Vibrational Structure in the Dissociative Attachment of Electrons in Hydrogen*

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A series of resonances with spacing 0.3 eV has been observed in the 11.2- to 12.5-eV range of the cross section for production of H^- by dissociative attachment of electrons in H_2. Comparison is made with resonances in the elastic scattering and vibronic excitation. Mechanisms involving vibrational levels of quasibound, excited states of H_2^- are discussed.

I. INTRODUCTION

Resonant scattering of electrons by atoms and molecules has been studied extensively in recent years by several investigators.[1] The phenomena observed are usually sharp peaks or dips in the elastic or inelastic scattering cross sections. The resonances are attributed to short-lived negative-ion states formed from excited states of the target atom or molecule. Because the temporary negative ion often can decay into several exit channels, resonances may occur at the same energy in cross sections for several processes. For example, the temporary negative molecule ion formed by electron impact may decay *by auto-ionization* into the molecular ground state (elastic scattering), into a higher vibrational level of the ground electronic state (vibrational excitation), into an excited electronic state of the molecule (electronic excitation), or into neutral fragments (dissociation). Another possibility is decay *without auto-ionization* into a neutral fragment and a negative-ion fragment (dissociative attachment).

In molecular hydrogen, resonances in several channels have been found in the 11- to 13-eV region. Resonances in elastic scattering have been reported by Kuyatt, Simpson, and Mielczarek[2] and also by Golden and Bandel.[3] Resonances in vibrational excitation of the $v=1$ and $v=2$ levels of the ground state were found by Menendez and Holt.[4] Heideman, Kuyatt, and Chamberlain[5] have observed resonances in the excitation of the two lowest vibrational levels of the $B^1\Sigma_u^+$ state. We report here what appear to be vibrational resonances in the H_2 dissociative attachment cross section in the same energy range. To our knowledge, this is the first reported observation of a series of vibrational resonances in dissociative attachment.

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[1] Two recent reviews of the subject are: P. G. Burke, Advan. Phys. **14**, 521 (1965); K. Smith, Rept. Progr. Phys. (GB) **29**, 373 (1966).

[2] C. E. Kuyatt, J. A. Simpson, and S. R. Mielczarek, J. Chem. Phys. **44**, 437 (1966).

[3] D. E. Golden and H. W. Bandel, Phys. Rev. Letters **14**, 1010 (1965).

[4] M. G. Menendez and H. K. Holt, J. Chem. Phys. **45**, 2743 (1966).

[5] H. G. M. Heideman, C. E. Kuyatt, and G. Chamberlain, J. Chem. Phys. **44**, 440 (1966).

II. APPARATUS

The apparatus used for this investigation is shown in Fig. 1. It is similar to that used in the past in this laboratory for absolute positive- and negative-ion cross-section measurements.[6] An oxide-coated cathode and four plates with rectangular slits constitute the electron gun. The electron beam is collimated by an axial magnetic field of typically 500 G. The size of the beam is determined by a 5×100-mil slit in the second gun plate. Electrons may be retarded at this plate to cut off part of the electron-energy distribution, yielding a distribution of typically 0.15-eV full width at half-maximum. The electron beam passes through the ion detection region and the ion suppressor, and is collected on the electron collector. Complete electron collection is indicated by saturation of electron current with electron collector potentials. The ion suppressor prevents ions formed in the electron collector from entering the ion-detection region.

The ion-detection region consists of two parallel plates with appropriate guard plates. Ions formed in this region are drawn to one plate by the voltage drop between the plates. The ion current is measured with a vibrating reed electrometer. (Figure 1 shows a slit in one of the plates through which ions may be drawn into a 1-in.-radius, 180° mass spectrometer. This feature was not used for the present data.) Complete collection of ions formed in the detection region is indicated by saturation of ion current with drawout fields. This is achieved with about 10 V/cm for H^- ions having thermal kinetic energies, and with more than 20 V/cm for H^- ions having several eV kinetic energy.[7] Use of drawout fields greater than 10 V/cm noticeably broadens the electron-energy distribution.

