

H_2^- FORMATION IN ELECTRON IMPACT IONIZATION OF H_2 NEAR THRESHOLD

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New features in near threshold ionization spectra of H_2 which can be correlated with two series of H_2^- states proceeding across the H_2^+ threshold, indicate a need for coincidence experiments that differentiate between one and two electron decay modes of H_2^- .

The mechanisms for the near threshold ionization of H_2 have been a subject of controversy for over a decade [1–3]. We here present evidence from electron impact ionization and electron transmission experiments indicating that in the near threshold region, electron impact ionization of H_2 proceeds in part via H_2^- formation as originally suggested by Stevenson [4]. Typically reproducible results of the present experiments are shown together with other ionization [2] and photoionization [5] work in fig. 1. All the observed features, which include five new ones, are collected in table 1 for comparison with those reported by other groups [2, 3, 5–8].

The ionization results were obtained by cross-finding a 10^{-7} A electron beam with a thermal H_2 beam at 10^{-5} torr, analyzing the ions in a 60° sector type spectrometer and detecting them with a Daly detector. The measured ionization curve was corrected for the energy spread in the electron beam by the EDD method with differentiation steps of 0.026 eV [9]. The transmission results were obtained with a new double modulation technique in an apparatus previously described [3, 10]. The energy resolutions of the ionization and transmission experiments are about 130 and 25 meV respectively.

The observed ionization and transmission features can be assigned to the two known series [3, 7]. Those labeled "f" correlate very well with each other, with

the photoionization data, with the anharmonic oscillator vibrational levels predicted [3] for the $2^2\Sigma_g$ state [8, 11] of H_2^- , and proceed across the ionization threshold (see table 1). The overlapping band "g" seen clearly in the transmission data but, with present resolution, barely discernible (as indicated by parentheses in table 1) in the ionization spectrum, also coincides with the autoionization series. Two members of this band lie *below* the ionization threshold. These cannot autoionize, yet seem to fit in the same band with structures seen above the threshold in all three experiments. The present results thus suggest that features due to autoionizing states may be obscured in electron spectra by formation of nearly coincident or overlapping H_2^- states which then decay to either autoionizing levels of H_2 or to H_2^+ directly.

This conjecture is supported by the fact that despite the different resolutions of our two experiments the apparent widths (~ 100 meV) of such H_2^- states are the same, consistent with other lifetime estimates (10^{-14} – 10^{-13} sec) [4, 7] and about three orders of magnitude larger than those of the longer lived (10^{-11} sec) [6, 12, 13] autoionizing states. Note that in this case, some of the structure reported by McGowan et al. [2] can, because of the 60 meV resolution of their experiment, be also attributed to H_2^- formation.

To identify the ionization mechanisms experiments

Table 1
Positions of structures in the H_2^+ and e^- spectrum in eV.

ν	H_2^+		H_2^-		present ionization	H_2^-		Golden [3]	Sanche and Schulz [7]		present transmission		empirical formula [3]
	Dibeler et al. [5]	Chupka and Berkowitz [6]	McGowan et al. [2]	$n = 1$		"f"	"g"		Weingarts-hofer et al. [8]	AI	"f"	"g"	
0													
1													
2													
3													
4													
5													
6													
7	15.48		15.47	15.49									
	15.60	15.58	15.61	15.58		(15.60)							
8			15.65	15.65		(15.60)		15.59					
			15.72	15.75		(15.77)							
9	15.86	15.88	15.86	15.89									
	15.94	15.96	15.96	15.97		(15.93)							
10	16.08	16.09	16.07	16.04									
		16.19		16.17		(16.12)							
11	16.22	16.24	16.20	16.23									
	16.32	16.33											
12	16.46	16.45											
13													
14													
15													
16													

