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On the Angular Momentum Transfer upon Excitation of Electronic States of Molecules by Electrons of Various Energies

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Abstract—The intensities of lines $I_{Q(1)}$ and $I_{Q(3)}$ of the vibrational transition $v' = 0 \to v'' = 0$ of the Fulcher band system upon excitation of hydrogen molecules by an electron beam are measured. The beam electron energy is $\varepsilon_e = 15...30$ eV ($\Delta\varepsilon_e \sim 1$ eV). The effective cross sections of H_2 ($d^3\Pi_u$, $v = 0$) state excitation by electron impact are estimated both without changing the molecule angular momentum and with an appreciable angular momentum transfer. Processes with an appreciable angular momentum transfer are most efficient in the subthreshold excitation energy range ($E_{\mathrm{thr}} =$ 14 eV $< E_e \leq 18$ eV) and are related to the formation of an intermediate composite system, i.e., a negative ion in the quasi-discrete state.

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Introduction. Excitation of electronic states of molecules by electron impact was studied repeatedly (see, e.g., [1–8]). Interest in these studies is caused mainly by the fact that measurements of intensities of rotational lines of vibronic bands of molecular spectra underlie the spectral methods of plasma and gas flow diagnostics [5]. The most comprehensive information is extracted from experiments with electron beams propagating in gases of molecules under study or with crossed electron–molecular beams. Measurements of emission band intensities in excited spectra depending on the electron energy (optical excitation functions) yield information on the probability of electron–molecular inelastic collisions. In such experiments, molecules are mostly in the ground vibronic state; to determine the excitation cross sections of individual vibrational levels of excited electronic states, a monochromatized electron beam energy of ∼0.1–0.3 eV is sufficient, which corresponds to the possibility of detecting appearing luminosity [9]. At the same time, the characteristic scale of the rotational structure of not too light molecules is $\sim 10^{-3}$ eV; therefore, as a rule, a significant number of rotational levels are populated in the ground vibronic state. This circumstance complicates the determination of the cross sections of individual rotational transitions. In this situation, the point of view dominated for a long time that the light electron does not transfer any appreciable angular momentum to a molecule upon excitation of vibronic states.

Let us to characterize the molecular state by the total angular momentum (without spin) $\mathbf{K}$ (with quantum number K), i.e., by the sum of the orbital momentum of bound electrons and the angular momentum of nuclei. Then the selection rule $\Delta K = K' - K^0 = 0$ (primed quantities correspond to the excited state, the subscript "0" corresponds to the electronic ground state) should be satisfied upon electron-impact excitation. From this it follows that when the rotational distribution in the electronic ground state is Boltzmannian, the relation

$$T_R^0 B_v' = T_R' B_v^0, \tag{1}$$

is satisfied between the rotational temperatures T_R^0 and T_R' of the ground and excited states, where B_v' and B_v^0 are the corresponding rotational constants. This statement was in particular among the conclusions in the known monograph [6]. Relation (1) is used to determine the neutral plasma component

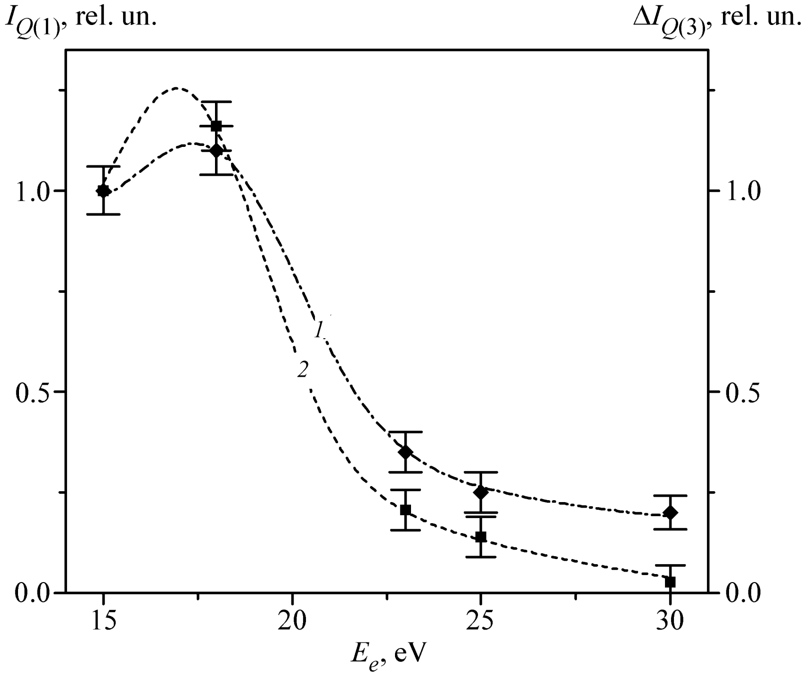

Fig. 1. Dependences of (1) the $I_{Q(1)}$ line intensity and (2) $\Delta I_{Q(3)}(\Delta K = 2)$ on the electron energy (in relative units).

