hydrogen.

The ratio of the ortho- and para-hydrogen densities in the $X^1\Sigma$ state, calculated in accord with (5) using the values of $x=g_0/g_1$ and T obtained from the minimum-M condition, amounts to 3.8:1, in agreement with the experimental value of this ratio for the state $d^3\pi(v'=0)$ (see above). This result is quite unexpected, inasmuch as under equilibrium conditions this ratio does not exceed 3 and decreases to 0 as $T\to 0$. A similar reduction of the data on the (2, 2) band leads to an orth-para ratio ~3.2, which also agrees with the experimental data for $d^3\pi$ ($v'=2$), while the values of $\overline{S_r}$ agree, within the limits of the indicated errors, with the values obtained for the (0, 0) band. The deviation of the ratio of the densities of ortho- and para-hydrogen from the equilibrium value and the dependence of this ratio on the vibrational level can be due to several causes. The relatively low rate of the vibrational relaxation in the state $X^1\Sigma$ can cause the excitation of an appreciable number of vibrational levels, and in general the excitation and deactivation of the vibrational levels can proceed differently in the ortho- and para-hydrogen. Owing to the difference between the Franck-Condon factors, this can lead to different band intensities for the ortho- and para- modifications, and under these conditions the minimum of M will correspond to only a certain effective value of the ortho/para concentration ratio in the ground state.

Since the H_2 nuclei are light, one should expect a noticeable vibrational-rotational interaction, and as a consequence, a dependence of the Franck-Condon factors on the rotational numbers. To estimate this dependence, calculations were made of the Franck-Condon factors of the $X^1\Sigma\to d^3\pi$ transitions with allowance for the vibrational-rotational interaction, using the program described in Ref. 20. It turned out that for most transition allowance for the vibrational-rotational interaction, within the accuracy limits indicated above, is unnecessary (for certain transitions with $K'-K_0\geqslant 3$, the change of the cross section can slightly exceed 40%, but the cross sections themselves are small). This dependence was therefore not taken into account in the final calculations. One must also bear in mind the possibility of deviations from the Franck-Condon principle, due to the dependence of the electronic matrix element on the distance between nuclei. The relevant data are not yet available.

According to Ref. 21, a number of levels of the $d^3\pi$ state are subject to perturbations, and the perturbation of the levels with $v'=2$ is stronger than with $v'=0$. This can also affect the results, since (3) is valid, generally speaking, only in the case of unperturbed terms and a pure type of coupling. In principle, the error may be due also to the presence of narrow resonances of the electronic cross sections, if these are present when Fulcher bands are excited, inasmuch as the applicability of Eq. (3) in this case is not clear beforehand. The described results, however, allow us to state that, within the cited accuracy, Eq. (3) and the electronic partial cross sections given above can be used for the case of excitation of the investigated levels.

IV. EXCITATION OF $H_2(I^1\Pi)$

In contrast to the $d^3\pi$ state, which belongs to the pure type-b coupling according to Hund, the $I^1\pi$ state pertains to an intermediate (between b and d) type and much of the information necessary for spectral measurements are lacking for this state. In the $I^1\pi$ state, the excited electron is weakly coupled to the "core," its orbital angular momentum is not quantized along the molecule axis, and a noticeable role is assumed by the interaction between the electron motion and the molecule rotation. The wave function can then be approximately written as

$$\Psi=\Psi_0\Psi_e, \tag{7}$$

where Ψ_0 pertains to the molecular residue and Ψ_e describe the Rydberg electron. In the presence of configuration interaction, the function Ψ_e can depend on K'. In this case the level lifetime also depends on K':

$$\tau^{-1}_{e'v'K'}=\frac{64\pi^4}{3h(2K'+1)}\sum_{e''v''K''}(\nu^{e''v''K''}_{e'v'K'})^3S^{e''K''}_{e'K'}\,q_{v'v''}, \tag{8}$$

where $q_{v'v''}$ is the Franck-Condon factor, $S^{\cdots}_{\cdots}$ is the strength of the electronic transition, $\nu^{\cdots}_{\cdots}$ is the frequency of the transition, and e is the electronic quantum number; the summation is over all the low-lying states. This situation has hardly been investigated in spectroscopy up to now (see, e.g., the reviews 22, 23). Exceptions are the measurements[14,15] made for $H_2(I^1\pi)$, but the results obtained there are fragmentary and contradictory. Nor do we know the relative probabilities of the radiative electron-vibrational-rotational transitions $I^1\pi\rightarrow B^1\Sigma$, which are the most suitable for investigations of the $I^1\pi$ state.

