Structures in the electron transmission spectrum of H_2 near the H_2^+ threshold

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The energy dependence near the ionization threshold of the electron-scattering cross section of H_2 has been investigated. Two series of structures which proceed across the H_2^+ threshold have been observed which can be correlated with structures observed previously in the ionization efficiency function. These results suggest that in the threshold region a significant portion of the ionization process by electron collision proceeds via the various decay modes of temporary H_2^- states. Furthermore, these structures can also be correlated with some structures in the photoionization cross section. Those H_2^- states that decay to autoionizing levels of H_2 and then to H_2^+ may account for the correlation with some of the photoionization data. To differentiate experimentally between one- and two-electron decay modes of H_2^- leading to H_2^+ formation, coincidence experiments between H_2^+ ions and electrons with specific energy losses will be necessary.

I. INTRODUCTION

The threshold region in the ionization of H_2 by electrons has been the subject of considerable attention and controversy for approximately 15 years.[1] In 1957 Krauss and Kropf[2] considered the consequences of a direct-ionization model for the threshold region. They took the excitation of each vibrational state of H_2^+ to be proportional to the incident energy (relative to the threshold energy) and invoked the Franck-Condon principle. The resulting ionization cross section consisted of a series of straight-line segments starting at each of the thresholds for the vibrational states of H_2^+. Shortly thereafter, Stevenson[3] remeasured the ionization cross section in the vicinity of the ionization threshold and found a linear function of incident energy (relative to the ionization threshold). Thus Stevenson's results were in agreement with the much earlier measurements of Bleakney.[4] Furthermore, Stevenson postulated short-lived (10^{-14}–10^{-13} sec) negative-ion states in order to explain the experimental results.

The first high-resolution electron-energy work (which claimed an energy resolution of 0.03 eV) by Marmet and Kerwin[5] showed breaks in the cross section for the production of H_2^+, which were interpreted by them as the thresholds for the individual vibrational states of H_2^+. Their results and interpretation were consistent with the earlier calculations of Krauss and Kropf.[2] In order to help settle this difference in experimental results and subsequent interpretation, Briglia and Rapp[6] repeated the measurements using retarding potential difference (RPD) techniques and found the ionization cross section to be a linear function of incident energy (relative to the ionization threshold), in agreement with the results of Bleakney[4] and Stevenson[3] and in disagreement with the high-resolution results of Marmet and Kerwin[5] and the direct-ionization model of Krauss and Kropf. Furthermore, Briglia and Rapp suggested that mechanisms such as autoionization and intermediate negative-ion formation might be necessary in order better to describe the ionization process in the threshold region.

Subsequently, further high-resolution work by McGowan and Fineman[7] (~0.06 eV) showed a nearly straight line for the ionization cross section in the threshold region. However, they found a break and a short linear region very close to threshold, which they interpreted as being due to the competition between direct rotational and vibrational excitation of the molecular ion and autoionization. Further work by McGowan *et al.*[8] showed a marked similarity between the photoionization data of Dibeler *et al.*[9] and the first derivative of their electron-impact data. They concluded that the structure in the ionization-threshold region was due to autoionization of long-lived Rydberg states of H_2 (lifetimes 10^{-7}–10^{-6} sec).

The original suggestion of Stevenson[3] that the ionization of H_2 by electrons in the threshold region may proceed partly via the temporary formation of H_2^- has been recently reopened by one of the present authors.[10] Structures were observed in the transmission of electrons through H_2 both below and above the ionization threshold. The structures below the threshold agree very well with a series of H_2^- resonances observed by Ehrhardt and Weingartshofer and by Weingartshofer *et al.*[11,12] which was identified by these authors as a $^2\Sigma_g$ compound state. It was suggested in Ref. 10 that some of the structures observed above the ionization threshold may be due to higher members of this vibrational resonance series. Other struc-

tures seem to correspond to autoionization peaks, as observed in photoabsorption experiments by Dibeler *et al.*[9] and by Chupka and Berkowitz.[13] It was also suggested in Ref. 10 that the rejection of the temporary formation of H_2^- as a contributing mechanism for ionization by McGowan *et al.*[8] may have been premature, because the details of the structures in the electron scattering cross section near the ionization threshold had not been known at the time of their experiment.

