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Temporary Formation of H_2^- above the H_2^+ Threshold by Electron Impact*

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The energy-differentiated electron impact spectra of H_2 has been studied near the H_2^+ threshold in a transmission experiment. Eleven structures with spacings characteristic of the $^2\Sigma_g$ state of H_2^- have been found starting at about 13.6 eV. Five of these structures are above the H_2^+ threshold. It is suggested that some of the structure previously found in the cross section for the production of H_2^+ near threshold is due to autoionization of this state of H_2^-.

The experimental arrangement used in the present work is shown schematically in Fig. 1. The essential details of the apparatus with the exception of the construction of the scattering cell and the modulation scheme have been described previously.[1] The present technique is briefly described below and a more complete description of the technique will be given in a later publication.[2,3]

The low-energy electrons from the cathode distribution are eliminated by the application of a dc retarding potential at the electrode *R*. The energy in the interacting region is determined by a ramp generator connected between the cathode

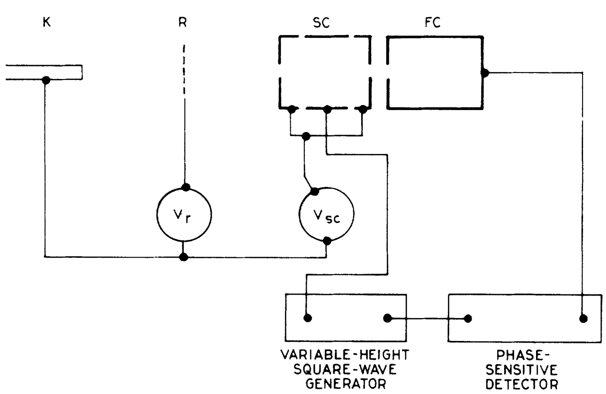

FIG. 1. Schematic diagram of the experiment.

K and the two cylindrical end caps of the scattering cell *SC*. The central cylindrical portion of the scattering cell is insulated from the end caps, and a variable-height square-wave modulation (typically about 55 mV) is applied between the two end caps and the central cylinder. A phase-sensitive detector measures the modulated transmitted current collected by the Faraday cup *FC* in phase with the applied square wave. Electrically, *FC* is at the same potential as the two end caps of the scattering cell. The output signal of the phase-sensitive detector is proportional to the derivative of the transmitted electron current with respect to the interaction energy. Thus only structure in the cross section is observed. The information obtained with this ac detection technique is essentially the same as that obtained by Golden and Bandel using a dc detector and bucking out the slow variation in current due to the slow variation in the total cross section.[4] However, the sensitivity obtained in the present case is much larger. The maximum resolution obtained thus far with the present technique is 45 meV.[2] The technique used to differentiate the transmitted spectra is similar to that recently used by Sanche and Schulz to study resonances in CO and O_2.[5]

The differentiated transmitted current in H_2 is plotted versus electron energy on Fig. 2, for a range of electron energies from 11 to 16 eV, at a pressure of about 5.5×10^{-3} Torr. The energy scale was determined by comparison with the 19.3-eV He resonance in a mixture of He and H_2.[6] The lower-energy series of resonances was first observed,[7] and later resolved into two closely adjacent series,[8] by Kuyatt, Mielzyareck, and Simpson. At the resolution used in the present case, these two series cannot be resolved. However, the data were purposely taken at poor resolution in order to obtain a sufficiently large signal-to-noise ratio so as to observe the smaller effects which have not previously been observed in transmission experiments[4,7-9] because of a lack of a sufficient signal-to-noise ratio. The higher series of resonances beginning at about 13.6 eV was recently found by Weingartshofer, Ehrhardt, Hermann, and Linder[10] by measuring the energy loss and angular distirbution of scattered electrons for various incident energies. Weingartshofer *et al.* designated the associated state of H_2^- as $^2\Sigma_g$. If we use the results of the measurements of Golden and Bandel[4] for the cross-section changes of the lower-energy series of resonances, the largest of the higher-energy series of resonances corresponds to a cross-section change of about 2.5×10^{-19} cm^2.