1. Radiative lifetimes

The radiative lifetimes of the rotational levels of H_2 ($I^1\pi$, $v'=0,K'$) were determined by the method of level crossing in a zero magnetic field (Hanle effect). The effect manifests itself in a change of the degree of polarization of the radiation by the particles that are in a coherent superposition of states ($\Delta M=2$), when the degeneracy is lifted in an external magnetic field.[27] An ensemble with a coherent superposition of states is referred to as "aligned." The alignment of atoms in a gas-discharge plasma was observed and interpreted in Ref. 28. The mechanism of alignment in gas-discharge tubes is connected with the anisotropy of the reabsorption of the light by the excited states, owing to the difference between the light fluxes in the radial and axial directions. The disruption of the alignment was observed experimentally in the form of a dependence of the intensity of light with a given polarization on the field H (the alignment signal). An analysis of alignment in cylindrical discharge tubes was carried out in Ref. 27, where the excitation tensor $\mathscr{F}^{\varkappa}_q(\mathrm{e}_0)$ was calculated for the plasma volume element. Here $\varkappa$ is the rank of the tensor, $q=0$ corresponds to longitudinal alignment, $q=\pm2$ to the transverse, and e_0 is the polarization vector of the exciting light. Longitudinal uniaxial alignment is produced along the tube axis, and biaxial alignment on the periphery. An axial magnetic field does not disrupt the longitudinal alignment, but does disrupt the biaxial one. A magnetic field perpendicular to the tube axis disrupts the longitudinal alignment. Since the alignment signal in the last case is maximal, the discharge was placed in our experiments in a transverse field.

If x is the discharge axis and z the observation axis (see Fig. 3) then, using the formulas given in Ref. 29, we can obtain a relation for the difference of the light intensity I of two orthogonal polarizations

$$I_x-I_y=5^{1/2}I_0(-1)^{J_1+J_2}\begin{Bmatrix}1 & 1 & 2\\ J_1 & J_1 & J_2\end{Bmatrix}\frac{\mathscr{F}^2_2(\mathrm{e}_0)\Gamma(2)}{\Gamma(2)^2+4\Omega^2}. \tag{9}$$

Here I_0 is the integral (with respect to the directions and polarizations) intensity of light; J_1 and J_2 are the angular momenta of the initial and final state of the particle in the radiative transition; $\Gamma(\varkappa)$ is the width of the radiating level ($\varkappa=2$); $\Omega=egH/2mc$; g is the Landé factor; m and e are the mass and charge of the electron; c is the speed of light.

In a transverse magnetic field, the alignment signal has a Lorentz contour with a width determined by the alignment relaxation time $\tau=\Gamma^{-1}$ (see Fig. 4):

$$\Delta H_{1/2}=mc/eg\tau(2). \tag{10}$$

The level width is determined by the radiation and by the collisions, $\Gamma=\Gamma_{\mathrm{rad}}+\Gamma_{\mathrm{col}}$, therefore in an experi-

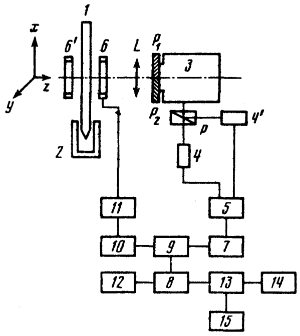

FIG. 3. Diagram of setup for the determination of the radiative lifetimes: 1—discharge tube, 2—dewar, 3—monochromator; $P1$, $P2$—Polaroids, 4, 4'—photomultipliers, 5—differential amplifier, 6, 6') Helmholtz coils, 7) voltage-to-frequency converter, 8) pulse analyzer, 9) control block, 10) generator, 11) current amplifier, 12, 15) printing units, 13) computer, 14) external memory, L) lens; p) optical analyzer.

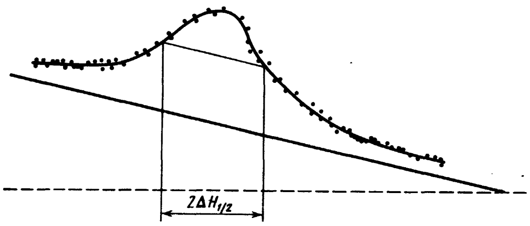

FIG. 4. Typical experimental plot of alignment signal.

mental determination of τ_{rad} the results must be extrapolated to zero pressure.