In this work we have further examined the structure in the total electron scattering cross section in the ionization-threshold region by doing transmission experiments using a new and more sensitive double-modulation technique.[14] These new measurements are compared with structures in previous electron-ionization cross-section measurements and photoionization measurements.

II. APPARATUS AND PROCEDURE

These new measurements of the electron transmission spectrum have been made using a new double-modulation technique which has recently been described in detail.[14] The apparatus is essentially the same as described previously,[10,15] except that the scattering cell has been shortened to 1.52 cm. Electrons from the cathode are focused into a parallel beam at the retarding plane where a square-wave modulation is applied. After additional focusing and acceleration, the electrons pass into the scattering cell where a second square wave, differing in phase by $\frac{1}{2}\pi$ from that at the retarding plane, is applied. The transmitted electrons are then detected by an electron multiplier. The output of the electron multiplier is applied through a current-to-voltage converter to the input of a phase-sensitive detector which is gated at twice the frequency of the square waves applied to the retarding element and the scattering cell.

A straightforward analysis shows that the output of the phase-sensitive detector, I_{out}, is in this case proportional to the derivative of the transmitted current, with a resolution determined only by the two modulation amplitudes; for small modulation amplitudes[14]

$$I_{\text{out}} = \Delta E \int_{E+E_1}^{E+E_2} F(E'-E)\,\frac{g(E'+\Delta E)-g(E')}{\Delta E}\,dE', \tag{1}$$

where $F(E'-E)$ is the electron energy distribution from the cathode shifted by energy E at the scattering cell, E_2-E_1 the peak-to-peak amplitude of the modulation applied at the retarding electrode, ΔE the peak-to-peak amplitude of the modulation applied to the scattering cell, and

$$g(E') = e^{-\sigma_t(E')nx}. \tag{2}$$

The function $\sigma_t(E')$ is the total scattering cross section, n the gas density in the scattering cell, and x the path length of the electron beam through the scattering cell. Equation (1) shows that the output of the phase-sensitive detector approaches the derivative of the transmitted current as ΔE and E_2-E_1 tend to zero. For the present work both modulation amplitudes were 25 mV. The energy scale was obtained by using a mixture of He and H_2 and calling the energy of $He^-(1s2s^2)^2S$ 19.35 eV.[16]

III. RESULTS AND DISCUSSION

Figure 1 shows one run of the present electron-transmission results together with the results of the previous electron-ionization experiment of McGowan *et al.*[8] and the photoionization results of Dibeler *et al.*[9] The positions of features found in the present electron-transmission work which are reproducible from run to run are collected with the results of other workers in Table I.

In the first and second columns, the energies of the autoionizing states of H_2 as seen in the photoionization work of Dibeler *et al.*[9,17] are compared with some of the stronger autoionizing states measured in the more recent and higher-resolution photoionization work of Chupka and Berkowitz.[13] Also shown for comparison are the peaks found in the electron-ionization work of McGowan *et al.*[8] (assuming either an $n=1.127$ or an $n=1$ power-law ionization-threshold dependence).

The positions of the vibrational levels of the H_2^- state observed by Weingartshofer *et al.*[12] in their electron-scattering experiment are also listed, together with those found in subsequent electron transmission experiments of Golden,[10] Sanche and Schulz,[18] and the present work. The positions given in the last column were taken from the empirical formula given in Ref. 10, obtained by fitting an anharmonic-oscillator term scheme to the positions of the "f"-series structures.[19] This series of resonances has been designated "f" in the subsequent work of Sanche and Schulz,[18,20] who were able to separate two distinct series of resonances ("f" and "g"). The H_2^- state giving rise to the "f" series is most probably a $^2\Sigma_g$ state, as suggested by the stabilization-method calculations of Eliezer *et al.*[21] and confirmed in the angular-distribution measurements of Weingartshofer *et al.*[12]

In the present work, 23 reproducible features have been found in the transmission spectrum between 13.5 and 17 eV. Of these features, 14 lie above the threshold for the ionization of H_2 (15.43 eV) and six have not been observed previously in electron scattering. The positions of the structures found in the present electron-transmission experiment and the older electron-ionization ex-

