Resonances in the Dissociative Recombination of $H_2{}^+$ with Slow Electrons

In a recent Letter [1] Van der Donk, Yousif, Mitchell, and Hickman presented high-resolution merged beam measurements for the dissociative recombination of $H_2{}^+(v=0)$ with slow electrons. The efficient vibrational relaxation achieved with a rf ion trap allows definite resonance features, due to the temporary formation of near-threshold Rydberg levels of H_2, to be clearly resolved in the cross section. Together with these outstanding experimental results, a theoretical calculation is presented in order to "associate particular features of the cross section to specific Rydberg states." Unfortunately, we think that these calculations are incomplete, and therefore misleading in the resonance assignment. We base this Comment on a similar calculation [2] for this process, using the same method [3] derived from multichannel quantum defect theory (MQDT).

This method assigns resonances to "closed ionization channels," each of them corresponding to a Rydberg series defined by the orbital quantum numbers $(l\lambda)$ of the external electron and by the series threshold, a given vibrational level v of the ion (here, as in Refs. [1] and [2], the molecular rotation is neglected and $\lambda=\sigma_g$ will be understood in the resonance assignment). A (n,l,v) resonance, with n the principal quantum number, may show up in the calculation *only if the corresponding* (l,v) *closed channel has been included.* In Ref. [1] only the lowest closed ionization threshold $(v=1)$ is considered such that only Rydberg states with $(n\geq 7,v=1)$ seem to participate in the resonance structure below 100 meV. Actually, as first pointed out by O'Malley [4], the (low n, high v) Rydberg states are likely to play a dominant role in the so-called "indirect" dissociative recombination process in spite of their weak vibrational coupling to the ion ground state $(\Delta v>1)$: They are the most strongly coupled to the valence dissociative channel due to the n^{*-3} scaling law for the electronic width.

For convergence purposes as well as proper identification of the resonances, we found it necessary to include up to 15 ion vibrational levels, i.e., a total of 31 channels (among which 28 are closed) instead of 5 in Ref. [1]. This led us to assign the following dominant character to the three features observed in the cross section below 100 meV: (i) 18 meV: Rydberg state $(5s,v=2)$, instead of $(7s,v=1)$ in [1], which we find below threshold. (ii) 45 meV: $(3s,v=6)$ instead of $(8d,v=1)$ in [1]. (iii) 66 meV: unresolved composite resonance $(8d+8s,v=1)$. It is unlikely that this broad feature corresponds to the single $(8s,v=1)$ as suggested in [1].

Another severe limitation of the calculation in [1] is the neglect of the R dependence of the quantum defects, which amounts, in the MQDT approach, to neglect of any vibrational coupling between ionization channels. We found that vibrational interaction significantly contributes to the resonance shift (see Fig. 5 of [2]). Thus no useful comparison between experimental and theoretical resonance energies can be made, in particular to discuss the molecular data used [5], unless their R dependence is introduced.

Finally, the second-order electronic coupling between ionization channels does not appear to be fully included, since diagonal terms g_{vv} are missing in the K matrix (10) of [1], as well as the $K_{lv,l'v}$ matrix elements corresponding to indirect l mixing.

In conclusion, we wish to emphasize that the latest merged beam measurements presented in [1] provide a highly needed test of the role of Rydberg states in near-threshold e-molecular-ion processes like dissociative recombination and associative ionization [6]. Molecular hydrogen is particularly suitable for this test because accurate molecular data are available. We thus find it unfortunate that the calculations in [1] do not make full use of the theoretical tools available nowadays and overlook the important role of the low Rydberg states as well as the combined effect of vibrational and electronic interactions.

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