A diagram of the setup for the measurements of the level lifetimes is shown in Fig. 3. The radiation of the (0, 0) band of the $I^1\pi \rightarrow B^1\Sigma$ transition is observed through the side wall of the discharge tube 1 (diameter 40 mm, length 400 mm, dc discharge $J=80$ mA in hydrogen). Part of the tube is placed in vessel 2 with liquid nitrogen to clear the discharge better. The radiation is focused onto the entrance slit of a DFS-12 monochromator (3). Half the slit is covered by a Polaroid P_1 that transmits x-polarized radiation, and the second half by Polaroid P_2, which transmit the y-polarized radiation. The differently polarized radiation is registered by two FEU-79 photomultipliers (4 and 4′), whose signals are fed to differential amplifier 5. The signal at the output of the amplifier is proportional to $U \sim I_x - I_y$. The magnetic field is directed along the z axis and is produced by Helmholtz coils 6 and 6′. The laboratory magnetic field is compensated for by additional coil. The signal from the amplifier goes to a voltage-to-frequency converter 7 and is recorded by pulse analyzer 8. The control block 9 switches the analyzer memory channels in synchronism with the stepwise increasing voltage from generator 10. The voltage is applied to amplifier 11, which sets the current (and the magnetic field) in coils 6 and 6′, i.e., each analyzer memory channel corresponds to a definite value of the field. The accumulated information is fed to an oscilloscope, to a digital printer 12, or to a computer 13, followed by rewriting in the external memory 14. After rewriting, the data are processed in the computer and fed to the printout unit 15.

The alignment signals registered in the experiment are those for the lines $Q(2)$, $Q(4)$, $Q(6)$, $P(2)$, $P(4)$, $P(6)$, and $P(3)$. For each of the investigated levels, a series (from 6 to 14) of alignment signals is plotted at a set hydrogen pressure. A typical single plot of the alignment signal is shown in Fig. 4. The signal has the form of a Lorentz contour on an inclined "base." The base is due to the motion of the discharge plasma in the magnetic field. The width of the Lorentz contour is determined by the computer by least squares. The true width of the alignment signal is obtained by extrapolating the data to a value corresponding to zero gas pressure. The radiative lifetime is determined from formula (10). The hydrogen pressure in the discharge ranges is varied from 0.6 to 0.08 Torr. The necessary spectroscopic data are given in Refs. 12, 13, and 30.

The measurement results are listed in Table I, which gives for comparison the lifetimes obtained in Ref. 24. The following is noteworthy. Owing to the large value of the Λ splitting in the $I^1\Pi$ state, the usual sequence of the rotational terms is disturbed.[12] The dependence of the lifetimes of the rotational levels of the state H_2 $(I^1\Pi, v'=0, K')$ on the rotational energy is shown in Fig. 5. As seen from the figure, the radiative lifetimes are determined, within the limits of the experimental error, only by the rotational energy. An increase of the lifetime is observed with increasing energy. For levels with close energies (but with different K') the lifetimes are practically equal.

TABLE I. Widths $\Delta H^{1/2}$ of alignment signals and radiative lifetimes τ_{rad} of $H^2(I^2\pi, v'=0)$.

K'	Line	λ, Å	$\Delta H_{1/2}$, Oe	τ_{rad}, nsec	
				present work	[24]
1 (ortho)	$P(2)$	4582.6	3.1±0.5	36±6	9*
2 (ortho)	$Q(2)$	4579.9	4.1±0.7	34±6	33.5
3 (ortho)	$P(4)$	4568.6	2.1±0.2	85±10	–
4 (ortho)	$Q(4)$	4572.7	3.0±1.0	74±28	–
5 (ortho)	$P(6)$	4549.8	~3	~120	–
6 (ortho)	$Q(6)$	4550.9	3.2±1.1	100±30	–
2 (para)	$P(3)$	4575.2	~2.2	~190	~100

*The identification of the transition in Ref. 24 raises doubts.

It should be noted that in fluorescence-quenching meameasurements reported in the already cited Ref. 25 and in a recent paper,[26] no difference was observed between the lifetimes of the rotational levels of H_2 $(I^1\Pi)$. Although no systematic measurements in a wide range of K' were made in Refs. 25 and 26, the question of the difference between the results given by the two methods is worthy of investigation.

