Measurement of Threshold Electrons in the Photoionization of H_2 and D_2^*

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Measurements of electrons produced in the photoionization of H_2 and D_2 are reported. The experimental technique employs a differential electron-energy analyzer to detect photoelectrons produced with nearly zero initial kinetic energy ($\lesssim 0.1$ eV). By varying the photon energy a spectrum of "threshold" photoelectrons is recorded exhibiting the vibrational structure of the H_2^+ and D_2^+ ions. From these spectra values of $I(H_2)$, $I(D_2)$, $\omega_e(H_2^+)$, $\omega_e(D_2^+)$, $\omega_ex_e(H_2^+)$, and $\omega_ex_e(D_2^+)$ are derived. In favorable cases the relative vibrational transition probabilities are also reported and compared with theoretical predictions as well as with other experiments. Some disagreements are noted in comparing the results obtained by this method with theoretical Franck-Condon factors based on potential curves appropriate to nonrotating molecules. It is suggested that the vibration-rotation interaction should be taken into account in calculations pertaining to electronic transitions in light molecules.

I. INTRODUCTION

Photoionization experiments in H₂ have revealed a complex spectrum in the energy region above ionization threshold.^{1,2} This structure has been interpreted, following Beutler,³ in terms of preionization of excited hydrogen molecules. That is, in addition to the direct ionization process

$$H_{2}(X \, {}^{1}\Sigma_{g}^{+}, v''=0) + h\nu \rightarrow H_{2}^{+}(X \, {}^{2}\Sigma_{g}^{+}, v') + e^{-}, \quad (1)$$

one must consider also the autoionization process

$$\mathbf{H}_{2}(X \, {}^{1}\Sigma_{\boldsymbol{\varrho}}^{+}, \boldsymbol{v}^{\prime\prime} = 0) + h\boldsymbol{\nu} \rightarrow \mathbf{H}_{2}^{*} \rightarrow \mathbf{H}_{2}^{+}(X \, {}^{2}\Sigma_{\boldsymbol{\varrho}}^{+}, \boldsymbol{v}^{\prime}) + \boldsymbol{e}^{-},$$

$$\tag{2}$$

where H₂* may refer to any of several known states of the molecule⁴ which are energetically degenerate with the ionization continuum.⁵ While the process represented in Eq. (1) is expected to vary smoothly with excess photon energy, the second process is known to have a resonance character. That is, ionization occurs only at those discrete photon energies which correspond to formation of the intermediate excited state. Recently there has been direct experimental confirmation of this interpretation.⁶ The extensive occurrence of autoionization in H₂ has been the dominant feature of

experimental observations of the probability of photoionization when the photon energy is varied. As a consequence, these experiments have yielded little information concerning the detailed behavior of the cirect ionization process and no information concerning the structure of H_2^+ .

Recent studies of photoelectron energy spectra have altered the situation.^{7,8} Using a fixed photon energy well in excess of the minimum ionization energy, measurements of the kinetic-energy distribution of photoelectrons produced in H₂ have revealed the vibrational structure of H_2^+ . These experiments also indicate qualitative agreement between theory and experiment. Discrepancies between theory and experiment have been found in the case of the apparent relative probabilities of transitions to distinct vibration states of the ion. One possible explanation of this result is that Franck-Condon factors based on potential curves appropriate to a nonrotating molecule do not describe the experimental situation. An alternative explanation would take into account the variation of cross section above the thresholds for formation of the different vibrational states of the ion.7

A different experimental approach is possible. In particular, one can vary the photon energy and observe electrons of fixed initial kinetic energy T only. Such electrons are produced at photon energies $T+I_j$ where I_j is the energy of the *j*th ionization limit. This paper reports results obtained with T=0 in which case the number of electrons produced at the photon energy I_i is proportional to the cross section for that threshold. To a first approximation the results are expected to be independent of variations of the cross section with excess energy. Data are presented for H_2 , para- H_2 and D_2 . Results obtained using this technique for the rare gases Ar, Kr, and Xe were reported in a previous publication.9

^{*}Supported in part by a grant from the National Science Foundation and in part by the Advanced Research Projects Agency.

[†] Submitted to the Department of Physics, The University of Chicago, in partial fulfillment of the requirements for the Ph.D. degree.

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¹ V. H. Dibeler, R. M. Reese, and M. Krauss, J. Chem. Phys. 42, 2045 (1965).

²G. R. Cook and P. H. Metzger, J. Opt. Soc. Am. 54, 968 (1964).

³ H. Beutler and H.-O. Junger, Z. Physik 100, 80 (1936).

⁴ A. Monfils, J. Mol. Spectry. 15, 265 (1965).
⁵ For simplicity, we neglect rotational states in this qualitative discussion. Of course, whether or not a specific excited state of the molecule will in fact decay by preionization is determined by the appropriate selection rules. These pertain to the complete set of molecular quantum numbers, including rotational symmetry. ⁶ P. H. Doolittle and R. I. Schoen, Phys. Rev. Letters 14, 348

^{(1965).}

⁷ D. C. Frost, C. A. McDowell, and D. A. Vroom, Proc. Roy.

Soc. (London) A296, 566 (1967).
 ⁸ D. W. Turner and D. P. May, J. Chem. Phys. 45, 471 (1966).
 ⁹ D. Villarejo, R. R. Herm, and M. G. Inghram, J. Chem. Phys. 46, 4995 (1967).



FIG. 1. Schematic diagram of the apparatus. The planes of the ultraviolet monochromator and the energy analyzer intersect at right angles along the line AA. In order to represent the apparatus in this drawing these planes have been shown as if they coincide.

II. EXPERIMENTAL

Experiments were performed using a vacuum monochromator and an electrostatic energy analyzer. A schematic diagram of the arrangement is shown in Fig. 1. Radiation produced in the light source is dispersed by a monochromator and bombards the target gas. Photoelectrons produced in the ionization zone are accelerated and then analyzed. The analysis energy is chosen to equal the total acceleration energy.

A. Light Source and Monochromator

Hopfield continuum radiation was produced in a pulsed high-voltage discharge in He as previously described.¹⁰ The light source is equipped with a fast two-stage differential pumping assembly and is mounted on a 1-m Seya–Nanioka vacuum-ultraviolet mono-chromator. The monochromator design is equivalent to that described by Hurzeler *et al.*¹¹ except that no windows are used. A 1200-line/mm platinum-coated grating, blazed for 960 Å as used in this mounting, provides a first-order reciprocal dispersion of ~ 8

Å/mm. Observation of the profile of an isolated emission line showed a triangular peak shape with bandwidth (full width at half-maximum) approximately 2.5 Å.

