

# Transfer of appreciable angular momenta in electron excitation of molecules

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It was experimentally established with the  $H_2$  and  $D_2$  molecules as an example that when electron-vibrational-rotational states are excited by direct impact the angular momenta of the molecules can change by as much as (5–6) $\hbar$ .

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This communication is devoted to an elucidation of the correctness of the universally accepted premise that excitation of electron-vibrational rotational states in a low-temperature plasma by electron impact proceeds without change of the angular momentum of the molecule.<sup>1</sup> This question can be verified directly by experiment using as an example hydrogen in a gas-discharge plasma in a discharge tube cooled with liquid nitrogen. Under these conditions only rotational level of the ground state  $X^1\Sigma_g^+$  is populated in the hydrogen in practice. This makes it possible, by measuring the relative populations of the rotational levels of the excited electron states, to investigate quantitatively the possibility of transferring an angular momentum to the molecule when the latter is excited.

The molecule distribution over the rotational levels in the electron-excited state  $d^3\pi_u$  of hydrogen and deuterium was investigated by the method of relative intensities in the rotational structure of the electron-vibrational bands of the  $\alpha$  system of Foulcher ( $d^3\pi_u \rightarrow d^3\Sigma_g^+$ ). The setup and the measurement procedure are described in Refs. 2–4. The gas pressure in the discharge did not exceed several tenths of a Torr, to prevent collision-induced distortion of the rotational distribution of the electron-excited molecules produced upon excitation from the ground state by electron impact<sup>3</sup>

(the radiative lifetime of the  $d^3\pi_u$  state is less than the time between the gas-kinetic collisions).

Figure 1 shows plots of  $\ln[cN_{K'}/g_{K'}]$  ( $c = \text{const}$ ,  $N_{K'}$  and  $g_{K'}$  are the population and the statistical weight of the rotational level  $K'$ ), obtained by the method of relative intensities, against the energy of the rotational levels of the state  $\text{H}_2(d^3\pi_u, v' = 0)$ . It is seen from Fig. 1 that for both ortho- and parahydrogen the plots are not linear. When the rotational temperature  $T'_{\text{rot}}$  is determined from the relative populations of the different level pairs, the results differ substantially. Thus, for orthohydrogen the first pair of levels yields  $T'_{\text{rot}} = 200$  K, while the pair of levels with  $K' = 5$  and  $K' = 6$  yields 680 K. We note that at a gas temperature  $T_g = 160$  K in the ground state orthohydrogen has, accurate to 1%, one populated rotational level, as against two for parahydrogen. In the emission spectrum, on the other hand, we see a rather fully

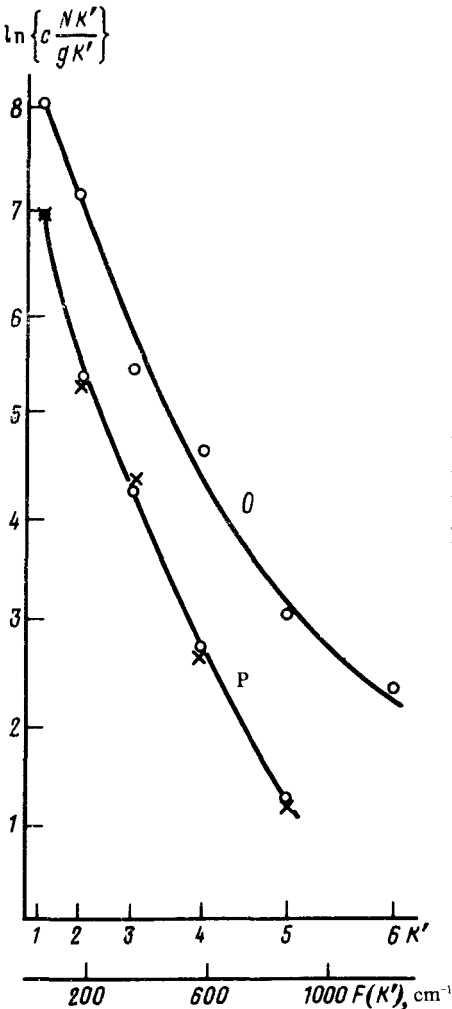


FIG. 1. Plot of  $\ln[cN_{K'}/g_{K'}]$  against the energy of the rotational terms  $F(k')$  for  $\text{H}_2(d^3\pi_u, v' = 0)$ . Discharge in an  $\text{H}_2$ -He mixture (1:3) at a pressure  $P = 0.5$  Torr and a current  $J = 30$  mA, and  $T_g = 160$  K. O—ortho-hydrogen, P—parahydrogen; ●—experimental values, ×—values calculated using  $a_{K'K''}$ .