Not shown in Fig. 1 are two side plates, or shields, perpendicular to the ion drawout plates and connected to the endplates of the collision region. The potential of these shields may be adjusted with respect to the drawout plates by means of a divider resistor. In this manner, the electron beam may be made to see either a potential well or a potential bump upon entering the

[6] (a) D. Rapp and P. Englander-Goldern, J. Chem. Phys. **43**, 1464 (1965); (b) D. Rapp and D. D. Briglia, *ibid.* **43**, 1490 (1965); (c) D. D. Briglia and D. Rapp, *ibid.* **42**, 3201 (1965).

[7] D. Rapp, T. E. Sharp, and D. D. Briglia, Phys. Rev. Letters **14**, 533 (1965).

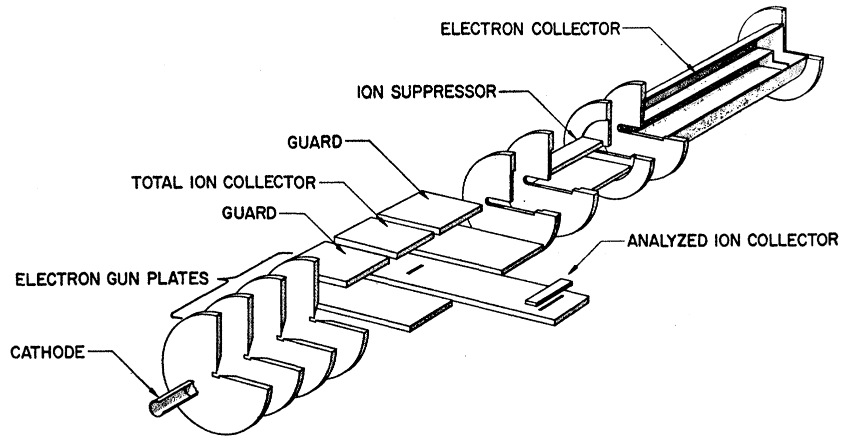

FIG. 1. Schematic view of experimental tube. The vertical spacing between the parallel plates in the ion-detection region is 1 cm.

collision region. The role this adjustment plays in the investigation is discussed below.

The apparatus is mounted in a bakeable vacuum system with a background pressure in the 10^{-9}-Torr region. Matheson reagent-grade hydrogen was used without further purification. The linearity of the ion current with gas pressure was checked over a factor of 15 in pressure. Electron-beam currents used were 1 to 5×10^{-7} A. The linearity of the ion current with electron current was checked up to 3 μA.

III. RESULTS AND DISCUSSION

The H^- production from dissociative attachment in H_2 has been the subject of several previous investigations.[7–10] There are three main features of interest in the 3- to 16-eV energy range of the cross section. The lowest-energy peak, at 3.75 eV, is associated with the unstable ground state ${}^2\Sigma_u{}^+(\sigma_g 1s)^2(\sigma_u 1s)$ of H_2^-, and is considered to have a vertical onset.[10] The large, sharp peak at about 14 eV is also thought to have a vertical onset.[9] This peak is probably associated with the repulsive part of a quasistable excited state of H_2^- which dissociates into $H^-(1s)^2$ and $H^*(n=2)$. The H^- ions forming these two peaks have very little kinetic energy. This is not the case for ions forming the broad peak in the 8- to 13-eV region. Dissociative attachment in this energy range occurs via the ${}^2\Sigma_g{}^+(\sigma_g 1s)(\sigma_u 1s)^2$ repulsive state of H_2^-, and the ions are formed with considerable kinetic energy. A drawout field of at least 23 V/cm is required for saturation of the ion current for this peak.[7] The energy spread of the electron beam is increased approximately 0.3 eV by a drawout field of this magnitude. Previously published data[7] on the 8- to 13-eV peak was taken with high drawout field. The data of Schulz,[9] which were taken with good energy resolution, show indications of structure on the high-energy side of this peak. In this study we used lower drawout fields in order to retain a reasonably narrow energy spread in the electron beam and yet collect an appreciable fraction of the ions formed.