Upon emerging from the monochromator exit slit, the photon beam passes through the ionization zone and is intercepted by the photon monitor. This device, which has been previously described,¹¹ consists of a clean inconel surface which yields photoelectrons when bombarded by sufficiently energetic quanta. The current of electrons leaving this surface is measured with a Carv Model 31 vibrating-reed electrometer whose output is displayed on a strip-chart recorder. The photocurrents measured are in the range of 1×10^{-13} to 2×10^{-11} A. Figure 2 shows a recorder tracing of the emission continuum used in these studies. Of special interest is the absence of atomic emission lines in the region 600-1000 Å. The often present impurity Ne I lines at 743.7 and 735.9 Å were eliminated by using commercial tank helium preselected for specially low Ne content.

The spectrum shown in Fig. 2 does not include a necessary correction for the variation of photoyield with photon energy. This correction was obtained by comparing spectra like that shown in Fig. 2 with spectra recorded using a sodium salycilate coated photomultiplier as detector. By assuming that the

¹⁰ D. Villarejo, R. R. Herm, and M. G. Inghram, J. Opt. Soc. Am. **56**, 1574 (1966).

¹¹ H. Hurzeler, M. G. Inghram, and J. D. Morrison, J. Chem. Phys. **28**, 76 (1958).



FIG. 2. Time-averaged photocurrent measurement of the Hopfield emission continuum. This spectrum has not been corrected for the wavelength sensitivity of the detector (see text). The peaks near 600 and 670 Å are believed to be due to the He₂ molecule. The He₁ 584.3-Å line and impurity H 1025.7-Å line are shown.

relative response of the latter detector is independent of wavelength in this region¹² one can obtain a measure of the wavelength sensitivity of the photon monitor used in these experiments. Over the region 685-810 Å, which encompasses the entire range of photon energies used in the experiments reported in this paper, the relative response of the inconel surface was determined in this manner to vary by less than 5%.

By admitting selected rare gases to the flowing He stream, atomic emission lines of known character could be generated to calibrate the wavelength scale. It is believed that the absolute wavelength scale is accurate to better than 0.5 Å and that the relative scale is accurate to 0.3 Å.

B. Ionization Chamber, Energy Analyzer, and Detector

As indicated in Fig. 1, a series of parallel 3.0- by 4.8-cm plates, spacing 5 mm, provide uniform field regions to draw out and accelerate electrons produced by photoionization of the target gas. A 0.7- by 1.0-cm aperture in each plate permits electrons to pass through. By using 0.0005-in.-diam W grid wires spaced 100/in., the uniform fields could be maintained in the aperture region. Upon emerging from the draw-out and acceleration zone, electrons are focused by means of an electrostatic quadrupole doublet lens13 onto the entrance slit of the energy analyzer.

The 127° cylindrical energy analyzer¹⁴ has a mean

radius of 4.3 cm and 0.5-mm by 1.5-cm slits. For a slit of zero length the resolving power of this system is approximately

$$W/\Delta W \sim 86,$$
 (3)

where ΔW is the transmitted energy bandwidth for electrons with energy W. For slits of finite length a somewhat smaller resolving power is expected.

Upon emergence from the analyzer exit slit, electrons are further accelerated and focused onto the first dynode of a 16-stage Cu-Be electron multiplier. Output pulses from the multiplier are electronically amplified and then counted with a fast scalar.

Since comparatively small electron acceleration and analysis energies are used ($\sim 5 \text{ eV}$), it was necessary to attenuate stray magnetic fields. By using three pairs of \sim 0.5-m-radius Helmholtz coils and annealed mumetal shielding¹⁵ the residual field along the mean electron trajectory was reduced to less than 0.010 G.

C. Method

Observation of threshold electrons (initial kinetic energy approximately equal to zero) is accomplished by adjusting the analysis energy to correspond to the total electron-acceleration energy. Once this condition is achieved, the ratio of electron count rate to photon flux is determined as a function of photon energy. The expected dependence of this ratio R(u) on photon energy u can be obtained by considering instrumental

¹² J. A. R. Samson, J. Opt. Soc. Am. 54, 6 (1964).
¹³ H. A. Enge, Rev. Sci. Instr. 30, 248 (1959).
¹⁴ A. L. Hughes and V. Rojansky, Phys. Rev. 34, 284 (1929).

¹⁵ Allegheny Ludlum Steel Corp., Pittsburgh 22, Pa,



FIG. 3. Convolution of instrument resolution function with the photoionization cross section. (a) Monochromator resolution function with bandwidth equal to (b) Energy-analyzer resolution Δu . function with bandwidth equal to ΔW . As used in this instrument only half of the resolution function is effective since the peak of $f(E, \Delta W)$ is set at zero. (c) Step-function cross section multiplied by resolution function of (b). Solid line corresponds to $\Delta W = \Delta u$ and dashed line to $\Delta W = 3\Delta u$. (d) Convolution of monochromator resolution function with product shown in (c). Solid line corresponds to $\Delta W = \Delta u$ and dashed line to $\Delta W = 3\Delta u$.

features in conjunction with known properties of the energy dependence of photoionization cross sections. Simple considerations indicate that

$$R(u) = A \int \sigma(E) f(E, \Delta W) g(E, u, \Delta u) dE, \quad (4)$$

where A is an instrumental constant, $\sigma(E)$ is the photoionization cross section at the photon energy E, $f(E, \Delta W)$ is the energy-analyzer transmission function of bandwidth ΔW , and $g(E, u, \Delta u)$ is the monochromator transmission function of bandwidth Δu . This integral may be evaluated for the idealized conditions illustrated in Fig. 3. Both monochromator and energyanalyzer transmission functions are regarded as triangular [see Figs. 3(a), 3(b)]. To a first approximation the cross section for photoionization to a single ionic state may be represented by a Heaviside function¹⁶ as shown in Fig. 3(c). That is, the cross-section is zero below the ionization limit, discontinuous at the limit, and independent of energy above the limit. Since the energy analyzer is set to correspond to ionization onset, the product of $\sigma(E)$ and $f(E, \Delta W)$ is the right triangle shown in Fig. 3(c). Convolution of $g(E, u, \Delta u)$ with this product results in the peak shown in Fig. 3(d). The solid line corresponds to the case $\Delta W = \Delta u$, while the broken line is the case $\Delta W = 3\Delta u$. Qualitatively, we may regard the result of this type of electron-energy analysis to be differentiation of the curve obtained without energy analysis.