developed rotational structure, with rotational lines having  $K'$  up to 6. This shows that the excitation is accompanied by appreciable changes in the angular momentum of the molecule.

Using the condition of stationary population of the levels and the result of Ref. 5,<sup>1)</sup> we readily obtain equations for relative excitation rates  $a_{K^0 K'}$  of the rotational level  $K'$  in the transition  $K^0 \rightarrow K'$  under the influence of electron impact.

$$f'(K') = \sum_{K^0} a_{K^0 K'} f^0(K^0), \quad (1)$$

where  $f(K)$  is the distribution function of the molecules over the rotational levels,  $K$  is the rotational quantum number,  $a_{K^0 K'} = \langle v_e \sigma_e^{K^0 K'} \rangle (\sum_{K'} \langle v_e \sigma_e^{K^0 K'} \rangle)^{-1}$ , and  $v_e$  is the electron velocity. The quantities labeled "0" pertain to the state  $X^1\Sigma_g^+$ , and the primed ones to  $d^3\Pi_u$ . It is obvious that  $\sum_{K'} a_{K^0 K'} = 1$ .

Under the investigated conditions, the orthohydrogen has only one populated rotational level,  $K^0 = 1$ , so that Eq. (1) takes the simple form  $f(K') = a_{1K'}$ . By measur-

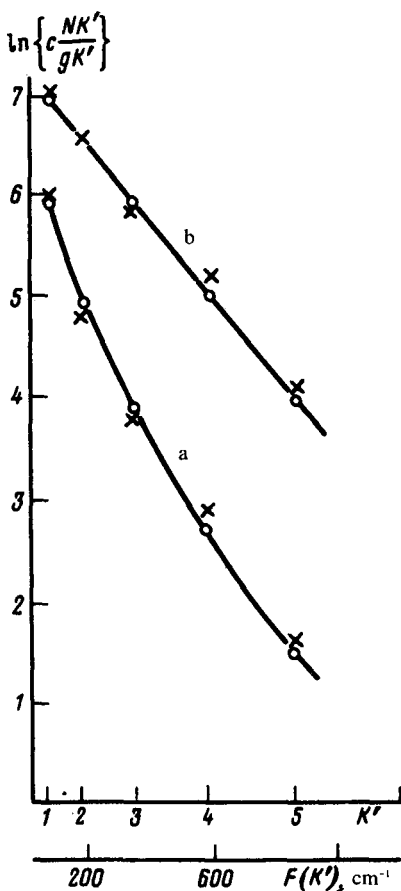


FIG. 2. Plot of  $\ln\{cNK'/gK'\}$  against  $f(K')$  for orthohydrogen  $H_2(d^3\Pi_u, v' = 0)$ . Discharge in  $H_2$  at  $P = 0.5$  Torr and  $J = 30$  mA. a)  $T_g = 300$  K, b)  $T_g = 800$  K,  $T_2 = 410$  K.