Present data for dissociative attachment in the 9- to 13-eV region are shown in Fig. 2. These data were taken on an XY plotter with the ion current being automatically divided by the electron current. The 3.75-eV peak was used for electron-energy calibration. The energy of this peak was verified to better than ±0.1 eV by comparison with the positive ion onset, and by measurement of the contact potential by retarding the electron beam. A series of peaks and dips in the negative-ion current is evident in the 11.2- to 12.3-eV region. Another set of data taken with lower drawout field and with suppressed zero on the ion current scale is shown in Fig. 3. Estimates of the energies of the peaks and dips are indicated by the arrows in the figure. The uncertainty in the energy scale, considering both systematic and random error, is estimated to be ±0.1 eV.

The question arises whether this structure is real or spurious. It has been observed over a wide range of electron-beam current and over a factor of 15 in pres-

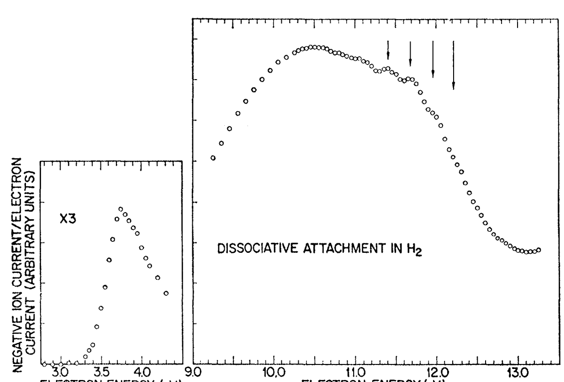

FIG. 2. Normalized negative-ion current versus electron energy in H_2. The energy scale is calibrated by assuming the low-energy peak to be at 3.75 eV.

[8] V. I. Khvostenko and V. M. Dukel'skii, Zh. Eksperim. i Teor. Fiz. **33**, 851 (1957) [English transl.: Soviet Phys.—JETP **6**, 657 (1958)].
[9] G. J. Schulz, Phys. Rev. **113**, 816 (1959).
[10] G. J. Schulz and R. K. Asundi, Phys. Rev. Letters **15**, 946 (1965); Phys. Rev. **158**, 25 (1967).

TABLE I. Resonance energies (in eV) for electron scattering from H_2.

Dissociative attachment; this work		Elastic scattering[a] Kuyatt *et al.*[c] 1st series	2nd series	Golden *et al.*[d]	Excitation[b] of $B\ ^1\Sigma_u^+$ Heideman *et al.*[e] $v=0$	$v=1$
Peaks	Dips			10.93		
	11.27±0.02	11.28		11.22		
11.40±0.01			11.46	11.48		
	11.57±0.02	11.56			11.56	11.56
11.70±0.01			11.72	11.76		
	11.87±0.03	11.84			11.84	11.87
12.00±0.01			11.99	12.04		
	12.12±0.03	12.11			12.13	12.15
12.25±0.02			12.27	12.31		
		12.37				12.42
			12.53	12.58		
		12.62				
			12.77	12.81		
		12.86				
			12.97			

[a] Energies correspond to peaks in transmission, which are dips in the scattering cross section.
[b] Energies correspond to peaks in scattering cross section.
[c] Reference 2.
[d] Reference 3.
[e] Reference 5.

sure. The shape of the curve is constant over these ranges for a given electron-energy resolution. However, trapped electrons can contribute to the observed negative-ion current. This effect may be studied by adjusting the potential of the side shields in the collision chamber so that the beam electrons see a small potential well, say 0.05 V. Electrons which suffer inelastic collisions in the chamber, and whose final energies are less than 0.05 eV, will be trapped in the potential well and will eventually reach the ion-collector plate.[11] The trapped electron spectrum in the 11- to 13-eV energy range in H_2 exhibits a series of sharp peaks, spaced approximately 0.3 eV. These peaks are due to excitation of the vibrational levels of the $c^3\Pi_u(\sigma_g 1s)(\pi_u 2p)$ state.[11] Any residual trapped electron current might easily be mistaken for resonances in the negative-ion cross section. We rule this out for two reasons. Firstly, the lowest energy, strong resonance in the dissociative attachment data is at 11.4 eV, whereas the lowest-energy, pronounced peak of the vibrational series of trapped electrons is at 11.75 eV. Secondly, one can let the electron beam see a potential bump in the collision chamber instead of a potential well. Then the trapped electron current vanishes completely,[12] but the structure in the negative-ion current is not changed.