As is clear from Fig. 3, the energy coordinate of the peak maximum is slightly larger than the value of the ionization limit. This shift, which we define as ΔE , depends on the ratio $\Delta W/\Delta u$. In the case $\Delta W=0$ we may represent $f(E, \Delta W)$ as a δ function centered at the ionization threshold and the convolution integral becomes

$$R(u) = A\sigma(I_0)g(I_0, u, \Delta u), \qquad (5)$$

where I_0 is the energy of the ionization limit. That is, in this limiting case the peak is centered at the ionization limit and has the shape of the monochromator transmission function. Hence ΔE is bounded according to

$$0 < \Delta E < \Delta u,$$
 (6)

where the upper bound applies strictly when $\sigma(E)$ may be represented by a Heaviside function or when $\sigma(E)$ decreases with increasing photon energy. The above features, including the magnitude of the peak shift, were confirmed and reported in a previous publication.⁹

¹⁶ On this point see, for example, the discussion in J. D. Morrison, J. Appl. Phys. **28**, 1409 (1957).



Fig. 4. Threshold photoelectron in H_2 . The analysis and acceleration energy used was 6 eV.

D. Procedure

Commercial-research-grade gases¹⁷ were admitted through a bakeable, glass-metal, high-vacuum, gashandling system (volume \sim 7 liters). Using a flow rate of roughly 1 µliter/sec, a sample pressure of 1×10^{-5} torr at room temperature could be maintained in the source region. The observed electron count rate was proportional to sample pressure up to 1×10^{-4} torr and was also proportional to photon intensity at constant sample pressure. For the experiments reported in this paper a sample pressure of about 1×10^{-5} torr was used.

A background count rate ≤ 30 counts/min was observed. This count rate was found to be a linear function of photon intensity although nearly independent of wavelength and background gas pressure for source pressures up to 1×10^{-5} torr (ion-gauge reading). Of this rate, about 2 counts/min were found to be attributable to cosmic rays and the remainder are believed to arise from photoelectrons produced from surfaces in the ionization zone.

The scattered-light background was estimated by measurement of the average apparent intensity in the wavelength region near 400 Å. The observed intensity attributed to scattered light was found to be about 0.2% of the peak continuum intensity near 825 Å and was systematically subtracted from all intensity measurements in the region of interest.

With the analysis energy adjusted to correspond to the total acceleration energy, the electron count rate and photon intensity were simultaneously measured on a point-by-point basis. Average wavelength intervals of 0.5 Å were used. Peak count rates up to $10^3/\text{min}$ were obtained when using 3-eV acceleration and analysis energy. In the limit of zero-energy analyzer bandwidth (δ function) the angular distribution of ejected photoelectrons cannot influence measurements using this technique. This follows from the fact that, in this idealized limit, only electrons with zero initial kinetic energy would be detected. The actual angular distribution is unknown and its effects cannot be accurately taken into account. It is believed that the experimental test of the observations (such as variation of drawout field strength) suggest that possible effects of this distribution are not significant. The energy-analyzer bandwidth was varied by changing the acceleration and analysis energy as expressed in Eq. (3). However, it is important to note that for a fixed choice of these parameters all electrical potentials in the instrument are fixed. Only the photon energy is varied. The electron-collection efficiency is believed to be fixed and independent of photon energy under these conditions.

III. RESULTS AND INTERPRETATION

A. Hydrogen

Figure 4 shows results obtained in H_2 when using 6-eV acceleration and analysis energy. The observed structure is interpreted as arising from production of

¹⁷ Reagent-grade H₂ furnished by The Matheson Co., Joliet, Ill. was stated to have a maximum impurity level of 3 ppm; C.P.grade D₂ furnished by Air Products and Chemical Co., Allentown, Pa. was specified to have a minimum purity of 99.5%.



FIG. 5. Dependence of peak position and amplitude on excess analysis energy for fixed acceleration energy. The behavior of the Kr⁺ ${}^{2}P_{1/2}$ peak and of the indicated peaks in H₂, where v is the apparent vibrational quantum number of the ion.

threshold-energy electrons in forming H_2^+ in each of several vibrational levels. Nine such levels are clearly indicated by the data. The observed peaks may be labeled according to the interpreted vibrational quantum number of the residual H_2^+ beginning with v=0for the peak near 803.5 Å. Additional peaks at 784 and 797 Å are interpreted as arising from the production of low-energy electrons in the autoionization of electronically excited H_2 formed by the absorption of radiation at those wavelengths. Such autoionizing states will be detected if the energy of the released electron is sufficiently small so as to fall within the energy-analyzer bandwidth. The peak at 797 Å could be produced by autoionization of the $B'' \, {}^{1}\Sigma_{u}^{+}$, v'=5 level or the $D^{1}\Pi_{u}$, v' = 7 level of H_{2} while the peak at 784 Å could be produced by the $D' \, {}^{1}\Pi_{u}, v' = 5$ level.⁴

Possible ambiguities of interpretation can be at least partially resolved experimentally in the following manner. Instead of tuning the analysis energy to correspond to the acceleration energy, the analyzer can be adjusted for the acceleration energy plus some small increment ϵ . With these settings a sweep of the photon energy should show a shift in the peak position if the peak corresponds to a direct ionization transition. Figure 5 illustrates this behavior for the isolated ${}^{2}P_{1/2}$ state of Kr⁺. The peak shift as a function of analyzer excess energy behaves qualitatively as expected, i.e., the magnitude of the peak shift asymptotically approaches the magnitude of the excess analysis energy as the latter increases Also shown is the decrease of the peak amplitude as a function of analyzer excess energy reflecting the decreased instrument collection efficiency for electrons of appreciable initial kinetic energy. The application of this technique to the intense peaks in the hydrogen spectrum is also shown in Fig. 5. The behavior of the peaks identified with v=0 and v=2 is clearly quite different than the behavior of the peaks labeled v=3, 4, 5. The absence of a wavelength shift¹⁸ for the peak corresponding to v=0 is interpreted as showing that the predominant contribution to this peak is from low-energy electrons produced by autoionization of electronically excited hydrogen molecules. For the peak corresponding to v=2 the shift ΔE is much larger than expected and the variation of peak position with excess electron energy is again consistent with autoionization as an important contribution. Moreover, the amplitude of this peak increases with increasing analysis energy reaching a maximum at roughly 0.080-eV excess electron energy. The amount of the peak shift is very nearly 0.076 eV, corroborating the former value. The wavelength position of the peak could correspond to autoionization of the as yet unreported $D' \Pi_u$, v'=6 level of H_2 .⁴ In rather sharp contrast, the peaks labeled v=3, 4, 5 clearly follow the pattern shown for the isolated ionic state of Kr⁺ and is interpreted as supporting the view that direct ionization is the predominant contribution to these peaks.