2. Relative probabilities of the radiative transitions

For an experimental determination of the relative probabilities of the radiative transitions we used a quartz discharge tube heated by a nichrome coil, and a DVS-25 spectral lamp.

Considering, for the sake of argument, the ortho-modification of H_2 and the stationarity condition in the case of electron-impact excitation and radiative decay of the rotational levels K' in $I^1\Pi$, we can (for a Boltzmann distribution over the rotational levels K_0 in $X^1\Sigma$) write

$$N_{K'}=\text{const}\cdot n_e n_0^{\text{ortho}} \tau_{K'} \sum_{K_0} (2K_0+1)\exp\{-F_0(K_0)hc/kT\}\langle v_e\sigma_{K_0K'}\rangle, \qquad (11)$$

where $F_0(K_0)$ is the value of the rotational term in $X^1\Sigma$; $\langle v_e\sigma_{K_0K'}\rangle$ is the rate constant for the excitation of the K'

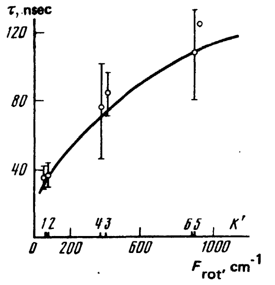

FIG. 5. Radiative lifetime of $H_2(I^{2\pi}, v'=0)$ vs. the number K' of the rotational level and the enrgy F_{rot} of the rotational term.

levels by electron impact from the K_0 levels; n_0^{ortho} is the density of the ortho-hydrogen molecules in the state $X^1\Sigma$; $\tau_{K'}$ is the lifetime of H_2 $(I^1\Pi, v'=0, K')$; n_e is the electron density.

Using the obtained values of $\overline{S}_\gamma$ for the singlet-triplet transition, we can show that under the condition $2B_0K_0 \ll kT$ the value of $\langle v_e\sigma_{K_0K'}\rangle$ decreases with changing K_0 (at fixed K') more rapidly than the Boltzmann factor $\exp\{-F_0(K_0)hc/kT\}$, i.e.,

$$\left|\frac{d}{dK_0}(\langle v_e\sigma_{K_0K'}\rangle)\right| \gg \left|\frac{d}{dK_0}\exp\left\{-\frac{F_0(K_0)hc}{kT}\right\}\right|. \tag{12}$$

If the condition (12) is satisfied also for a singlet-singlet transition, then the following relation holds:

$$N_{K'}=\text{const}\cdot n_e n_0^{\text{ortho}}\tau_{K'}\exp\{-F_0(K')hc/kT\}\sum_{K_0}(2K_0+1)\langle v_e\sigma_{K_0K'}\rangle. \tag{13}$$

It follows from Ref. 4 that under electronic excitation

$$\sum_{K_0}\frac{2K_0+1}{2K'+1}\sigma_{K_0K'}=\text{const}, \tag{14}$$

and the constant does not depend on K'. Combining (13) and (14), we obtain

$$N_{K'}=\text{const}\cdot n_e n_0^{\text{ortho}}\tau_{K'}(2K'+1)\exp\{-F_0(K')hc/kT\}. \tag{15}$$

On the other hand, the intensity of the spectral line $I_{K'K''}$ is

$$I_{K'K''}=N_{K'}A_{K'K''}h\nu_{K'K''}, \tag{16}$$

where $A_{K'K''}$ is the Einstein coefficient of the optical transition $K' \to K''$, and $\nu_{k'k''}$ is the frequency of the transition $k' \to k''$. Combining (15) and (16), we obtain

$$A^*_{K'K''}=\frac{\text{const}\cdot I_{K'K''}}{\tau_{K'}\nu_{K'K''}(2K'+1)\exp\{-F_0(K')hc/kT\}}. \tag{17}$$