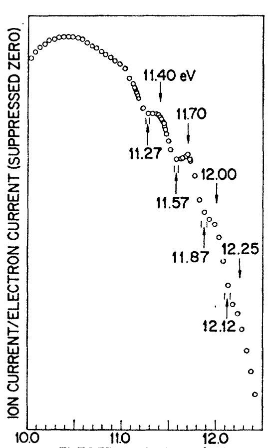

FIG. 3. Normalized negative-ion current (with suppressed zero) versus electron energy in H_2. Energies of the peaks and dips are indicated by arrows, and uncertainties by lines bracketing the arrows.

[11] J. T. Dowell and T. E. Sharp, J. Chem. Phys. 47, 5068 (1967).

Careful investigation of the dissociative attachment in energy regions other than 11.0 to 13.5 eV yielded no evidence of further structure.

In the data of Rapp, Sharp and Briglia,[7] the cross section for dissociative attachment in the 8–12.5-eV region showed two peaks for H_2, HD, and D_2. By examining H_2 with reduced ion drawout field, we have been able to resolve the peak lying at higher energy into a series of resonances. We have also examined HD and D_2 with reduced ion drawout voltage. In the 11.3- to 12.5-eV region we have found evidence of resolvable resonances in HD, but none in D_2. Even at very low ion drawout fields, the cross section in D_2 continues to exhibit two smooth peaks. The failure to observe in D_2 any hint of the vibrational structure seen in H_2 is most probably due to the difficulty of resolving the more closely spaced vibrational levels with an electron beam having an intrinsic energy spread comparable with the spacing itself.

It should be noted that the energies of the peaks in Fig. 3 are not necessarily the significant energies for comparison with resonances in other channels. Resonances may be manifested as peaks or dips in the cross sections, depending on the phase shifts involved. Resonances at the same energies in different channels may differ in shape. The energies of the dips in the elastic scattering cross section are compared with the present data in Table I. The dips in the present data appear to

[12] To show that the trapped electron current vanishes completely under these conditions, a check was made in helium. With a potential well, larged trapped-electron peaks appear, as in Ref. 11. With a potential bump, the peaks disappear and no residual negative ion current can be observed.

agree very closely in energy with one series of dips in the elastic cross section observed by Kuyatt *et al.*[2] Because of the uncertainties in assignment of absolute energies, the agreement may be fortuitous. The energy resolution is not good enough in the present experiment to determine whether there is more than one series of resonances in the dissociative attachment.

Some relevant potential energy curves[13] are shown in Fig. 4. The heavy lines represent H_2^- curves. The upper $^2\Sigma_g^+$ state of H_2^- is that calculated by Taylor and Williams.[14] Their calculation places the lowest vibrational level of this state at 11.4 eV.

Either of two qualitatively different mechanisms which have been proposed recently[15,16] would account for the observed resonances. Both mechanisms require a specific arrangement of potential energy curves: an attractive negative-ion state having vibrational levels must lie in the Franck-Condon region at nearly the same energy as a repulsive negative-ion state. These requirements are probably fulfilled by the attractive $^2\Sigma_g^+(\sigma_g 1s)(\pi_u 2p)^2$ and the repulsive $^2\Sigma_g^+(\sigma_g 1s)(\sigma_u 1s)^2$ of H_2^-.

O'Malley[15] has predicted that this arrangement of potential curves could give rise to structure in the dissociative attachment cross section. He pictures the process as a resonant elastic scattering of, or vibrational excitation by, the electron from a vibrational level of the attractive state of H_2^-, followed by ordinary dissociative attachment from the ground state of H_2. The structure produced in dissociative attachment by this mechanism should be identical with the structure observed in resonant elastic scattering or vibrational excitation. The resolution in the present experiment is not sufficient to allow one to determine whether this is the case.