The behavior of the peak amplitudes with analyzer excess energy shows, independently, evidence supporting the same conclusions. The relative amplitudes

¹⁸ Wavelength values for the expected thresholds were calculated using a preliminary experimental value of the ionization potential reported by W. A. Chupka; namely, $I(H_2) = 124400$ cm⁻¹. This value was quoted in his invited paper: W. A. Chupka, Bull. Am. Phys. Soc. **12**, 273 (1967). Recently, the interpretation leading to that value has been modified on the basis of further experimental evidence [W. A. Chupka (private communication)].



F16. 6. Threshold photoelectron spectrum in H₂. The analysis and acceleration energy used was 3 eV.

of the peaks corresponding to v=3, 4, 5 change by less than 15% when ϵ changes from 0 to 0.16 eV. In contrast, the relative amplitude of the peak corresponding to v=0 with respect to the peak labeled v=3 decreases from 1.8 to 0.5 for the same range of ϵ and continues to zero as ϵ increases further. Large variations in the relative amplitude of the v=2 peak with respect to the v=3 peak are also observed when ϵ is varied. From these and other similar results it is concluded that the peaks corresponding to r=-3, 4, 5, 6 arise from direct transitions while the peaks labeled v=0, 2 are influenced by contributions from autoionizing states. Measurements for the peak corresponding to v=1 were not possible since the spectrum in this region becomes dominated by the peak at 784 Å as ϵ increases from zero. Inasmuch as this latter peak does not show a shift with increasing ϵ , a substantial contribution of autoionization to the $\tau = 1$ peak is indicated.

To further test these conclusions the relevant portion of the H₂ spectrum was measured using 3-eV acceleration and analysis energy which, by Eq. (3), halves the energy-analyzer bandwidth. The results are shown in Fig. 6. The smaller "valley-"to-peak ratio in this curve as well as the further suppression of the autoionizing peaks at 797 and 784 Å illustrate the improved resolution. The qualitative features of the spectrum are not fundamentally changed. That is, the peaks corresponding to v=3, 4, 5, 6 of the ion show rather similar relative amplitudes as compared with the spectra obtained using 6-eV acceleration and analysis energy. On the other hand the peaks corresponding to v=0, 1, 2 have somewhat smaller amplitudes relative to the v=3 peak. These features are wholly consistent with the results expected on the basis of the experiments using excess analysis energy.

A further test of the relative amplitudes was also effected. In order to achieve a wholly different rotational population of the neutral molecule, a threshold photoelectron spectrum was recorded in para-H2. A sample of para-H₂ was obtained by evaporation of aged liquid hydrogen. To minimize conversion to ortho-H2 the sample reservoir was directly connected to a liquidhydrogen Dewar and was continuously pumped. The sample inlet branch leading to the ionization source completed a "tee" configuration. In this way freshly evaporated para-H₂ could be continually maintained in the sample reservoir. Results obtained using 3-eV acceleration and analysis energy are shown in Fig. 7. Qualitatively the spectrum is very much like that obtained in normal H₂ although the peak corresponding to v=0 of the ion is somewhat reduced. Otherwise there are no pronounced effects which can be attributed to the drastically altered rotational population of the initial state.

In a separate series of experiments the amplitudes only of each of the maxima corresponding to v =1, 2, 3, 4, 5, 6 of the ion were determined. The acceleration and analysis energy was 3 eV. The relative amplitudes of the peaks labeled v=3, 4, 5, 6 were found to be independent of instrumental parameters within the available range of variation. Specifically, variation of the drawout field, at constant acceleration energy, over the range 0.2 to 3.0 V/cm produced no change in



FIG. 7. Threshold photoelectron spectrum in para-H₂. The analysis and acceleration energy used was 3 eV.

relative peak heights. The same ratios were obtained when the quadrupole focusing system was rendered inoperative. The results, normalized to the peak corresponding to v=3 of the ion, are shown in Table I. Also shown are the wavelengths of peak maxima and peak intervals expressed in electron volts. Because the peak at 803.7 Å is predominantly due to very lowenergy electrons produced by autoionizing states, meaningful measurements of peak amplitude were not possible. For similar reasons, only upper bounds for the relative amplitudes of the v=1, 2 peaks can be given. The quoted errors for the peak amplitudes are somewhat larger than the indicated measurement precision and take into account certain features of the data. First, the peaks are not completely resolved, i.e., the valleys between peaks do not reach the base line. Second, the relative areas contained by the peaks can be regarded as the quantities of primary interest. Finally, the fixed 2.5-Å monochromator bandwidth corresponds to a changing energy bandwidth according to the relation

$$\Delta u = (u/\lambda) \,\Delta \lambda = (C/\lambda^2) \,\Delta \lambda. \tag{7}$$

With respect to the peaks corresponding to v=3 and v=6 this effect represents an 8% change in energy bandwidth.

A possible alternate interpretation of the observed relative intensities has been suggested to the author by Chupka. If there are a large number of autoionizing peaks roughly equally spaced and of comparable intensity on the high-energy side of each ion vibronic level, then averaging with a bandwidth of roughly 0.05 eV might produce an effective cross section nearly independent of energy above each vibronic level. To interpret the data of the present paper from that viewpoint would also require that the

 $\begin{array}{l} \text{TABLE I. Photoionization of molecular hydrogen:} \\ H_2 \langle {}^1\Sigma_{\varrho}{}^+, \, v'' = 0 \rangle {\rightarrow} H_2{}^+ ({}^2\Sigma_{\varrho}{}^+, \, v) \, . \end{array}$

Ũ	Threshold wavelength ^s (Å)	Energy interval $v+1 \rightarrow v$ (eV)	Relative peak amplitude ^b	Theoretical Franck- Condon factor ^e
0	(803.7 ± 0.5)	•••	•••	0.57
1	789.3 ± 0.5	0.254 ± 0.006	≤0.63	1.03
2	776.8 ± 0.5	0.235 ± 0.006	≤0.73	1.13
3	765.6 ± 0.5	0.225 ± 0.006	1.00	1.00
4	755.1 ± 0.5	0.206 ± 0.006	0.73 ± 0.04	0.79
5	745.7 ± 0.5	0.193 ± 0.007	0.42 ± 0.05	0.58
6	737.2±0.5	•••	0.16 ± 0.03	0.41

^a The threshold wavelength is the measured value corresponding to the peak maximum plus 1.2 Å. This latter quantity is the instrumental peak shift discussed in the text. The value quoted for v = 0 is the measured value at the peak maximum without this peak-shift correction.

^b Normalized to the value at v = 3.

^e See Ref. 22. The values have been normalized such that the factor corresponding to v=3 is equal to 1.00 in order to facilitate comparison with the experiments reported in this paper.



