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ROTATIONAL EXCITATION OF H_2 BY SLOW ELECTRONS IN A BEAM EXPERIMENT

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Rotational excitation and de-excitation $J_f - J_i = \pm 2$, $J_i = 0, \cdots, 3$, of H_2 by slow electrons with and without the simultaneous excitation of one vibrational quantum has been measured. The absolute total cross section for pure rotational excitation $J = 3 \leftarrow 1$ in the energy range 1-10 eV is presented. The measurements of angular dependences indicate s-, p-, and d-wave scattering.

Pure rotational excitation of H_2 molecules by slow electrons has been investigated theoretically[1] using various approximations and electron-molecule interactions. The derived cross sections depend strongly on the approach and range,[1] for example, at about 2-eV collision energy they lie between 7×10^{-18} cm^2 and 2×10^{-16} cm^2 for $\sigma(J' = 2 \leftarrow J = 0)$. On the other hand, it seems difficult to extract quantitative cross-section data from electron swarm experiments,[2,3] since rotational excitations are masked by other energy-loss processes. In the present paper we report the results of a beam experiment in which for the first time we are allowed to observe separate rotational transitions due to single collisions of slow electrons (1-10 eV) with H_2. The energy and angular dependence were measured for rotational excitation with and without the excitation of one vibrational quantum.

In an 127° electrostatic energy selector an electron beam is produced with an energy inhomogenity of 20 meV and a beam current of 10^{-9} A. This beam crosses the molecular beam at right angles (10^{-3} Torr). The scattered electrons enter a second 127° electrostatic energy analyzer, which can be rotated in the angular range from 0° (forward scattering) to 120°. Single pulses are counted, integrated by a ratemeter, or stored in a 400-channel analyzer. The overall energy resolution of the apparatus for energy-loss spectra is 30 meV. Detailed descriptions of the electron spectrometer have been given in earlier papers.[4,5]

The occupation of the rotational state J is given by

$$N(J) \propto (2I+1)(2J+1)e^{[-BJ(J+1)]/kT},$$

where I is the nuclear spin $I = 0$ for $J = 0, 2, \cdots$, and $I = 1$ for $J = 1, 3, \cdots$. Since the gas beam is at room temperature, the population of the rotational states is as follows: $J = 0$, 13.6 %; $J = 1$, 67.1 %; $J = 2$, 11.3 %; and $J = 3$, 7.7 %; the contribution of higher states is lower than 0.3 %. These numbers are of importance for the discussion of Fig. 1, which shows the energy-loss spectrum for collision energy $E_p = 4.42$ eV and scattering angle 20°. The large elastic peak (energy loss zero) contains all contributions from $J' \leftarrow J$ with $J' = J = 0, 1, 2, 3$. The instrumental peak shape, especially in the wings, has been measured separately using argon (dotted lines). At the right side of the elastic peak are the visible contributions from superelastic collisions ($J = 0 \leftarrow 2$ and $1 \leftarrow 3$); at the left side, from inelastic collisions

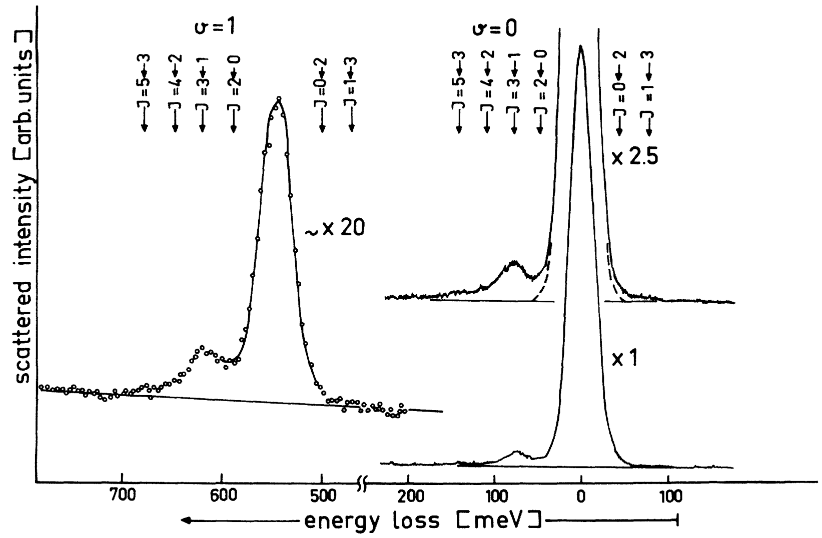

FIG. 1. Energy-loss spectrum of 4.42-eV electrons from H_2 molecules at a scattering angle of 20°. Pure rotational $\Delta J = 2$ excitations and de-excitations appear to the left and right, respectively, of the elastic peak. The instrumental curve shape of this peak has been measured using argon (dotted line). Around 545-meV energy loss, rotational transitions occur accompanied by the transition of one vibrational quantum. The expected positions of energy losses for the different processes are indicated by arrows. The curves $\Delta v = 0$ are recorder traces using the ratemeter; for $\Delta v = 1$ the pulses have been stored in a multichannel analyzer for about 3 h.