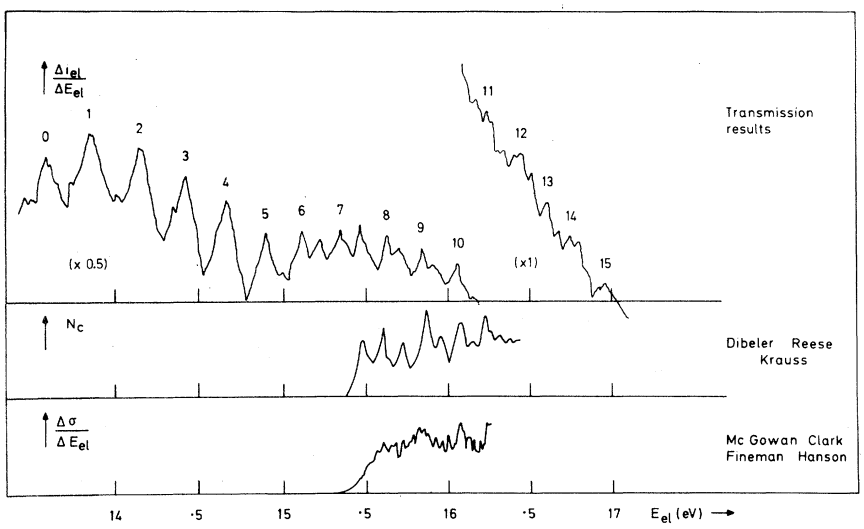

FIG. 1. Electron-transmission curve near threshold (upper curve: present results); photoionization curve (second curve: Dibeler *et al.*); ionization curve (third curve: McGowan *et al.*). As indicated on the vertical axes, the transmission and ionization curves are energy differentiated.

TABLE I. Positions of structures in the H_2^+ and e^- spectrum in eV.

H_2^+							H_2^-				
Dibeler *et al.*[a] AI[g]	Chupka and Berkowitz[b] AI[g]	McGowan *et al.*[c] $n=1.127$	$n=1$	Weingartshofer *et al.*[d] H_2^-	Golden[e] H_2^-	AI[g]	Sanche and Schulz[f] "f"	"g"	Present transmission "f"	"g"	Empirical formula[e] "f"
				13.63	13.62		13.66		13.62		13.62
				13.93	13.91		13.94		13.91		13.91
				14.20	14.19		14.20		14.19		14.19
				14.47	14.46		14.45		14.46		14.46
				14.70	14.72		14.65		14.72		14.72
				14.92	14.97		14.93		14.97		14.97
								15.09		15.06	
					15.21		15.18		15.21		15.21
								15.32		15.31	
15.48	15.48	15.47	15.49		15.44		15.43		15.44		15.44
15.60	15.58	15.61	15.58			15.59		15.57		15.57	
	15.66	15.65	15.65		15.66		15.65		15.67		15.66
15.72	15.74	15.72	15.75			15.79		15.77		15.74	
15.86	15.88	15.86	15.89		15.87		15.85		15.88		15.87
15.94	15.90	15.96	15.97			16.02				15.96	
16.08	16.11	16.07	16.04		16.07				16.08		16.07
			16.17							16.16	
16.22	16.21	16.20	16.23		16.26				16.26		16.26
16.32	16.36									16.34	
16.46	16.45								16.44		16.44
	16.64								16.61		16.61
									16.77		16.77
									16.92		16.92
											17.06

[a]Reference 9.
[b]Reference 13.
[c]Reference 8.
[d]Reference 12.
[e]Reference 10.
[f]Reference 18.
[g]AI stands for autoionization

periment of McGowan *et al.*[8] agree quite well with each other. These positions also agree with those given in the recent preliminary ionization measurements of Boesten and Heideman,[22] which extend to higher impact energies than those of McGowan *et al.*[8] As can be seen from Table I, the positions can also be correlated both with the photoionization peaks of Dibeler *et al.*[9] and with some of those reported by Chupka and Berkowitz.[13]

Above 16.64 eV there are three additional peaks which cannot be compared with photoionization peaks, but whose positions agree very well with the semiempirical predictions given in the last column. That these peaks can be identified as higher vibrational members of the $^2\Sigma_g$ "*f*" state of H_2^-, as observed in the electron-scattering work, is further confirmed by Fig. 2. The vibrational spacings of the "*f*" series found in the various experiments are plotted in Fig. 2 as a function of the vibrational quantum number. This so-called Birge-Sponer plot indicates that more than 20 vibrational levels exist for this H_2^- state. Thus one might expect H_2^- formation to be significant within about 6 eV of the ionization threshold.

