tron beam. Within the statistics, this source of error was eliminated by properly degassing the electron gun. An estimate of systematic errors such as instrument inaccuracies, nonlinearities, etc., gives between +10 and -2%from these sources.

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PHOTOELECTRON SPECTROSCOPY WITH A SPHERICAL ANALYZER. THE VIBRATIONAL ENERGY LEVELS OF H₂⁺

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This Letter reports the use of a spherical energy analyzer to study the photoelectron-energy distribution in an ionized gas. This has enabled us to measure the separations of the first five vibrational energy levels of $H_2^{+(2\Sigma_g^+)}$ and the relative probabilities of ionization to them.

The photon source is a microwave discharge in helium, which emits essentially 584 Å (21.21 eV) in the energy range above the hydrogen ionization potential. To a very close approximation, the photoelectrons will have kinetic energies equal to 21.21 eV minus the ionization potential of hydrogen. If H_2^+ can be formed in more than one vibrational state, we expect a group of photoelectrons corresponding to each. The differences between the group energies should give the vibrational level spacing, and the relative intensities will be proportional to the transition probabilities from $H_2({}^{1}\Sigma_g^{+})$ for 584Å radiation.

In this work we have restricted ourselves to observations on the ${}^{2}\Sigma_{g}^{+}$ ground electronic

state.

All previously reported work on photoelectron kinetic-energy distributions in gases has been done using cylindrical-grid energy analyzers.¹⁻⁴ Although vibrational structure can be clearly seen in some differential retarding curves,⁴ the resolution has not been sufficient to permit accurate measurements on vibrational energylevel spacings or transition probabilities.

The low resolution stems primarily from the photoelectron spatial distribution being close³ to that predicted theoretically,⁵ i.e. dependent on $\sin^2\theta$ (θ = angle between photon and electron). Since retarding fields using cylindrical grids affect only the radial component of kinetic energy, electrons expelled over a considerable range of angles will cause a smoothing out of what would be a stepped retarding curve for electrons ejected in one direction only.

To overcome this difficulty we have built an analyzer wherein photoelectrons are produced in a small volume at the center of a spherical grid system, so that initial ejection is always



FIG. 1. Diagram of the microwave photon source and the spherical photoelectron energy analyzer.

normal to the retarding field. This gives rise to greatly improved resolution, as our results show (see Fig. 2). Figure 1 shows a diagram of the apparatus, a full description of which will appear elsewhere.

Several groups⁶⁻⁸ have recently studied the threshold ionization of hydrogen by using essentially monoenergetic electron bombardment. At this time, however, it is by no means certain how much preionization, rotational excitation, and other factors are contributing to the ionization efficiency curves. Much of the data appears to be contradictory.

Since preionization completely obscures H_2^+ vibrational structure in the photoionization curves of Cook⁹ and Dibeler,¹⁰ and a spectrum of H_2^+ has never been observed optically (probably since the stable excited states have quite low dissociation energies), the approach of photoelectron spectroscopy, where preionization may be avoided, shows great promise.

A photoelectron retarding curve for H_2 is shown in Fig. 2. We have established the threshold energy for H_2^+ as 15.44 ± 0.01 eV in a subsidiary experiment. The accurately known ionization potential of argon is used to fix the energy scale on a retarding curve for a hydrogenargon mixture.

The adiabatic ionization potential for H_2 is



FIG. 2. Tracings of a photoelectron retarding curve for hydrogen obtained with both cylindrical and spherical retarding grids. Clearly the photoelectron groups are resolved much better with the latter arrangement, where it is possible to measure the relative intensities of the groups and so obtain relative transition probabilities.

known to be 15.427 eV so our threshold must refer to the 0-0 transition.

In Table I we compare the threshold energies of the five energy groups clearly visible in Fig. 2 with the calculated¹¹ vibrational spacings of H_2^+ and the electron-impact data of Kerwin.⁷ The three sets of data are in very good agreement.

The relative intensities of the photoelectron groups are measured directly from the retarding curve, and they are taken to correspond to the relative transition probabilities from $H_2(v=0)$ to various vibrational states of H_2^{+} . In Table II we compare our data with the Franck-Condon factors recently calculated by Wacks.¹¹ We estimate the uncertainty in our figures to be ±0.1. The electron impact results of Kerwin, Marmet, and Clarke⁷ are included for comparison, although, as already mentioned,

Table I. H_2^+ vibrational energy levels.

	Vibrational interval (eV)				
Levels	This work ^a	Electron impact ^b	Calculated ^C		
0-1	0.27	0.268 ± 0.01	0.269		
1-2	0.26	0.266	0.254		
2-3	0.24	0.235	0.239		
3-4	0.22	0.245	0.223		
4-5	0.21	0.20	0.208		

 a Each is the mean of eight determinations, and each is reproduceable to 0.01 eV.

^bSee reference 7.

^cSee reference 11.

Table II.	Relative transition probabilities for	
$H_2(1\Sigma_{cr}^+, v')$	$= 0) \rightarrow H_2^+(^2\Sigma_{\sigma}^+, v = 0-5).$	

Transition	Expe This work	rimental Electron impact ^a	Theoretical Franck-Condon factor ^b
0-1	0.47	0.53	0.47
0-2	0.83	0.91	0.89
0-3	1.00	1.00	1.00
0-4	0.78	0.35	0.87
0-5	0.71	0.35	0.65

^aSee reference 7.

^bSee reference 11.

it is not known to what extent preionization is contributing to the ion-efficiency curve. As the electron-impact 0-4 and 0-5 probabilities seem to be low, it appears that preionization is relatively more important at the lower levels.

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SATURATION OF A RESONANT OPTICAL DOUBLE-QUANTUM TRANSITION

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We have observed production of violet and infrared radiation from potassium vapor which can be attributed unambiguously to a resonant double-quantum absorption transition. The output of a giant-pulse ruby laser is used to generate stimulated Stokes emission in the near infrared. The two simultaneous pulses are employed then to excite potassium atoms in the ground state $(4s_{1/2})$ to an excited state $(6s_{1/2})$. The excited atoms subsequently cascade down, and intense infrared (6s-5p) and violet (5p-4s)radiation is observed. The fact that both the red ruby and the Raman-Stokes pulses are required for the excitation is a clear indication of the double-quantum process. We present theoretical arguments for the saturation of the excitation, and then describe the experimental arrangement.

Multiple quantum transitions were discussed first by Goeppert-Mayer¹ in 1929, and were observed first in the laboratory in the microwave region by Hughes and Grabner.² The the-

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ory of these transitions occuring under the influence of highly coherent applied fields has been discussed in the experimental papers 2,3 and in detail by Salwen,⁴ Hack,⁵ Javan,⁶ and others.⁷ The observation of double-quantum transitions in the optical region of the spectrum has been made possible by the development of lasers, and the simple energy-level scheme of cesium vapor was employed in the experiment of Abella,⁸ which followed the first observation of double-quantum absorption into a broad band in an inorganic crystal.⁹ Subsequently, such absorption has been found in a wide variety of materials: other doped inorganic crystals,¹⁰ organic crystals,¹¹ and organic liquids.¹² Saturation of the absorption transition has not been possible. Only in part is the absence of saturation a consequence of the breadth of the upper levels. Another crucial factor in determining the saturation is the position of the intermediate state with respect to the quantum energies in the radiation fields. Yatsiv¹³ has

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