temperature by relative intensities of rotational lines of electron-vibronic bands of molecule emission spectra. However, an analysis of the results of further experiments on excitation of electronic states of molecules showed that the actual situation is more complex. Experiments of [10] showed that significant angular momenta can be transferred under conditions of gas-discharge plasma upon electron-impact excitation of electronic states of molecules. An analysis of the experimental data on population rates of electronic—vibrational—rotational levels of the hydrogen molecule by electron impact, performed in [11], made it possible to identify the physical mechanism of the angular momentum transfer to molecules upon their excitation in low-temperature plasma and to develop a model for calculating relative excitation probabilities of rotational levels. This model is based on the assumption that the dominant process of electronic state excitation in plasma should occur via the formation of an intermediate composite system, i.e., a negative ion in the quasi-discrete state; in this case, the electron temperature was assumed to be specified. In the present paper, we study the effect of the electron energy on the angular momentum transfer efficiency.

Experimental. We performed experiments on electron-beam excitation of H_2. The measurement technique is described in [12]. The hydrogen pressure in the beam—gas interaction chamber was $(5-9)\cdot 10^{-3}$ Torr, the beam current was $(4-5)\cdot 10^{-6}$ A. Under conditions of low currents and low molecule densities, the gas temperature in the chamber was $T \approx 300$ K. The $I_{Q(1)}$ and $I_{Q(3)}$ line intensities of the vibrational transition $v' = 0 \to v'' = 0$ of the Fulcher band system $d^3\Pi - a^3\Sigma$ were measured. The study was performed at $\varepsilon_e = 15...30$ eV; the energy spread in used electron beam was $\Delta\varepsilon_e \sim 1$ eV. The energy is limited from below by the threshold of the reaction

$$H_2(X^1\Sigma_g^+) + e \to H_2(d^3\Pi_u) + e', \tag{2}$$

which is $E_{\text{thr}} = 13.97$ eV. The upper limit (30 eV) excludes the possibility of hydrogen excitation by secondary electrons formed during ionization

$$H_2(X^1\Sigma_g^+) + e \to H_2^+(X^2\Sigma) + e' + e''. \tag{3}$$

The reaction (3) threshold is $E_i = 15.43$ eV. If primary electrons e have energies $\varepsilon_e > E_i + E_{\text{thr}}$, electrons e' or (and) e'' can contribute to process (2).

Results and discussion. Figure 1 shows the dependence of the $I_{Q(1)}$ line intensity on the exciting electron energy in relative units (dependence 1). The experimental data are normalized by the condition that $I_{Q(1)}$ be equal to unity at $E_e = 15$ eV. We can see that the line intensity initially increases with E_e; then, a significant decrease near $E_e \approx 23$ eV is observed; at 23 eV$< E_e \leq$30 eV, the line intensity rather slowly decreases. Thus, as the electron energy increases from $E_e = 18$ eV to $E_e = 23$ eV, the $I_{Q(1)}$ intensity more than threefold decreased; as the electron energy increased from $E_e = 23$ eV to $E_e = 30$ eV, $I_{Q(1)}$ decreased by a factor of 1.75.

The homonuclear molecule Hamiltonian invariance with respect to permutation of nuclei causes different degeneracy multiplicities of rotational levels. According to the symmetry of the coordinate part of the total wave function (symmetric (s) and antisymmetric (a)) with respect to permutation of nuclei with half-integer nuclear spin I, nuclear statistical weights of the molecule relate as