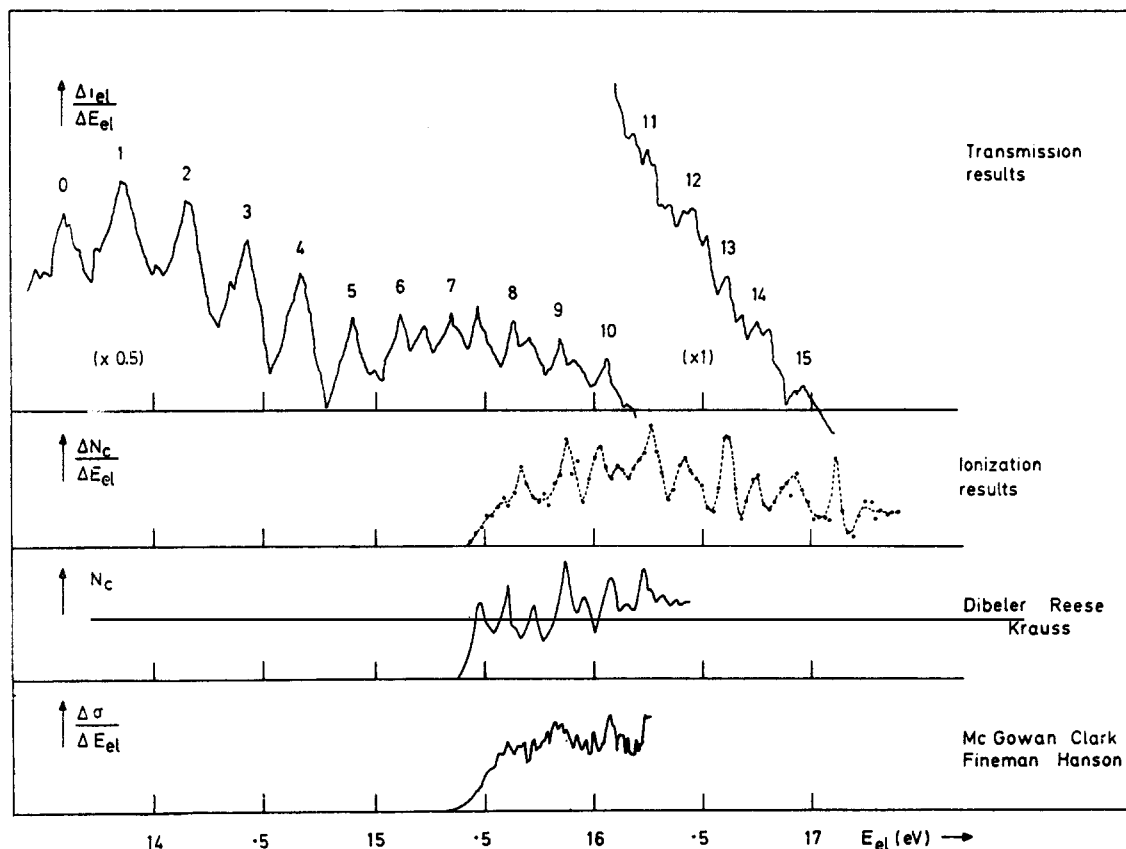


Fig. 1. Structures in H_2 ionization near threshold. Upper curve: present results – electron transmission; Ionization – second curve: present results; fourth curve: McGowan et al. ref. [2]; Photoionization – third curve: Dibeler et al., ref. [5]. As indicated on the vertical axes, the transmission and ionization curves are energy differentiated.

are, therefore, necessary to clearly distinguish between the processes $e + H_2 \rightarrow (H_2^{*+} + e) \rightarrow H_2^+ + 2e$ or $e + H_2 \rightarrow H_2^+ + 2e$, or $e + H_2 \rightarrow H_2^- + e$, of $e + H_2 \rightarrow H_2^- \rightarrow H_2^{*+} + e \rightarrow H_2^+ + e$. In particular, coincidence experiments between H_2^+ ions and electrons with specific energy losses that distinguish between the one and two electron decay modes of H_2^- , as well as similar experiments in D_2 where the “f” and “g” series do not overlap [14], would verify the present suggestions.

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