($J = 2 \leftarrow 0, \cdots, 5 \leftarrow 3$). Their expected positions are indicated by arrows. Since, within experimental error,[6] the relative intensities for the inelastic processes are the same as the rotational population distribution of the initial states, we conclude that the cross sections $\sigma(J' = 3 \leftarrow J = 1)$, $\sigma(J' = 4 \leftarrow J = 2)$, and $\sigma(J' = 5 \leftarrow J = 3)$ are nearly equal. The processes $\sigma(2 \leftarrow 0)$ and $\sigma(0 \leftarrow 2)$ are not discussed because of the tail of the elastic peak. Since the intensity for $1 \leftarrow 3$ is about half the intensity for $5 \leftarrow 3$, although the initial state is the same, the cross section for the superelastic collision seems to be about half of the inelastic collision. Similar conclusions can be made at all other angles and collision energies measured.

The same discussion holds for rotational transitions accompanied by the transition of one vibrational quantum, the energy-loss spectrum of which is shown (with slightly different energy scale) on the left side of Fig. 1.

Figure 2 shows the energy dependence of the absolute total cross section for the rotational excitation $J' = 3 \leftarrow J = 1$ of the H_2 molecule in its electronic and vibrational ground states. These results have been derived from the following data: (i) measurements of the ratio of the intensity at 75-meV energy loss (contributions from the unresolved neighbor peaks $2 \leftarrow 0$ and $4 \leftarrow 2$ are <2 %) and the elastically scattered intensity; (ii) measurements of the angular distributions of the elastic and inelastic scattering, integrated over the angular range from 0° to 120° and extrapolated to 180° (which introduces an error in the integral of about 10 %); (iii) the normalization to the absolute total cross section (sum of elastic and inelastic processes) measured by Golden, Bandel, and Salerno.[7] Our total cross section curve (EL) is compared with the theoretical results of Lane and Geltman[1] (LG). The agreement, particularly in the shape of the curves, is very

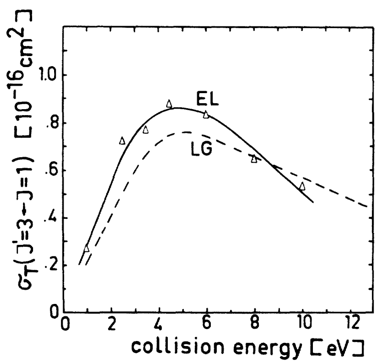

FIG. 2. Measured energy dependence of the total cross section for the rotational transition $J' = 3 \leftarrow J = 1$, $\Delta v = 0$ of the present paper (EL) compared with the theoretically predicted cross section of LG (Ref. 1). The experimental points have an accuracy of about 10 %.

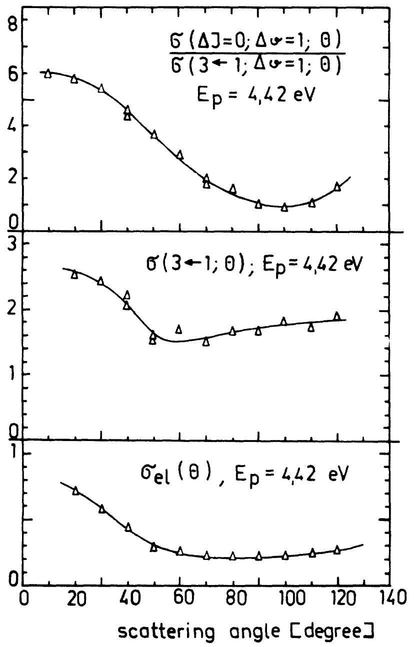

FIG. 3. Differential cross sections (arbitrary units) of 4.42-eV electrons for elastic scattering (lower curve) and for the rotational excitation $J'=3\leftarrow J=1$, $\Delta v=0$ (middle). These curves contain information about the partial waves which contribute to the relevant cross sections. The upper curve represents the angular dependence of the ratio of the cross sections for pure vibrational excitation, $v=1\leftarrow 0$, $\Delta J=0$, and for the simultaneous excitation $J'=3\leftarrow J=1$ and $v=1\leftarrow 0$.

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Figure 3 shows as an example the differential cross sections for elastic collisions (lower curve) and for the excitation $J=3\leftarrow 1$, $\Delta v=0$ (middle curve) at a collision energy of 4.42 eV. The curves contain information about the different partial-wave contributions for the two processes. Without recourse to a detailed analysis, the differential cross section $\sigma(3\leftarrow 1;\theta)$ seems to contain large s-, p-, and d-wave contributions. The curve shape does not change very much with energy between 2.5 and 10 eV, although it appears to be flatter at lower energies; at 1 eV $\sigma(3\leftarrow 1;\ \theta)$ is nearly constant. These results are qualitatively in agreement with theoretical predictions.[1,8,9]

The upper curve of Fig. 3 shows some exciting and unexpected results. First, the simultaneous excitation of two rotational quanta and one vibrational quantum ($\Delta v=1$) is rather large compared with the pure vibrational excitation of H_2; second, the angular dependence for the two processes is very different. For example, at 90° scattering angle the two intensities are about equal, whereas in the forward direction the intensity of the pure vibrational excitation is about six times larger than for the transition $\Delta J=2$ and $\Delta v=1$.

The angular dependence of the scattered electrons for pure vibrational excitation shows pronounced p-wave character corresponding to the $H_2^-({}^2\Sigma_u^+)$ resonance state, as has been shown in earlier measurements,[10] whereas the angular dependence for the process $\Delta J=2$, $\Delta v=1$ is relatively flat. A detailed one-value analysis of the resonance scattering, which is responsible for the vibrational excitation, must take into account the different angular dependences for the two processes $\Delta J=0$ and $\Delta J=2$. Measurements with this aim are in progress.

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[6] At the present state of the work only the transition $J'=3\leftarrow 1$ could be measured with an accuracy of about 5%; for the other transitions the error is larger.

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