FIG. 8. Threshold photoelectron spectrum in D_2 . The analysis and acceleration energy used was 3 eV.

released autoionized electron have the minimum possible initial kinetic energy. There is not, at present, experimental evidence available which tests this latter requirement for the v=3, 4, 5, 6 levels of H_2^+ . While the results presented above support the interpretation previously outlined, this alternative viewpoint cannot be conclusively excluded. Therefore, the relative peak amplitudes and associated uncertainties quoted in this paper can only be regarded as relative transition probabilities within the framework of the former interpretation.

B. Deuterium

Experimental results obtained in D2 using 3-eV acceleration and analysis energy are shown in Fig. 8. The 10 clearly resolved peaks are interpreted as corresponding to the production of low-energy electrons in forming $D_{2^+}(^{2}\Sigma_{g}^{+}, v)$ where v=0-9, inclusive. By studying the dependence of peak amplitude and position on analyzer excess energy ϵ (as in the case of H_2), it was possible to conclude that the first two peaks are predominantly due to low-energy electrons produced by autoionization of electronically excited D2. Of the remaining peaks, it is believed that measurable contributions of low-energy electrons produced by autoionization are observed only at the peaks corresponding to v=2, 3. The relative amplitudes of the remaining peaks are comparatively insensitive to experimental conditions including ϵ . For example, normalizing to the v=5 peak, we find that the v=0 peak decreases by a factor of 2 and the v=1 peak by 60% when ϵ increases

TABLE II. Photoionization of molecular deuterium: $D_2({}^1\Sigma_{\varrho}{}^+, v''=0) \rightarrow D_2{}^+({}^2\Sigma_{\varrho}{}^+, v).$

		·····		and the second s
v	Threshold wavelengthª (Å)	Energy interval $v+1 \rightarrow v$ (eV)	Relative peak amplitude ^b	Theoretical Franck– Condon factor°
0	(801.2 ± 0.5)	•••		0.29
1	(791.4 ± 0.5)	• • •	•••	0.72
2	782.4 ± 0.5	0.178 ± 0.006	<0.75	1.06
3	773.7 ± 0.5	0.176 ± 0.006	<0.81	1 19
4	765.3 ± 0.5	0.162 ± 0.006	0.98 ± 0.05	1.15
5	757.7 ± 0.5	$0.157 {\pm} 0.006$	1.00	1.00
6	750.5 ± 0.5	0.148 ± 0.007	0.88 ± 0.05	0.81
7	743.9 ± 0.5	0.141 ± 0.007	≤0.55	0.63
8	737.7 ± 0.5	$0.134 {\pm} 0.007$	≤ 0.28	0.48
9	731.9 ± 0.5	•••	≤ 0.20	0.36

^a The threshold wavelength is the measured value corresponding to the peak maximum plus 1.2 Å. This latter quantity is the instrumental peak shift discussed in the text. The values quoted for v=0, 1 are the measured values without this additional peak-shift correction.

^b Normalized to the value at v = 5.

^e See Ref. 22. The values have been normalized such that the factor corresponding to v=5 is equal to 1.00 in order to facilitate comparison with the experiments reported in this paper.

from zero to ~ 0.08 eV. On the other hand the v=4, 6 peak amplitudes remain invariant for the same change in ϵ .

Table II presents a summary of the results of measurements of peak amplitudes in D_2 . Also, wavelength positions of peak maxima and peak intervals in electron volts are reported. Since the peak spacing is somewhat smaller in D_2^+ as compared with H_2^+ , the effective resolution is not sufficient to permit an accurate measurement of peak amplitudes. Thus, the quoted error is larger than the measurement precision.

IV. DISCUSSION

A. Ionization Energies and Vibrational Constants

The measured peak intervals can be used to directly determine experimental values of ω_e and $\omega_e x_e$ for both D_2^+ and H_2^+ . Figure 9 shows a plot of these intervals as a function of $(v+\frac{1}{2})$. In addition, least-squares fits of the form

$$A(v) = a_0 + a_1(v + \frac{1}{2}) \tag{8}$$

are also shown. The derived values of a_0 and a_1 for both molecules are listed in Table III. If the peak maxima are interpreted as corresponding to the $J''=0 \rightarrow J'=0$ transitions, where J'', J' are the rotational quantum numbers of the neutral and ion, respectively, then¹⁹

$$a_0 = \omega_e - \omega_e x_e, \tag{9}$$

$$a_1 = -2\omega_e x_e. \tag{10}$$

In deriving Eqs. (9) and (10) higher-order anharmonic corrections have been neglected. Using the values re-

ported in Table III we then find, in this interpretation,

$$\omega_e x_e = 0.2034 \pm 0.0027 \text{ eV}; \qquad \omega_e x_e = 0.0039 \pm 0.0005 \text{ eV}$$
(11)

and

ω,

D₂+:

$$\mathrm{H}_{2}^{+}$$
:

$$\omega_e = 0.2829 \pm 0.0030 \text{ eV}; \qquad \omega_e x_e = 0.0075 \pm 0.0004 \text{ eV}.$$
(12)

If, on the other hand, the observed peak maxima are interpreted as corresponding to transitions terminating in the rotational level J' of the ion, then it can be shown that¹⁹

$$a_0 = \omega_e - \omega_e x_e - \alpha_e J'(J'+1), \qquad (13)$$

$$a_1 = -2\omega_e x_e, \tag{14}$$

where the higher-order anharmonicity corrections have been neglected. The constant α_e represents the influence of the vibration-rotation interaction. Experimental values of α_e cannot be derived from the data presented in this paper. However, the value $\alpha_e \approx 1.4$ cm⁻¹ has been estimated for H₂⁺ by extrapolation of the values observed in a Rydberg series in molecular hydrogen.²⁰ For H₂ at 300°K, about two-thirds of the molecules are excited with one rotational quantum. If



FIG. 9. Measured peak intervals as a function of $(v+\frac{1}{2})$. The dashed lines are the least-squares linear fits.

²⁰ O. W. Richardson, Proc. Roy. Soc. (London) 152, 503 (1935).

¹⁹ G. Herzberg, Spectra of Diatomic Molecules (D. Van Nostrand Co., Inc., Princeton, N. J., 1950), 2nd ed.

TABLE III. Vibrational constants of H_2^+ and D_2^+ .