$$\frac{g_s}{g_a} = \frac{i}{i+1}. \tag{4}$$

For hydrogen, $i = 1/2$ and $g_s/g_a = 1/3$. The total nuclear spin I of the molecule can take the values $I = 0$ and 1 (para- and orthohydrogen, respectively). These values corresponds to symmetric (K is even) and antisymmetric (K is odd) rotational levels, respectively [13]. Due to extremely weak interaction of nuclear spins with electrons, the probability of changing the total nuclear spin of the molecule upon electron-impact excitation is very low, i.e., ortho- and paramodifications do not transform to each other under molecule excitation, and they can be considered as two different gases. Table 1 lists the relative populations N_K^0 of rotational levels K^0 of the H_2 electronic ground state $\mathrm{H}_2(X^1\Sigma_g^+, v = 0)$ at $T = 300$ K. For orthohydrogen, the experimental data are normalized by the condition that the sum of rotational level populations is unity; in this case, the corresponding sum for parahydrogen appears three times lower. For convenience of comparison, the divisor of 3 is placed outside parentheses. We can see that only two rotational levels ($K^0 = 1, 3$) are populated in the H_2 electronic ground state $\mathrm{H}_2(X^1\Sigma_g^+, v = 0)$ of orthohydrogen under the conditions under study; the levels $K^0 = 1$ and $K^0 = 3$ are populated by 90% and 10% of molecules, respectively.

Table 1. Relative populations N_K^0 of rotational levels K^0 of the H_2 electronic ground state $\mathrm{H}_2(X^1\Sigma_g^+, v = 0)$ at $T = 300$ K

K^0	N_K^0
0, parahydrogen	(0.5397):3
1, orthohydrogen	0.8946
2, parahydrogen	(0.4479):3
3, orthohydrogen	0.1046
4, parahydrogen	(0.0124):3
5, orthohydrogen	$8 \cdot 10^{-4}$

Since the level population of the ground state $X^1\Sigma_g^+, v = 0$ with $K^0 = 1$ is almost ten times higher than the population of $X^1\Sigma_g^+, v = 0$ with $K^0 = 3$, it can be considered that the $d^3\Pi_u, v = 0$, $K' = 1$ level is populated due to orthohydrogen molecule excitation by direct electron impact without changing the molecule angular momentum, i.e., during the transition $K^0 = 1 \to K' = 1 (\Delta K = K' - K^0 = 0)$. Hence, the dependence for the $Q(1)$ line, shown in Fig. 1, represents the effective cross section for electron-impact excitation of the $d^3\Pi_u, v = 0$ state without changing the molecule angular momentum.

The $d^3\Pi_u, v = 0$, $K = 3$ level is populated during the transitions $K^0 = 3 \to K' = 3 (\Delta K = K' - K^0 = 0)$ as well as the transitions $K^0 = 1 \to K' = 3 (\Delta K = K' - K^0 = 2)$. In [11], it was found that transitions with $\Delta K > 1$ can occur only via the stage of the formation of short-lived negatively charged molecular ions in quasi-discrete states. The contribution ΔI of processes with $\Delta K > 1$ to the intensity $I_{Q(3)}$ is easily calculated by the formula

$$\Delta I_{Q(3)}(\Delta K = 2) = I_{Q(3)} - I_{Q(1)} \frac{N(K' = 3)}{N(K^0 = 1)}. \tag{5}$$

The quantity $\Delta I_{Q(3)}(\Delta K = 2)$ can be used as a characteristic of the efficiency of processes going through the formation of short-lived negative molecular ions. Figure 1 shows the dependence $\Delta I_{Q(3)}(\Delta K = 2)$ (dependence 2) on the electron energy in relative units. The dependence is normalized by the condition $\Delta I_{Q(3)}(\Delta K = 2) = 1$ at $E_e = 15$ eV. This dependence characterizes the effective cross section for excitation of the $d^3\Pi_u, v = 0$ electronic state of hydrogen molecules with an appreciable angular momentum transfer. It can be seen from Fig. 1 that the efficiency of such processes is very high at $E_e \leq 18$ eV; as the electron energy increases from $E_e = 18$ eV to $E_e = 23$ eV, a sharp drop is observed, $\Delta I_{Q(3)}(\Delta K = 2)$ decreases almost six times; at $E_e > 30$ eV, the excitation processes through the formation of short-lived negatively charged molecular ions almost do not occur. The $X^1\Sigma_g^+, v = 0$ level with $K^0 = 1$ can be populated both with the formation of short-lived negatively charged molecular ions and due to ordinary processes of electron-impact excitation. A comparison of dependences 1 and 2 in Fig. 1 shows that the $X^1\Sigma_g^+, v = 0$ electronic state excitation by electrons with energies $E_e \leq 18$ eV occur through the formation of an intermediate system, i.e., a negative ion in the quasi-discrete state. At 18 eV $< E_e \leq 23$ eV, the contributions of the processes with the formation of short-lived negatively charged molecular ions and due to ordinary electron-impact excitation are approximately identical; at $E_e > 25$ eV, the latter processes become dominant.

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