Here $A^*_{K'K''}$, naturally, coincide with the Einstein coefficients $A_{K'K''}$ (in relative units) only provided that the relation (15) obtained under the assumption (12) is valid. Thus, in the study of the temperature dependences of $A^*_{K'K''}$ obtained experimentally in accord with (17), one should expect the $A^*_{K'K''}$ to remain constant when the temperature changes, starting with a certain value $\tilde{T}$. It is this which corresponds to the true values of the relative probabilities. Figure 6 shows plots of the relative probabilities of the radiative transitions of the lines $P(2)$, $P(4)$, $P(6)$, $Q(2)$, $Q(4)$, and $Q(6)$ on the gas temperature, obtained using a discharge tube and a DVS-25 lamp. It is seen from the figure that, first, the discharge tube and the lamp yield results that are in good agreement and, second, that $A^*_{K'K''}$ is constant at $T > 950$ K. This behavior of $A^*_{K'K''}$ confirms the validity of the assumptions (12) in this temperature region.[1)] The values of the relative probabilities $A_{P(2)}$, $A_{P(4)}$, $A_{P(6)}$, $A_{Q(2)}$, $A_{Q(4)}$, and $A_{Q(6)}$ for the transition $I^1\pi$ $(v'=0, K') \to B^1\Sigma$ $(v'=0, K'')$ are respectively $A_{P(2)}$ is taken equal to unity:

1; 0.91±0.1; 0.25±0.08; 1.98±0.12; 1.79±0.36; 3.1±1.5.

We note that the method proposed here for determining the relative probabilities of the optical transitions does not call for the presence in the radiation source of the thermal equilibrium that is traditional for such measurements. The development of similar equilibrium sources for the excitation of high-lying electronic states entails great difficulties, since the excitation energy of the radiating states frequently exceeds the molecule dissociation energy. For hydrogen, in particular, the energy of the state $I^1\pi$ $(v'=0)$ is 13.7 eV, and the dissociation energy is 4.25 eV. The described method can therefore be useful in the determination of the relative probabilities of optical transitions from states with high excitation energy.

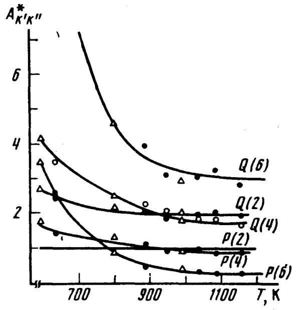

FIG. 6. Temperature dependences of the values of $A^*_{K'K''}$ determined experimentally in accord with Eq. (1): ●, ○) DIV-25 lamp, △) heated discharge tube.

3. Excitation of the levels $I^1\Pi$, $v'=0$, K'' from the levels $X^1\Sigma$, v_0, $K_0=1$ by electron impact

The information obtained on the lifetimes and probabilities of transitions from various H_2 $(I^1\pi,\ v'=0)$ rotational levels makes it possible, in accord with (1), to determine experimentally the relative probabilities $a1K'$ of the electron-vibrational-rotational transitions $K_0=1 \to K'$ from the ground state in ortho-hydrogen, in a discharge cooled with liquid nitrogen. The measurement results are:

K':	1	2	3	4	5	6
$a_{1K'}$:	0.311±0.040	0.320±0.050	0.221±0.044	0.081±0.022	0.051±0.018	0.018±0.011

These data were obtained in the discharge under the same conditions as when $a_{1K'}$ was determined for the singlet-triplet transition. For comparison, the results are shown together in Fig. 7. With increasing ΔK, the value of $a_{1,1+K}$ for the singlets decreases noticeably more slowly than for the triplets, i.e., in direct electron impact the rotation is excited more intensely in the $X^1\Sigma \to I^1\pi$ transition than in the $X^1\Sigma \to d^3\pi$ transition. The excitation of H_2 $(I^1\pi)$ by electron impact from the ground

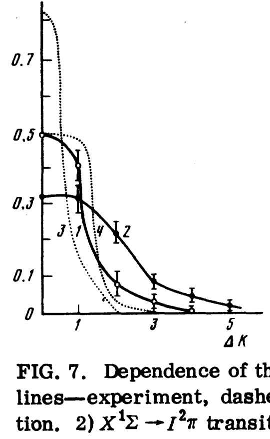

FIG. 7. Dependence of the values of $a_{1,1+\Delta K}$ on ΔK. Solid lines—experiment, dashed—calculation; 1) $X^3\Sigma \to d^3\pi$ transition. 2) $X^1\Sigma \to I^2\pi$ transition. 1, 2) present data, 3) data of Ref. 6, 4) data of Ref. 7. Curves 3 and 4 correspond to the parameter value $\beta = 0.5$.[6,7]

state was monitored by experiments aimed at the study of the dependences of the line intensities on the discharge current and at investigations of the shapes of the spectral-line contours. The same figure shows the theoretical results[6,7] for the $^1\Sigma \to {}^1\pi$ transition. The data of Ref. 6 (curve 3 in Fig. 7) were renormalized to a unity sum. Curve 4 was plotted in accord with the formulas proposed in Ref. 7, using the parameter $\beta = 0.5$ recommended in the same reference, and also corresponds to normalization to unity sum. The difference between theory experiment is larger for the $^1\Sigma \to {}^1\pi$ transition than for the singlet-triplet transition. Although the results obtained in Refs. 6 and 7 differ, it can be stated nevertheless that this theory predicts a less effective rotational excitation than is observable in experiment.