S]	oecies	<i>a</i> ₀	a_1	ωe	$\omega_e x_e$	
	H_{2}^{+}	0.2754±0.0029 eV	$-0.0150 \pm 0.0008 \text{ eV}$	$2290 \pm 26 \text{ cm}^{-1}$	$60\pm5 \text{ cm}^{-1}$	
	D_2^+	0.1995±0.0026 eV	$-0.0078 \pm 0.0005 \text{ eV}$	$1643 \pm 22 \text{ cm}^{-1}$	$31 \pm 4 \text{ cm}^{-1}$	

⁸ The quoted error limits for a_0 and a_1 represent one standard deviation for the least-squares fit. The errors quoted for ω_e are somewhat larger and take into account the possible influence of the vibration-rotation interac-

tion (see text). The quoted error for ω_{e^Xe} is sufficiently large to include estimated effects of higher-order anharmonicity corrections as well.

the rotational angular momentum of the molecule is preserved in direct ionization, then we expect J'=1. However, since the outgoing electron may carry off angular momentum, rotational excitation cannot be excluded. For J'=3 this interpretation would lead to $\omega_e = 0.2850$. Applying the isotope relations¹⁹ to obtain an approximate α_e value for D_2^+ , these arguments lead to a slightly larger ω_e value for that molecule. Table III shows adjusted vibrational constants for both molecular ions as determined in this investigation. The possible influence of higher-order anharmonicity corrections, believed to be small, has not been taken into account. These vibrational constants are in good agreement with Richardson's²⁰ indirectly determined values for H_2^+ , namely $\omega_e = 2297 \text{ cm}^{-1}$ and $\omega_e x_e = 62 \text{ cm}^{-1}$. By applying the isotope relations to these indirect determinations, one can obtain estimates of the D_2^+ constants which are also in good agreement with the values determined in this investigation. Also, measurements of the kineticenergy distribution of photoelectrons produced in photoionization have shown good agreement for vibrational intervals predicted from Richardson's data and observed values.7,8

The monochromator bandwidth used in these experiments was sufficiently broad as to not allow a highly accurate determination of the ionization potential of H_2 . On the other hand, agreement with previous more accurate determinations is expected if the observations do in fact correspond to the interpretation outlined above. Therefore the determination of ionization energies constitutes a reasonable internal check of the experimental method.

The peak corresponding to v=0 as observed in the H_2 investigation was interpreted as being predominantly due to production of low-energy electrons by autoionizing states of the excited molecule. The peak expected to correspond to the direct transition would occur at a slightly different photon energy. Thus, the H_2 ionization energy was not directly determined. An indirect determination is possible. From Table I we find the photon energy for the threshold of the process

$$\mathbf{H}_{2} ({}^{1}\Sigma_{g}^{+}, v''=0) + h\nu \rightarrow \mathbf{H}_{2}^{+} ({}^{2}\Sigma_{g}^{+}, v=3) + e^{-} (15)$$

to be equal to 16.194 ± 0.010 eV. From the least-squares fit of the vibrational intervals in H₂⁺, see Table III, we extrapolate 0.759 ± 0.007 eV to be the energy interval between the v=3 peak and the unobserved v=0 direct ionization peak. This leads to

$$I(H_2) = 15.435 \pm 0.012 \text{ eV}$$
 (16)

if the peak maxima are interpreted as corresponding to the $J''=0 \rightarrow J=0$ transition. A small correction to this value is required if the peaks actually correspond to a different pair of rotational quantum numbers. By studying the v=0 peak amplitude as a function of analyzer excess energy (see Fig. 5), it is concluded that the energy of the low-energy electrons produced by autoionization is consistent with zero and experimentally less than 0.015 eV. From the observed peak position we arrive at a second indirect determination of $I(H_2)$, namely

$$I(H_2) = 15.426 \pm 0.018 \text{ eV},$$
 (17)

where the somewhat larger error limit reflects the unknown energy of the autoionized electrons as well as the possibility that the photon energy required to produce the autoionizing state may be less than the photon energy required for direct ionization owing to rotational excitation of the ground state. The average value is regarded as the ionization energy of H_2 determined in these experiments:

$$I(H_2) = 15.431 \pm 0.022 \text{ eV},$$
 (18)

where the quoted error is the rms error of the independent indirect determinations.

A completely analogous situation is found in D₂. In this case, the photon energy corresponding to the v=2peak is used: 15.846 ± 0.010 eV. From the least-squares fit of the vibrational intervals in D₂⁺, the extrapolated energy interval between the v=2 peak and the unobserved v=0 peak is found to be 0.383 ± 0.006 eV. If the peak maxima correspond to $J''=0 \rightarrow J=0$ transitions, we get

$$I(D_2) = 15.463 \pm 0.012 \text{ eV}.$$
 (19)

The v=0 peak is observed to be produced by low-energy electrons (probably less than 0.015 eV) from autoionizing states of the excited neutral. As in the case of H₂, this is used to arrive at a second, independent, determination of the ionization energy of D₂,

$$I(D_2) = 15.474 \pm 0.018 \text{ eV}.$$
 (20)

The average of these values is regarded as the ionization

energy of D₂ as determined in these experiments:

$$I(D_2) = 15.468 \pm 0.022 \text{ eV},$$
 (21)

where, as before, the quoted error is the rms error of the independent determinations.

The measured difference $\Delta I = I(D_2) - I(H_2) = 0.037$ eV should correspond to the following difference in zero-point energies, denoted by E_0 :

$$\Delta = [E_0(\mathbf{H}_2) - E_0(\mathbf{D}_2)] - [E_0(\mathbf{H}_2^+) - E_0(\mathbf{D}_2^+)]. \quad (22)$$

Herzberg and Monfils have reported accurate values of $E_0(H_2)$ and $E_0(D_2)$.²¹ From Table III, we calculate values of $E_0(H_2^+)$ and $E_0(D_2^+)$ where the uncertainty is sufficiently large that higher-order anharmonic corrections may be ignored. We obtain

$$\Delta = 316 \text{ cm}^{-1} = 0.039 \text{ eV}, \qquad (23)$$

in excellent agreement with the difference in ionization energies. Clearly the values of $I(H_2)$ and $I(D_2)$ determined in this investigation form a self-consistent set together with the vibrational constants. As previously indicated the value of $I(H_2)$ reported in this paper is in good agreement with more accurate determinations.^{3,18}

B. Relative Intensities

In contrast with the rather good agreement between previously reported ionization energies and vibrational constants and the values determined in this work, the observed relative intensities do not agree with theoretical expectations. Calculated Franck-Condon factors22 pertaining to transitions between rotationless states of the neutral and molecular ion are indicated in Tables I and II. It is evident that there is considerable disagreement. The departures from theoretical relative intensities reported by Frost et al.7 are considerably smaller than the discrepancies indicated by the results of this research. Their results are not, however, strictly comparable inasmuch as their experiments are, in principle, of a different character. That is, they measure the distribution according to vibrational level of ions formed by absorption of photons whose fixed energy is about 5.8 eV in excess of the minimum ionization energy. The results of the research reported in this paper pertain to those different photon energies which correspond to the ionization thresholds of the different ion vibrational levels. Possible unknown variations of the cross section with excess energy above these different thresholds might resolve some of the apparent disagreements (see the discussion of this point in Ref. 7). It is also possible that very rapid variations of the cross section within the experimental bandwidth of the threshold could influence the observed peak intensities. On the other hand, the very close qualitative correspondence of the threshold electron spectra observed in H_2 as compared with D_2 suggests that the relative

transition probabilities indicated in Tables I and II might be associated with features of the relevant potential curves and not in cross-section variations.