Another explanation has been offered by Taylor, Nazaroff, and Golebiewski.[16] The negative-ion production in the 7- to 11-eV region is considered as due to dissociative attachment through the repulsive $^2\Sigma_g^+$ state of H_2^-. Taylor *et al.* argue, from consideration of the united atom configuration, that the potential curve of

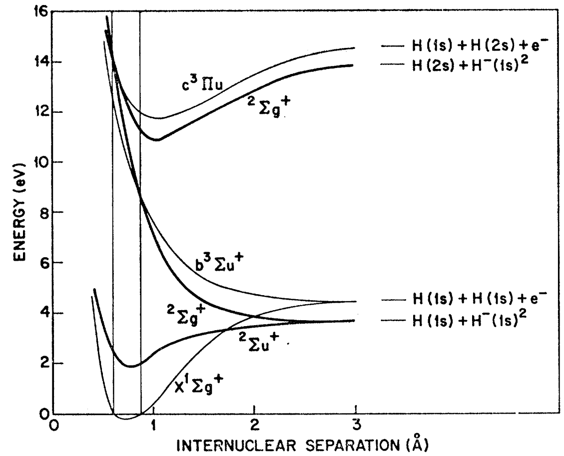

FIG. 4. Potential-energy curves for H_2 and H_2^-. The heavy lines represent H_2^- curves. Sources for the curves are cited in Ref. 13.

this state must cross that of the $b^3\Sigma_u^+$ state of H_2. The large dip appearing at 11.0 to 11.5 eV in the HD and D_2 dissociative attachment cross sections and the small dip in the H_2 cross section presumably occur at the energy of crossing of the two potential curves. At this energy a new channel is opened, e.g., $H_2^-(^2\Sigma_g^+) \rightarrow H_2(^3\Sigma_u^+)+e^-$, with the final products $H+H+e^-$. In addition, the H_2^- repulsive curve is believed to approach closely the quasibound $^2\Sigma_g^+$ state of H_2^-; thus, molecules excited to the repulsive state could undergo inverse predissociation to the quasibound state. Also, molecules excited to the quasibound H_2^- state could predissociate to the repulsive state. Resonances in the dissociative attachment cross section would be expected at the energies of the vibrational levels of the quasibound state. The shapes of the resonances would not necessarily be the same as those of the resonances in other channels.

Various authors[2,16] have suggested the possibility of other H_2^- states lying slightly lower in energy than the $^2\Sigma_g^+$ quasibound state. The existence of more than one negative-ion state in this energy range is indicated by the double series of resonances in the elastic cross section.[2] It would be of interest to repeat the present measurements with higher-energy resolution to determine whether there is more than one series of resonances in the dissociative attachment and whether there is structure below 11.2 eV. Experiments with higher resolution would also yield information on the widths and shapes of the resonances.

ACKNOWLEDGMENT

The authors are grateful to Vincent Galea for his skillful technical assistance.

[13] The curves for the ground state $X^1\Sigma_g^+$ and the repulsive state $b^3\Sigma_u^+$ of H_2 are taken from W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965). The curve for the $c^3\Pi_u$ state is taken from J. C. Browne, *ibid.* **40**, 43 (1964), and adjusted slightly in energy to agree with the experimental term energy value cited therein. The part of the curve for the ground state of the H_2^- ion which lies below the curve for the ground state of the neutral molecule is taken from H. S. Taylor and F. E. Harris, *ibid.* **39**, 1012 (1963); the remainder of this curve is taken from I. Eliezer, H. S. Taylor, and J. K. Williams, Jr., *ibid.* **47**, 2165 (1967). The repulsive H_2^- curve is taken from J. C. Y. Chen and J. L. Peacher, Phys. Rev. **167**, 30 (1968).

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[15] T. F. O'Malley, Phys. Rev. **150**, 14 (1966).

[16] H. S. Taylor, G. V. Nazaroff, and A. Golebiewski, J. Chem. Phys. **45**, 2872 (1966).