In the table the overlapping band beginning just above 15 eV, which Sanche and Schulz[18] have labeled band "*g*," can be seen to also coincide very closely with some of the autoionization data of Dibeler *et al.*[9] or Chupka and Berkowitz.[13] According to Chupka and Berkowitz, the autoionization of H_2 proceeds via Rydberg states such as $np\pi\ ^1\Pi_u$ and $np\sigma\ ^1\Sigma_u^+$. On the basis of this result one might conclude that these structures, as well as any other which fit in with this band, are due to autoionization. However, it should be noted that two members of this band lie *below* the ionization threshold. Since these two cannot autoionize, they would not appear in the photoionization data or the electron-ionization data, but they do seem to fit in

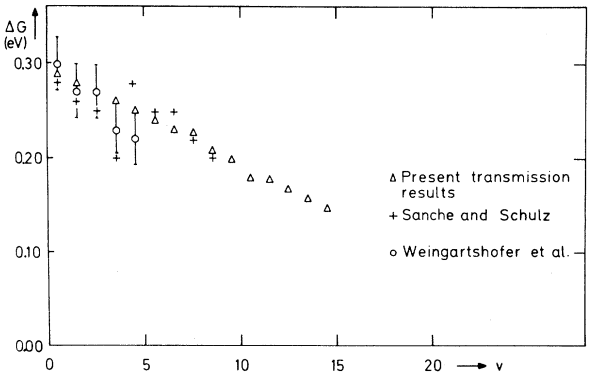

FIG. 2. Birge-Sponer plot for the H_2^- states based on Δ, present electron transmission results; +, electron-transmission results of Sanche and Schulz; O, electron-scattering measurements of Weingartshofer *et al.*

the same band with the structures above the ionization threshold which are seen in all three experiments. We therefore can say that these structures are either due to the opening of inelastic channels to double-excited states of H_2, i.e.,

$$e + H_2 \rightarrow H_2^{**} + e,$$

some of which may autoionize to H_2^+, or they are H_2^- resonances which decay either by one- or two-electron processes to H_2 or H_2^+, viz.,

$$e + H_2 \rightarrow H_2^- \begin{cases} \rightarrow H_2 + 2e \\ \rightarrow H_2^+ + e \end{cases}.$$

The one-electron decay of H_2^- may in this case also involve autoionization to H_2^+. Weingartshofer *et al.*[12] have concluded that the $^2\Sigma_g$ state of H_2^- ("*f*") almost exclusively decays to the *C* state of H_2 ($^1\Pi_u$) for $v = 0, 1, 2, 3, 4, 5$, with the vibrational quantum number of the final state being equal to the vibrational quantum number of the initial state. The $np\pi\ ^1\Pi_u$ Rydberg states considered significant in the autoionization of H_2 by Chupka and Berkowitz[13] have the same symmetries as the *C* state, and therefore one might expect at least a small amount of decay of the H_2^- state to some of these where energetically possible. However, for $v \geq 7$ a new decay channel for this state of H_2^- is open—i.e., two-electron decay to H_2^+. Above the ionization threshold of H_2^+, neither experiment can distinguish between the three possible decay mechanisms of H_2^- to H_2^+ discussed above. For those members of either the "*f*" or "*g*" series lying above the ionization threshold, either process could produce an H_2^+ ion and thus produce structure in the electron-impact-ionization curves.

Only doubly excited states which autoionize can show up in the photoionization spectra, but, since some of the structures of both series in the electron-impact data appear below the H_2^+ threshold and are attributable to H_2^- states which cannot be formed in photon-impact work, the present results support the point of view that the dominant effect in electron-impact ionization of H_2 is the formation of H_2^-, which can proceed to H_2 or H_2^+ via one- or two-electron decay. This suggestion is strengthened by consideration of the lifetimes of autoionizing and negative-ion states, as we now discuss.