To explore the idea more fully we outline the usual formulation of the photoionization cross section appropriate to these experiments. The cross section for a transition from a nondegenerate initial state of a diatomic molecule to a given final state may be written as^{23}

$$\sigma(\nu) = (8\pi^3 e\nu/3c) \left| \int \Psi_f^*(\mathbf{r}, \mathbf{R}) \mathbf{r} \Psi_i(\mathbf{r}, \mathbf{R}) d^3 \mathbf{r} d^3 \mathbf{R} \right|^2,$$
(24)

where ν is the frequency of the incident photon, **r** symbolizes a single electron coordinate, and **R** is the position vector of one nucleus relative to the others. For degenerate states this expression must be averaged over initial states and summed over final states. In the Börn-Oppenheimer approximation the total eigenfunction is separated according to

$$\Psi_i(\mathbf{r}, \mathbf{R}) = R^{-1} \Psi_i(\mathbf{r}, R) \phi_i(R) \chi_i(R^{-1} \mathbf{R}), \quad (25)$$

where χ_i , ϕ_i , ψ_i are the rotation, vibration, and electronic eigenfunctions of the molecule in the initial state and $R = |\mathbf{R}|$. An analogous expression may be written for Ψ_f . The Franck-Condon approximation permits separation of the integral over electronic coordinates from the integration over R. Also, since rotational structure is not resolved in these experiments the integrals over degenerate rotational levels are regarded as effected and averaged (see Ref. 19 for a discussion of the sum over rotational states for discrete-discrete transitions). The resulting averaged cross section then describes a transition from a vibrational level v' of the neutral molecule to a vibrational level v' of the form

$$\tilde{\sigma}_{\boldsymbol{v}^{\prime\prime}\boldsymbol{v}^{\prime}}(\nu) = q(\boldsymbol{v}^{\prime\prime},\,\boldsymbol{v}^{\prime})M(\nu)\,,\tag{26}$$

where the vibrational quantum numbers of the eigenfunctions ϕ_i , ϕ_f have been explicitly developed, i.e., the Franck-Condon factors are

$$q(v'',v') = \left| \int \phi_f^*(R)\phi_i(R)dR \right|^2.$$
(27)

The quantity $M(\nu)$ is presumed to contain the variation of the cross section with excess energy above threshold.

For the photoionization of H_2 , v'' = 0 and the relative cross section at threshold for transitions to two distinct vibrational levels of the ion, denoted by v_1' , v_2' is given by

$$\frac{\tilde{\sigma}_{0v_{1'}}(\nu_{0v_{1'}})}{\tilde{\sigma}_{0v_{2'}}(\nu_{0v_{2'}})} = \frac{q(0, v_{1'})}{q(0, v_{2'})} \frac{M(\nu_{0v_{1'}})}{M(\nu_{0v_{2'}})} \,. \tag{28}$$

 ²¹ G. Herzberg and A. Monfils, J. Mol. Spectry 5, 482 (1960).
 ²² G. H. Dunn, J. Chem. Phys. 44, 2592 (1966).

²³ M. R. Flannery and U. Opik, Proc. Roy. Soc. (London) 86, 491 (1965).

The two cross sections in this expression have been evaluated at different photon frequencies according to $h\nu_{0\nu'} = I + E(\nu')$, where I is the ionization energy and E(v') is the ion vibrational energy with respect to v'=0. If M(v) is nearly independent of v, then, for some range of ion vibrational levels, we expect

$$\bar{\sigma}_{0v_{1'}}(\nu_{0v_{1'}})/\bar{\sigma}_{0v_{2'}}(\nu_{0v_{2'}}) = q(0, v_{1'})/q(0, v_{2'}); \quad (29)$$

that is, the relative cross sections are proportional to the ratio of the appropriate Franck-Condon factors. It is important to realize that departures from the predictions of Eq. (29) may mean that Eq. (28) is a better representation of the situation in which case the variation of $M(\nu)$ with ν becomes significant.

While it is conceivable that unknown variations of $M(\nu)$ may explain the known experimental situations, it is appropriate to inquire whether the formulation of the overlap integrals as expressed in Eq. (27) is correct. The usually neglected vibration-rotation interaction is known to influence intensities in electronic bands of hydride molecules.²⁴ As pointed out by James, the ratio B_e/ω_e is an appropriate measure in estimating the possible importance of this effect.²⁵ For $RbH(X^{1}\Sigma^{+})$ this ratio is about 1/300 and computed Franck-Condon factors show a dependence on rotational quantum number. For H_2^+ and H_2 the ratio B_{e}/ω_e is even larger, roughly 1/75. There are no calculations for H₂ transitions which attempt to take this effect into account. To illustrate the large effects to be expected in H₂ ionization, Franck-Condon factors for harmonic oscillator potential functions have been calculated which include the dependence on rotation.

Following the treatment in Pauling and Wilson.²⁶ the Schrödinger equation for a harmonic oscillator including rotation may be written in the following form in the case of ${}^{1}\Sigma$ states:

$$\left(-\frac{\hbar^2}{2m}\frac{d^2}{d\eta^2}+\frac{\omega_e^2}{4B_e r_e^2}\eta^2+\frac{J(J+1)B_e}{\left[1+(\eta/r_e)\right]^2}\right)\psi=E\psi,\quad(30)$$

where ω_e , B_e , r_e have the usual significance, $\eta = r - r_e$, m is the reduced mass of the atoms, ψ is the eigenfunction appropriate to the energy E, and J is the rotational quantum number. The rotational energy is expanded in powers of η/r_e and is truncated after three terms. The new effective potential function has a minimum at

$$r = \left(1 + \frac{J(J+1)}{3J(J+1) + (\omega_e^2/4B_e^2)}\right) r_e.$$
 (31)

By means of a change of variable the effective potential is expanded about the new minimum. The Schrödinger equation becomes

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{d\xi^2} + \left(\frac{\omega_e^2}{4B_e r_e^2} + \frac{3J(J+1)B_e}{r_e^2}\right)\xi^2\right]\psi \\ = \left(E - J(J+1)B_e + \frac{J^2(J+1)^2B_e}{3J(J+1) + (\omega_e^2/4B_e^2)}\right)\psi. \quad (32)$$

This is the equation for a harmonic oscillator of frequency ω_e' where

$$\omega_{e}' = \omega_{e} \{ 1 + [12J(J+1)B_{e}^{2}/\omega_{e}^{2}] \}^{1/2}.$$
(33)