V. CONCLUSION

Table II lists the values of $a_{K0K'}$ obtained using the partial cross sections S_r for the excitation of the $X^1\Sigma \to d^3\pi$ transition in H_2, in relative units and with the normalization $a_{01} = 1$.

For the $1 \to K'$ transition, besides our data (a), the table lists the calculated results of Ref. 7 (b, c), renormalized in accord with the condition $\sigma_{01} = 1$.[3)] In case (b) we used for the parameter β (see Ref. 7) the value 0.5 recommended in that reference. In case (c), $\beta = 0.8$, which agrees better, according to the formulas of Ref. 7, with the ratio σ_{01}/σ_{02} obtained by us. It is seen that for $\Delta K = 0$ or 1 the data of Ref. 7 agree quite well with our results, whereas at larger ΔK a discrepancy appears. It is possible that the zero-radius-potential model used in Ref. 7 is not effective enough for the determination of electronic partial cross sections with large r. We note also that with increasing K the relation $a_{K_0K'} = f(|K_0 - K'|$ used in Ref. 7 begins to be approximately satisfied. This follows directly from formula (2) and from the asymptotic properties of the $3j$-symbols.[15]

It was remarked in Ref. 3 that the experimental data of Ref. 3 for the excitation H_2 $(d^3\pi)$ cannot be described by formula (3). This remark is worthy of a discussion. The task of determining the partial cross sections from experimental data, as in most inverse problems, is mathematically untenable. The simultaneous use, in the present paper, of data on ortho- and para-hydrogen, and the reduction of these data by least squares, have made it possible to obtain sufficiently stable results without the use of any special regularization technique. An important role is played here by the fact that, owing to the gas cooling, the overwhelming majority of the molecules are in the lowest rotational state. An attempt to carry out similar calculations for deuterium, whose rotational constant is half as large and in which higher rotational levels are more strongly populated at the same temperatures, was unsuccessful because of the instability of the results with respect to the experimental errors. At the same time, a calculation of the populations of the deuterium levels $D_2(d^3\pi)$ using the electronic partial cross sections obtained for hydrogen (the direct problem) turned out to be in satsifactory agreement with experiment. An attempt to determine the electronic partial cross sections by directly solving the insufficiently well founded system of equations (3), in which the $\bar{S}_r$ are assumed to be known and the free terms are taken to be the experimental data[3] for orthohydrogen, leads in fact to unstable results, in contrast to the procedure used in the present paper; it is this which can serve as an answer to the remark made in Ref. 5.

TABLE II. Values of $a_{K_0K'}$ for the excitation of the levels $d^3\pi(v' = 0,\ K')$.

K_0	K'					
	1	2	3	4	5	6
0	1	0.161	0,133	0.018	$<10^{-4}$	$<10^{-4}$
1^a	0.548	0,577	0.104	0,072	0.0096	$<10^{-4}$
1^b	0,515	0,508	0.029	0.0005	$<10^{-4}$	$<10^{-4}$
1^c	0.550	0,528	0,090	0.033	0.0005	$<10^{-4}$
2	0.171	0.535	0,454	0,087	0.058	0.008
3	0.044	0.194	0.529	0.406	0,080	0,052
4	0.013	0.047	0,215	0.527	0,381	0,076
5	0,001	0.017	0.050	0.228	0.526	0,365

It is seen from Table II that the selection rules proposed in Ref. 3 and in Refs. 5–7 ($\Delta K = 0, \pm 1$) are approximately satisfied in this case, although with a small margin. In addition, it follows from (3) that the lowest value of r for which S_r differs from zero is $|\Lambda_0 - \Lambda'|$ (we confine ourselves for simplicity to the case of Hund's b coupling). By the same token, even if only $S_{|\Lambda_0 - \Lambda'|}$ differ from zero, the more general selection rule is $\Delta K \leq |\Lambda_0 - \Lambda'|$.