The work of Stevenson[3] has shown that the average appearance potential of H_2^+ and the initial kinetic energy of the protons in the dissociative ionization spectrum were in disagreement with the expectations based on the conventional application of the Franck-Condon principle using the potential-energy diagrams of H_2 and H_2^+ taken from the work of Bates *et al.*[23] Stevenson found that the most probable internuclear separation for H_2^+ formed by

electrons of energy in the range 15–100 eV did not agree with that given by Bates *et al.* He therefore postulated the formation of H_2^- virtual states with lifetimes of the order 10^{-14}–10^{-13} sec determined by the time required by the slowly moving nuclei to assume a new distribution of states in the field of three electrons.

The results of Briglia and Rapp[6] and McGowan *et al.*[8] are in agreement as to the general shape of the ionization curve of H_2^+. McGowan *et al.* have attributed all the structures found by them to long-lived Rydberg states, which, however, as discussed by Stevenson, cannot explain the data. On the other hand, the existence of H_2^- states proceeding across the H_2^+ threshold can explain the data. As a matter of fact, the lifetimes of these H_2^- states, as measured by their apparent widths in the present experiments (~100 meV), are in agreement with the lower limit of Stevenson's estimate.

The suggestion by McGowan *et al.* of long-lived (10^{-6}–10^{-7} sec) autoionizing states is also not supported by more recent experimental[24] and theoretical[25] work, and thus their analysis of the discrepancies in the lifetimes derived from molecular-beam and closed-chamber ionization data has to be abandoned. We can argue that the resolution of 60 meV claimed by McGowan *et al.* implies that the structures seen by them could also be attributed to negative-ion formation because the widths of their structures are too large (~100 meV) to be consistent with the postulate of long-lived states. The widths of the structures seen in the present work are in agreement with those of McGowan *et al.*, as well as with those reported by Erhardt and Weingartshofer[11] and Sanche and Schulz,[18] and are indicative of lifetimes of the order of 10^{-14} sec, as postulated by Stevenson. Hence, we conclude that in the present experiments H_2^- states are created and decay by either one- or two-electron processes to H_2^+. Those states that decay by one-electron emission can then give rise to the autoionizing states which coincide with or lie close to the H_2^- levels seen here. However, the smaller widths (i.e., longer lifetimes ~10^{-11} sec) of the autoionizing levels are obscured by the larger widths (i.e., shorter lifetimes ~10^{-14} sec) of the H_2^- states. An experiment to study simultaneously the electron transmission and electron ionization spectra of H_2 should help further to resolve this point.[26]

IV. SUMMARY

The main result of this work is the suggestion that an important indirect contribution to the near-threshold electron-impact ionization of H_2 is the formation of H_2^- ions. Further verification of this result dictates the need for additional experiments and some calculations. In particular, coincidence experiments between H_2^+ ions and electrons with specific energy losses would permit one to distinguish between the one- and two-electron decay modes of H_2^- leading to H_2^+ formation. Similar experiments with D_2, where, as noted by Schulz,[20] the "*f*" and "*g*" series do not overlap, would clarify the situation further.

On the theoretical side, close-coupling calculations of electron scattering by H_2 in which H_2^- formation would manifest itself either as Feshbach or shape resonances would provide information on both the positions and lifetimes, while calculations on the e-H_2^+ system would yield the same information about the autoionizing states. Two sets of calculations are needed because current formalisms do not allow for simultaneous inclusion of all the final-state channels in the (e, H_2) problem. The first set, in particular, would establish whether the H_2^- states discussed here are shape resonances bound to the $C\,^1\Pi_u$ or Feshbach resonances bound to the $D\,^1\Pi_u$ state of H_2, as discussed by Ehrhardt and Weingartschofer[11] and Schulz.[20]

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[19]Note that the anharmonic-oscillator constants $w_e = 0.30$ and $w_e x_e = 0.005$ eV, determined by fitting the experimental H_2^- levels in Ref. 10, are quite close to those of the H_2 $C\,^1\Pi_u$ and $D\,^1\Pi_u$ states, thus further confirming the finding by Eliezer *et al.* (Ref. 21) that the potential-energy curve of H_2^- is very similar to those of the possible parent H_2 states. The small anharmonicity is also indicative of weak correlation between the incident and bound electrons. The near coincidence of w_e for the $C\,^1\Pi_u$ and H_2^- states suggests the latter might be core-excited shape resonances bound to the $C\,^1\Pi_u$ state rather than Feshbach states bound to $D\,^1\Pi_u$.

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