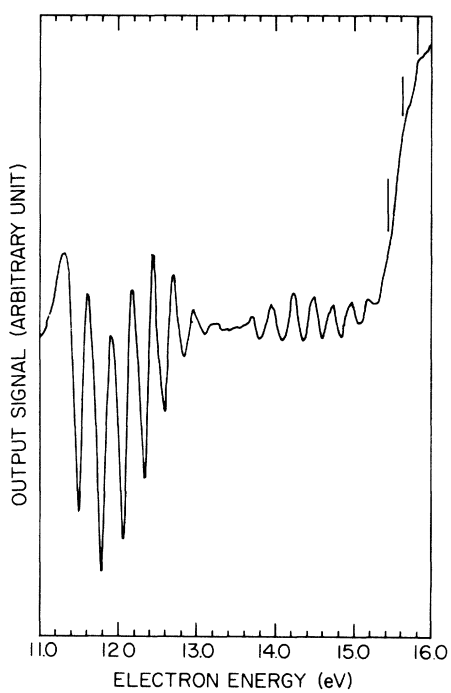

FIG. 2. Differentiated transmitted electron current in H_2 versus electron energy for electron energies from 11 to 16 eV for a pressure of about 5.5×10^{-3}Torr.

Above 15.4 eV the signal begins to rise rapidly as a result of the onset of ionization. Close inspection of the region above 15.4 eV has shown that there are additional structures, three of which are indicated by vertical lines on Fig. 2. Figure 3 shows the higher-energy portion of the curve run at increased gain with an expanded energy scale. The maxima in the signal are indicated by the vertical lines above the curve. Three additional smaller structures in the curve are indicated by the vertical lines below the curve at about 15.59, 15.79, and 16.02 eV. There may be additional structures in the curve but only the ones indicated have been found to be reproducible from run to run. The intersecting straight lines on the figure indicate the method of construction of the positions of the maxima. The positions of the maxima found in this work are listed in Table I. The corresponding spacings are also listed and compared to the spacings found by Weingartshofer *et al.* for the first six of the states.[10] The calculated spacings listed in Table I have been obtained by fitting the data with

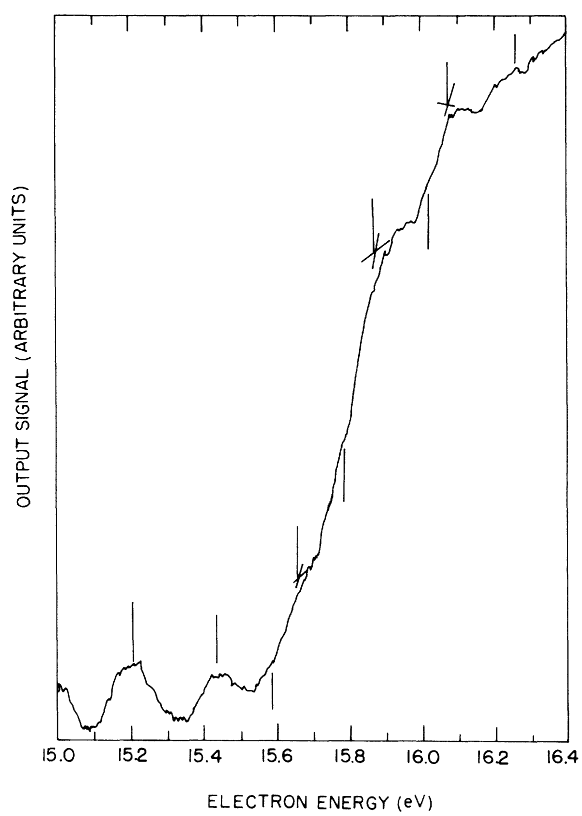

FIG. 3. Differentiated transmitted electron current in H_2 versus electron energy for electron energies from 15 to 16.4 eV for a pressure of about 5.5×10^{-3} Torr.

TABLE I. Observed positions of resonances in H_2, and a comparison between observed and calculated spacings.

v	Positions (maxima) (eV)	Measured spacing (eV)	Calculated spacing (eV)[a]	Measured spacing (eV)[b]
0	13.62			
		0.29	0.29	0.30
1	13.91			
		0.28	0.28	0.27
2	14.19			
		0.27	0.27	0.27
3	14.46			
		0.26	0.26	0.23
4	14.72			
		0.25	0.25	0.22
5	14.97			
		0.24	0.24	...
6	15.21			
		0.23	0.23	...
7	15.44			
		0.22	0.22	...
8	15.66			
		0.21	0.21	...
9	15.87			
		0.20	0.20	...
10	16.07			
		0.19	0.19	...
11	16.26			

[a]Eq. (1) [b]Ref. 10

an anharmonic-oscillator term scheme. The resulting term scheme is given by

$$T(v) = [0.30(v+\tfrac{1}{2}) - 0.005(v+\tfrac{1}{2})^2]\ \text{eV}. \quad (1)$$

The calculated and measured spacings can be seen to agree to two significant figures.