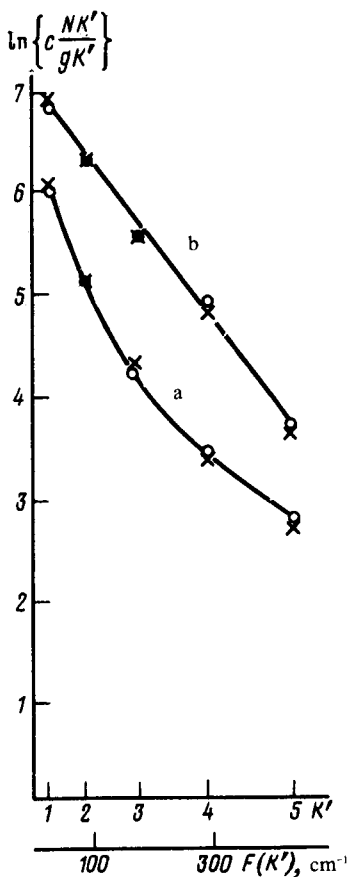


FIG. 3. Plot of  $\ln\{cN_{K'}/g_{K'}\}$  against  $F(k')$  for  $D_2(d^3\pi_u, v' = 0)$ . Discharge in  $D_2$ -He mixture (1:3) at  $P = 0.5$  Torr and  $J = 30$  mA: a)  $T_g = 170$  K, b)  $T_g = 340$  K;  $T'_{rot} = 190$  K. ●-experimental values, ×-values calculated using the  $a_{K^0K^0}$  obtained from the  $H_2$  spectrum.

ing the relative intensities  $I_{K^0K^0}$  of the rotational lines and using the analytic expression<sup>6</sup> for  $I_{K^0K^0}$ , we can determine all the  $a_{1K^0}$ , namely

$$a_{1K^0} = \text{const } I_{K^0K^0} \frac{2K^0 + 1}{S_{K^0K^0}}, \quad (2)$$

where the constant was determined from the normalization condition and the Henle-London factors  $S_{K^0K^0}$  were taken from Refs. 6 and 7.

The values of  $a_{1K^0}$  obtained by us were averaged over the bands (0,0), (2,2), and (3,3) and amount to  $0.528 \pm 0.050$ ,  $0.350 \pm 0.035$ ;  $0.69 \pm 0.014$ ,  $0.042 \pm 0.011$ , and  $0.011 \pm 0.004$  for  $K^0 = 1, 2, 3, 4$ , and 5.

To calculate  $a_{K^0K^0}$  at  $K^0 \neq 1$  from the measured values of  $a_{1K^0}$ , we have assumed that  $a_{K^0K^0}$  are symmetric (relative to  $\Delta K = K^0 - K^0$ ), i.e.,  $a_{K^0K^0 + \Delta K} = a_{K^0K^0 - \Delta K}$ , and are similar, i.e.,

$$\frac{a_{11 + \Delta K_1}}{a_{11 + \Delta K_2}} = \frac{a_{K^0K^0 + \Delta K_1}}{a_{K^0K^0 + \Delta K_2}}$$

A comparison of the calculation results with experiment in the temperature interval (160–800) K has shown that the agreement is satisfactory. Some results are shown in Fig. 2. It is seen from this figure that with increasing  $T_g$  the distribution of the  $H_2(d^3\pi_u)$  molecules acquires a Boltzmann form. In particular, at  $T_g = 800$  K (Fig. 2b) we have an almost-Boltzmann distribution, and  $T'_{rot}$  and  $T_g$  are connected by the known relation<sup>1</sup> (the deviation is less than 3%)

$$T_g = \frac{B^0}{B^*} T'_{rot} \quad (3)$$

It turned out, in addition, that the values of  $a_{K^0K^*}$  obtained from the emission spectrum of  $H_2$  are quite suitable also for the calculation of the rotational levels of  $D_2$  (see Fig. 3).

We now summarize the results of the investigations:

1. The excitation can be accompanied by an appreciable change in the angular momentum of the molecule (up to (5–6) $\hbar$ ).
2. The rotational distribution remains of the Boltzmann type and relation (3) is satisfied when the molecules are excited from the ground state only if  $kT_g \gg B^0 hC$ .
3. Experiments with  $D_2$  show that the value of  $B$  does not affect the relative excitation rates  $a_{K^0K^*}$ .

<sup>1</sup>It follows from Ref. 5 that  $\sum_K \sigma_e^{K^0K^*} = \text{const}$ , where  $\sigma_e^{K^0K^*}$  is the cross section for the excitation of the level  $K^*$  by electron impact in the transition  $K^0 \rightarrow K^*$ .

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