We note once more that the values of $\bar{S}_r$ cited in the present paper for the excitation of H_2 $(d^3\pi)$ have relatively low accuracy (see above). This is due both to the complexity of the investigated object (gas discharge) and to the already mentioned inadequate correspondence between the employed theoretical model and the real molecule. Further experiments are therefore advisable. It would be of interest to perform analogous measurements in monoenergetic beams. According to Ref. 32, calculations of the total cross sections for the excitation of the Fulcher bands agree well with the experimental data. It would be of interest to make an analogous comparison also of the electronic partial cross sections. If the electron-molecule scattering matrix with fixed position of the nuclei were to be known in some approximation or another, the calculation of the electronic partial cross sections would reduce to merely a computational problem (see Ref. 4).

It is difficult at present to carry out a theoretical interpretation of the results on the excitation of the state H_2 $(I^1\pi)$. The primary reason is the complicated scheme of the connection between the angular momenta and the possible interaction of the configurations. We confine ourselves in this paper therefore to a determination of the values of $a_{1K'}$. The important aspect here is the following. A comparison of the regularities of the rotation excitation in the singlet $I^1\pi$ and triplet $d^3\pi$ states leads to the conclusion that each type of transition is characterized by its own set of $a_{K_0K'}$. In contrast to radiative transition, for excitation of molecules by electron impact it is impossible to indicate at present universal selection rules with respect to the rotational quantum number K. Therefore the conclusions drawn in Refs. 5–7 that the optical selection rules are general enough do not seem to be fully justified. This can also be illustrated by the following example. We have investigated the rotational structure of the H_2 spectrum in the bands (0, 0), (1, 0), and (2, 1) of the $G^1\Sigma \rightarrow B^1\Sigma$ transition under the same conditions that obtained when the spectra that start out from the states $d^3\pi$ or $I^1\pi$ were obtained. The relative intensities of the rotational lines of the (0, 0) band of the transition $G^1\Sigma(v'=0) \rightarrow B^1\Sigma(v''=0)$ are the following:

$R(K'')$:	$R(0)$	$R(1)$	$R(2)$	$R(3)$	$R(4)$	$R(5)$	$R(6)$	$R(8)$	$R(10)$
$I^{\text{rel.}}_{K'K''}$:	41±4	33±4	100	14±2	33±2	6±1	7±1	6±1	3±1 .

The other bands give close values of the relative intensities. A special check has shown that the spectrum is excited by direct electron impact. Despite the fact that the lifetimes and probabilities of the radiative transitions for this system were not determined, so highly developed a rotational structure offers definite evidence of highly effective excitation of rotation in a transition $X^1\Sigma \rightarrow G^1\Sigma$ induced by electron impact.

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1) The restrictions on the validity of (15) are due to changes of the angular momentum of the molecule following excitation by electron impact. If this is disregarded and it is assumed that the rotational-quantum-number selection rule in electronic excitation is $\Delta K = 0$, the result is an incorrect conclusion (see, e.g., Ref. 31) that relations of the type (15) are valid without restrictions.

2) In Ref. 6 and 7 is considered case b of Hund coupling.

3) We recall that our data consititute excitation rates (cross sections averaged over the energies of the electrons), wheras in Ref. 7 are calculated the cross sections at a certain electron effective energy close to the threshold.

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[1] G. Herzberg, Molecular Spectra and Molecular Structure. 1. Spectra of Diatomic Molecules, 2 ed., Vau, Nostrand, N. Y. (1951).

[2] E. P. Muntz, Phys. Fluids 5, 80 (1962).

[3] D. K. Otorbaev, V. N. Ochkin, S. Yu. Savinov, N. N. Sobolev, and S. N. Tskhaĭ, Pis'ma Zh. Eksp. Teor. Fiz. 28, 424 (1978) [JETP Lett. 28, 392 (1978)]; FIAN Preprint No 161 (1978).

[4] P. L. Rubin, Zh. Eksp. Teor. Fiz. 65, 1375 (1973) [Sov. Phys. JETP 38, 684 (1973)].

[5] B. P. Lavrov, V. N. Ostrovskiĭ and V. I. Ustimov, Pis'ma Zh. Eksp. Teor. Fiz. 5, 355 (1979) [JETP Lett. 5, 293 (1979)].

[6] B. P. Lavrov, V. N. Ostrovskiĭ and V. I. Ustimov, Zh. Eksp. Teor. Fiz. 76, 1521 (1979) [Sov. Phys. JETP 49, 772 (1979)].

