Scattering of electrons from H_2 near rotational thresholds

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A previous theory for rotational excitation of molecules is modified to include the effect of the anisotropic polarization potential in addition to the quadrupole potential. This refinement results in better agreement with some new experimental data.

In a previous article,[1] it was shown that rotational excitation of molecules near threshold by electron scattering was accurately described in the Born approximation.[2] The theoretical cross section σ_{20} was found to be in excellent agreement with experiment.[3] However, a new experimental cross section,[4] σ_{31}, is found to differ from the previous theory by as much as five standard deviations. It is the purpose of this note to show that the simple theory can be refined, resulting in closer agreement with the new experiment without diminishing agreement with the old experiment.

According to theory,[1,2] the rotational cross section (in atomic units) is simply

$$\sigma_{j'j} = \tfrac{16}{45} K Q^2 (j0, 20|j'0)^2 \pi a_0^2, \tag{1}$$

where K is the ratio of the final-state wave vector k_f to the initial wave vector k_i, Q is the quadrupole moment which is 0.49 ea_0^2 for H_2,[5] and $(\ldots/\ldots)$ is a Clebsch-Gordan coefficient involving the initial and final rotational states, j and j', respectively. Conservation of energy requires K to be related to the incident energy $\frac{1}{2}k_i^2$ (in atomic units) by

$$K = k_i^{-1}(k_i^2 - 2E_{j'j})^{1/2}, \tag{2}$$

where $E_{j'j}$ is the rotational excitation energy, and is 0.439 eV for (2←0) and 0.0727 eV for (3←1). For these two transitions, the squared Clebsch-Gordan coefficients have the values 1 and 0.6, respectively. Equation (1) suggests that the scaled excitation cross sections defined by

$$\bar{\sigma} = (j0, 20|j+2, 0)^{-2}\sigma_{j+2,j} = 0.85K(\pi a_0^2) \tag{3}$$

should all fall on the same line shown in Fig. 1. As shown previously,[1] the experimental $\bar{\sigma}$ for (2←0) agrees well with Eq. (3). However, $\bar{\sigma}$ based on the new experimental results[4] for (3←1) lies about 25% higher, well outside of the quoted experimental error of ±5%.

The above theory is based on the fact that at threshold energies, the long wavelength of the electron explores only long-range potentials. Since rotational excitation can only be affected by anisotropic potentials, the longest-range one, the quadrupole potential, was accounted for in the theory. However, the potential with the next longest range, the anisotropic polarization potential, may have a significant effect since the rotational cross section depends on the coherent sum of these potentials.[6] Fortunately, this contribution from the anisotropic polarization potential, $(-\alpha_2/2)r^{-4}P_2$, has already been derived by Dalgarno and Moffet.[7] The scaled cross sections including this effect are

$$\sigma' = \bar{\sigma}\left[1 + 2\left(\frac{\pi\alpha_2 k_i}{32Q}\right)(3+K^2) + \left(\frac{\pi\alpha_2 k_i}{32Q}\right)^2 (1+K^2)\right], \tag{4}$$

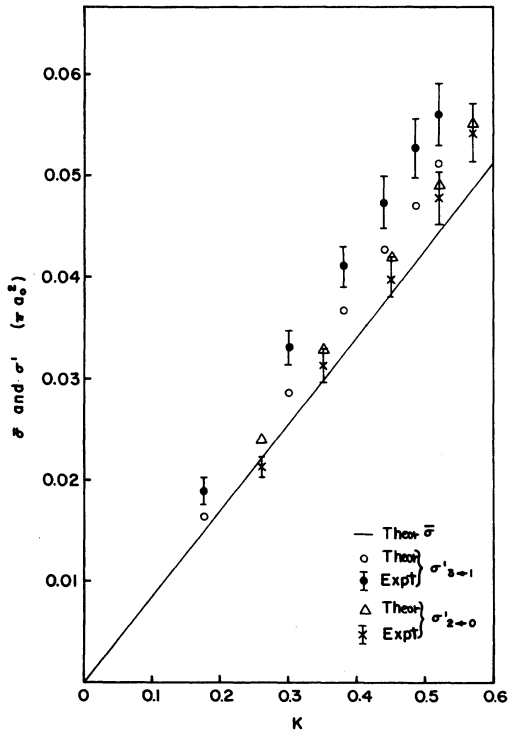

FIG. 1. Scaled rotational cross sections for the (2←0) and the (3←1) transitions. Experimental error bar of ±5% is shown.

where α_2 is the anisotropic polarizability equal to 1.4 a_0^3 for H_2. For $K \lesssim 0.5$, a typical value of $(\pi \alpha_2 k_i/32Q)$ is 0.02, therefore the third term in Eq. (4) is completely negligible. However, the second term increases $\bar{\sigma}$ by about 12% and so it is not negligible even for threshold energies. This contribution represents interference between the dominant quadrupole and the weaker anisotropic polarization potentials, and is due to incoming d waves and outgoing s waves in keeping with earlier results.[1] The scaled cross sections for the excitations $(2 \leftarrow 0)$ and $(3 \leftarrow 1)$ according to Eq. (4) are both shown in Fig. 1. They are virtually identical and lie between the two experimental results. Thus for the $(2 \leftarrow 0)$ transition, agreement between earlier theory $(\bar{\sigma})$ and experiment appears somewhat fortuitous, but the modified theory (σ') is still basically in agreement within the indicated experimental error of ±5%. For the $(3 \leftarrow 1)$ transition, the discrepancy between earlier theory and experiment has been reduced by a factor of about 2 in the modified theory. However, as shown in Fig. 1, the modified theoretical cross section still lies two standard deviations below experiment.

Comparison of the theoretical results here with those obtained from a close-coupling calculation[8] reveals no essential differences. This is not surprising since similar long-range anisotropic potentials are used, and as elucidated previously[1] excitation threshold cross sections should be indifferent to the use of the Born approximation, the presence of any isotropic potentials, or modifications of the anisotropic potentials at short range. Therefore the inclusion of questionable isotropic potentials in the close-coupling calculation could not have adversely affected σ_{31} as conjectured elsewhere.[4] These considerations lead us to believe that the theoretical results σ' presented in Fig. 1 should be accurate to a few percent. Moreover, the accuracy should improve towards threshold (as $K \rightarrow 0$), while the experimental results can be expected to be less accurate owing to smallness of the cross sections. It is precisely here that the discrepancy between theory and experiment is the largest. Therefore it is concluded that the experimental error in rotational cross sections near the thresholds is underestimated by about a factor of 2. However, at slightly higher energies, the claim of 5% in the experimental accuracy is probably well justified.

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