The measurements of the ionization of H_2 near threshold by McGowan *et al.*[11] showed structure which was attributed to autoionization. It had previously been suggested that the ionization might proceed through the temporary formation of H_2^-,[12]

$$H_2 + e^- \to H_2^- \to H_2^+ + 2e^-.$$

McGowan *et al.*[11] rejected that possibility because they found no resonance peaks in the ionization curve similar to those found in the elastic cross section for H_2.[8,9] However, the resonances just below ionization had not been observed at that time. The smallest changes in cross section above ionization due to vibrational resonances can be estimated to be of the order of 10^{-20} cm^2 from the cross-section changes estimated for the series of vibrational resonances at about 11 eV.[4] Such cross-section changes would thus appear to be significant factors in the measurement of the cross section for ionization near threshold. The other features in the data at 15.59, 15.79, and 16.02 eV are most probably due to autoionization. These features are reproducible from run to run and have been identified as major peaks in the photoionization spectra of Dibeler, Reese, and Krauss,[13] which only show up as small changes of slope in this work.

Since energy analysis is not available as yet for these new features, the possible decay schemes of the higher members of the series are not known. However, the heights of the peaks appear to decrease monotonically with increasing v for $v > 3$ giving support to the premise that the decay scheme observed previously for the first five members of the series is also correct for the higher members.[10]

Since the ionization cross section is determined by normalizing the ion current to the transmitted electron current,[14] it is suggested that the ionization threshold be reinvestigated with special attention to measurement of the transmitted electron current and positive ion current separately.

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[6]It should be noted that the positions of the maxima and minima in this work are at the positions of the inflection points in the usual transmission experiment. The shift in the absolute energy scale necessary to compare the two types of experiments for these resonances amounts to about 70 meV at this energy resolu-

tion.
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Small-Angle Charge Exchange in $He^+ + N_2$ Collisions*

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Small-angle charge-exchange measurements are made on the $He^+ + N_2$ collision in an energy range from 0.50 to 3.00 keV and in an angular region out to 2.0°. The experimental results directly show that charge exchange plays a major role in the collision. At each energy the probability of charge exchange increases monotonically with increasing angle of scattering and then attains a relatively constant value with further increase in angle.

A great deal of experimental and theoretical effort has gone into the study of charge-exchange scattering. Such scattering plays an important role in many phenomena; and in addition, since charge-exchange processes are generally inelastic, experimentally obtained results may serve as an important guide in the development of inelastic-scattering theory. While ion-atom charge exchange is understood for select systems (examples are the resonant case or when a curve crossing is responsible), much less is known about ion-molecule charge-exchange. To date the velocity dependence of the total cross section has been reported by many laboratories for a large variety of ion-molecule combinations; and although a great deal of information about charge exchange is extractable from such experiments, much more may be learned about the dynamics of the collision from studies of the angular distributions of the scattered charge-exchanged atoms. This paper presents results on the probability of charge exchange in small-angle scattering of He^+ by N_2. Recent experimentally determined total-cross-section results for this collision may be found in an article by Koopman,[1] while Inn[2] has provided information on optical excitations resulting from these collisions.

Figure 1 shows the experimental arrangement.[3] Helium ions are formed in an electron-impact ion source A, are extracted from the source at B, and focused at a suitable point in front of a mass spectrometer magnet D by ion optics at C. The mass-analyzed beam passes through additional ion optics E and is collimated by two small holes F and G before reaching the scattering chamber which is supplied with appropriate target gas. The beam scattered through an angle θ passes through holes H and I into a parallel-plate electrostatic analyzer terminated by separate multipliers for the neutral and ion signals. The half width at half-maximum is typically 0.07° for the incident beam. In this experiment the analyzer voltages are set to transmit only those ions with energies appropriate to the scattered He^+ beam. In addition the slits on the analyzer are made sufficiently wide to ensure collection of almost all the He^+ ions independent of small energy losses. The results are obtained by finding the ratio of neutral to total scattered signal at each of the angles investigated. Although the ratio of scattered neutral to scattered total signal gives the probability of a scattered particle being neutral, it is reasonable to assume that at the angles investigated this is the probability of charge exchange (since forward scattering of N_2 is unlikely). The experimental results contain information on the scattered beams as a function of angle and also on the probability of charge exchange. Although the measured angular dependence of the scattered ion and neutral beams may depend on apparatus conditions (beam stability,