When J is sufficiently small this may be written in the form

$$\omega_e' = \omega_e + [6J(J+1)B_e^2/\omega_e], \qquad (34)$$

which can be compared with the usual expression for the energy of the rotating anharmonic oscillator:

$$G_{J}(v) = \left[\omega_{e} - \alpha_{e}J(J+1)\right](v+\frac{1}{2}) - \left[\omega_{e}v_{e} - \gamma_{e}J(J+1)\right](v+\frac{1}{2})^{2} + \cdots + B_{e}J(J+1) + \cdots$$
(35)

Therefore, in this approximation, we find the vibrationrotation interaction constant of the rotating harmonic oscillator to be

$$\alpha_e = -6B_e^2/\omega_e. \tag{36}$$

The solutions of Eq. (32) must now be labeled according to both vibrational and rotational quantum numbers: ψ_{vJ} . Equation (27) must be modified to the form

$$q(v'', J''; v', J') = \int \phi_{v''J''}(R) \phi_{v'J'}(R) dR \Big|_{-\infty}^{2} .$$
 (37)

Franck Condon factors for harmonic-oscillator potentials including displacement of equilibrium coordinate may be directly computed.27 Using molecular constants of H_2 and H_2^+ we have calculated these factors for the rotating harmonic oscillator where the rotational energy is included in the manner outlined above. While it is known that the harmonic oscillator is a rather poor representation of the potential function of molecular hydrogen, the results are easily obtained and are rather striking. Table IV shows the results of this calculation for the (0, v') bands for v' = 0, 2, 4, 6. Only those transitions where $\Delta J = 0$, ± 2 are considered. Such transitions preserve the para or ortho spin states of the nucleii. A similar rule has been invoked in the consideration of rotational structure in the electronimpact study of H₂ ionization near threshold.²⁸ Clearly, large effects of the vibration-rotation interaction are apparent, especially for the higher v' levels. It is evident that a correct theory of intensities in ionizing transi-

²⁴ D. C. Jain and R. C. Sahni, Proc. Roy. Soc. (London) 88, 495

<sup>(1966).
&</sup>lt;sup>25</sup> T. C. James, J. Chem. Phys. 32, 1770 (1960).
²⁵ L. Pauling and E. B. Wilson, *Introduction to Quantum Mechanics* (McGraw-Hill Book Co., New York, 1935).

¹⁷ J. R. Henderson, R. A. Willet, M. Muramoto, and D. C. Richardson, "Tables of Harmonic Franck-Condon Overlap Integrals Including Displacement of Normal Coordinates," Develop Part Co. 1064 (mark) Douğlas Rept. SM-45807, Douglas Aircraft Co., 1964 (unpub-

Lished). ²⁸ J. W. McGowan and M. A. Fineman, Phys. Rev. Letters 15, 179 (1965).

Band		Franck-Condon factors for $J'' \rightarrow J'$				
 0–0	J' == 0	1	2	3	4	5
J'' = 0	0.0986	•••	0.0921	•••	•••	•••
1		0.0977	•••	0.0873	•••	•••
2	0.1028	•••	0.0960	•••	0.0821	•••
3	• • •	0.1046		0.0936	• • •	0.0857
02	J' = 0	1	2	3	4	5
J'' = 0	0.3483	•••	0.3469	• • •	• • •	•••
1	•••	0.3398		0.3454	• • •	•••
2	0.3490	•••	0.3479	•••	0.3433	•••
3	•••	0.3494	•••	0.3480	•••	0.3453
()-4	J' = 0	1	2	3	4	5
J'' = 0	0.0532		0.0609	•••	• • •	•••
1	•••	0.0524	•••	0.0672	•••	•••
2	0.0478	•••	0.0555	•••	0.0746	•••
3	•••	0.0455	•••	0.0582	•••	0.0689
06	J' = 0	1	2	3	4	5
J'' = 0	0.000776	•••	0.000472	•••	•••	•••
2		0.000733		0.000281	• • •	• • •
2	0.001029	•••	0.000698	•••	0.000118	• • •
3	•••	0.001172	•••	0.000621	• • •	0.000264

TABLE IV. Franck-Condon factors for a rotating harmonic oscillator.

tions in molecular hydrogen should take this effect into account. In this context it should be noted that calculations of Franck-Condon factors for electronic transitions in the neutral molecule have not included this effect and, again, it is suggested that a significant effect will be found at the higher vibrational levels.

In considering the rotating Morse oscillator, Pekeris has derived the following expression for the vibrationrotation interaction constant²⁹:

$$\alpha_e = (6\omega_e x_e/\omega_e) B_e (B_e/\omega_e x_e)^{1/2} - (6B_e^2/\omega_e), \quad (38)$$

which reduces to Eq. (36) when $\omega_e x_e \rightarrow 0$. For an anharmonic oscillator with $\alpha_e > 0$ the rotational distortion of the potential is such as to reduce the effective vibrational frequency and not increase it. Therefore, the model Franck-Condon factor calculation for the rotating harmonic oscillator probably does not correctly indicate the trend of the overlap integrals with increasing rotational quantum number. It is clear that the $J'' = 0 \longrightarrow J' = 0$ entries for the different (0, c') bands, corresponding to the usually calculated Franck-Condon factors, are often quite distinct from values found for other (J'', J') combinations. Since only 13% of H_2 at room temperature is in the J''=0 rotational state, the Franck-Condon calculations referring to rotationless potential curves may account for only a small part of the actual transition probability.

A correct theory of the photoionization of the hydrogen molecule should include consideration of all physically significant interactions. The cross section for the production of ions in a single vibrational-rotational level will be proportional to the modified Franck-Condon factor as indicated above and to the appropriate lines strength.¹⁹ Therefore, the cross section for production of a definite rotational-vibrational level of the ion will be sensitive to the line strength as well. As indicated in Eq. (38) the α_e value is expected to be sensitive to the anharmonicity of the potential function and thus calculations of overlap integrals including vibration-rotation interaction will be extremely sensitive to the detailed shape of rotationless potential curve. Clearly, more theoretical work is indicated.

ACKNOWLEDGMENTS

I wish to thank Professor Mark Inghram for his continuing encouragement and interest in this work. The assistance of T. Earp and J. Keane in the construction of the apparatus is gratefully acknowledged. Also, the enthusiastic participation of Ron Herm in the early stages of this work and of Roger Stockbauer in the latter part of the work is greatly appreciated. Finally, I wish to thank W. A. Chupka for constructive suggestions regarding the manuscript and especially for making available unpublished data pertaining to the photoionization of H_2 .

²⁹ C. L. Pekeris, Phys. Rev. 45, 98 (1934).