[7] B. P. Lavrov, V. N Ostrovskiĭ and V. I. Ustimov, Opt. Spektrosk. 47, 55 (1979) [Opt. Spectrosc. (USSR) 47, 30 (1979)].

[8] O. W. Richardson, Molecular Hydrogen and Its Spectrum, Yale University Press, 1934.

[9] B. Rosen, Spectroscopic Data Relative to Diatomic Molecules, N. Y. -London, Pergamon Press, 1970.

[10] G. H. Dieke and R. W. Blue, Phys. Rev. 47, 261 (1935).

[11] G. H. Dieke, J. Molec. Spectr. 2, 494 (1958).

[12] G. H. Dieke, The Hydrogen Molecule Wavelength Tables. Wiley-Interscience, N. Y. (1972).

[13] K. P. Huber and G. Herzberge, Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules, Vau. Nostrand, N. Y. (1979).

[14] R. L. Day, R. J. Anderson and F. A. Sharpton, J. Chem. Phys. 69, 5518 (1978).

[15] D. A. Varshalovich, A. N. Moskalev and V. K. Khersonskiĭ, Kvantovaya teoriya uglovogo momenta (Quantum Theory of Angular Momentum), Nauka, Leningrad (1975).

[16] L. G. H. Huxley and R. W. Crompton, The Diffusion and Drift of Electrons. in Gases, Wiley, 1974.

[17] G. J. Prangsma, L. J. Borsboom, H. F. P. Knaap, C. J. N. Van Den Maijdenberg, and J. J. M. Beenakker, Physica 61, 527 (1972).

[18] V. N. Ochkin, S. Yu. Savinov, and N. N. Sobolev, Zh. Eksp. Teor. Fiz. 75, 463 (1978) [Sov. Phys. JETP 48, 232 (1978)].

[19] D. V. Zhuk, D. K. Otorbaev, V. N. Ochkin, S. Yu. Savinov, and N. N. Sobolev, Pis'ma Zh. Eksp. Teor. Fiz. 31, 188 (1980) [JETP Lett. 31, 172 (1980)].

[20] S. G. Gagarin, Zhurnal structurnoĭ khimii, 16, 906 (1975).

[21] G, H. Dieke, Phys. Rev. 48, 610 (1935).

[22] L. A. Kuznetsova, N. E. Kuz'menko, Iu. Ia. Kuzyakov and Yu. A. Plastinin, Usp. Fiz. Nauk 113, 285 (1974) [Sov. Phys. Usp. 17, 405 (1974)].

[23] N. E. Kuz'menko, L. A. Kuznetsova, A. P. Monyakin, Yu. Ya. Kuzyakov and Yu. A. Plastinin, Usp. Fiz. Nauk 127, 351 (1979) [Sov. Phys. Usp. 21, 174 (1979)].

[24] C. W. T. Chein, F. W. Dalby and I. Van Der Linde, Can. J. Phys. 56, 827 (1978).

[25] G. Gomez-Reino and J. Campos, Anales de Fiscia, 72, 219 (1976).

[26] R. L. Day, R. J. Anderson and F. A. Sharpton, J. Chem. Phys. 71, 3683 (1979).

[27] M. P. Cahĭka, Interferentsiya vyrozhdennykh atomnykh sostoyaniĭ (Interference of Degenerate Atomic State), Leningrad Univ. Press 1975.

[28] M. P. Chaĭka and Kh. V. Kallas, Opt. Spektrosk. 27, 694 (1969) [Opt. Spectrosc. (USSR) 27, 376 (1969)].

[29] M. I. D'yakonov and V. I. Perel', Zh. Eksp. Teor. Fiz. 48, 345 (1965) [Sov. Phys. JETP 21, 227 (1965)].

[30] G. H. Dieke, S. P. Cungham and F. T. Burne, Phys. Rev. 92, 81 (1953).

[31] B. P. Lavrov and D. K. Otorbaev, Izmerenie gazovĭ temperatury plazmy nizkogo davleniya po intensivostyam molekularnykh polos H_2 i D_2, (Determination of Low Pressure Gas Temperature from Measurements of the H_2 and D_2 Molecular bands) izd. Ilim, Frunze (1978), str. 28.

[32] G. R. Möhlmann and F. J. De Heer, Chem. Phys. Lett. 43, 240 (1976).

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