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VIBRATIONAL INTENSITY DISTRIBUTIONS IN THE PHOTOELECTRON
SPECTRUM OF HYDROGEN.*

J. L. Gardner and James A. R. Samson
Behlen Laboratory of Physics
Lincoln, Nebraska 68508 U.S.A.

ABSTRACT

The intensity distribution over the H_2^+ vibrational levels up to $v = 15$ has been measured from H_2 photoelectron spectra at a photon wavelength of 584 Å. The data show reasonable agreement with recent calculations only in the range $v = 0$ through 8; the higher levels are populated significantly lower than predicted by theory.

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INTRODUCTION

A number of determinations of the vibrational intensity distribution of the 584 \AA hydrogen photoelectron spectrum have been reported in the literature.¹⁻³ The most recent measurement is that of Berkowitz and Spohr,³ who recorded intensities over the range $v = 0$ to 9 (where v is the vibrational quantum number of the H_2^+ ionic ground state). These data were compared with relative intensities calculated by Itikawa⁴ and were found to be in good agreement, although considerable scatter is present in the data at the higher vibrational levels.

The purpose of the present experiment was to extend the measured intensities to higher vibrational levels. The intensities calculated by Itikawa included the dependence of the electronic transition moment on the internuclear separation and on the kinetic energy of the departing electron, but did not include the effect of rotational coupling on the vibrational levels. This latter effect has been predicted to become significant in the photoionization to the higher vibrational levels of H_2^+ .⁵

EXPERIMENTAL

Hydrogen photoelectron spectra were recorded at a photon energy of 21.2 eV (584 \AA HeI radiation produced in a DC glow discharge and dispersed with a $\frac{1}{2}$ m Seya-Namioka monochromator) with a cylindrical mirror electron energy analyzer whose response is independent of the photoelectron angular distributions.⁶

The analyzer includes a lens between the ionization region and the deflection region; the lens voltage is scanned so that constant resolution is maintained across the spectrum and peak areas represent the electron intensity. The transmission of the analyzer has been calibrated to better than 5% over the energy range covered here.⁷

Spectra were recorded at analyzer resolutions of 30, 23 and 15 meV. It should be noted that good resolution is required to accurately measure intensities in the hydrogen photoelectron spectrum. The spectrum is dominated by the Q rotational branch⁸ whose extent increases as the vibrational separation increases. The Q branch includes members (N', N'') from (0,0) to (3,3), with the (3,3) member approximately 10% as intense as the dominant (1,1) member.⁸ At $v = 13$, the (0,0) and (3,3) members are separated by 0.072 eV, whereas the (0,0) members of the $v = 12$ and 13 vibrational levels are separated by 0.101 eV.⁹ Thus an analyzer resolution of the order of 20 meV is necessary to determine the baseline between the vibrational levels.

RESULTS

A number of spectra were recorded with the varying resolution and at varying gas pressures in the analyzer. The intensity distribution was found to be independent of the gas pressure, in contrast to previous measurements in CO and N₂.¹⁰ This was not surprising, as the electron scattering cross section of hydrogen shows little change over the range of energies covered by the photoelectrons¹¹ and the analyzer has been shown to be comparatively

insensitive to differential scattering when operated in the constant resolution mode.⁶

A spectrum recorded at a resolution of 30 meV is shown in Fig. 1; superimposed is a spectrum recorded over the higher vibrational levels at a resolution of 15 meV. The shoulder on the main peak is mainly due to the $(N', N'') = (3, 3)$ member of the Q rotational branch. No significant differences could be found in the population of the higher vibrational levels in the spectra recorded with resolutions of 15 and 23 meV, indicating that the baseline determination between the peaks was not being compromised by poor analyzer resolution.

Statistical averages were obtained for the vibrational intensity distribution by normalizing the total intensity of each spectrum to the same value. From 6 to 10 spectra were averaged to obtain the mean intensities reproduced in Table 1, where the data are normalized to 100 at $v = 2$. The errors quoted on these values represent standard deviations due to statistical variations only. The present intensity distribution is in reasonable agreement with that obtained by Berkowitz and Spohr³ for $v = 0$ to 9. Berkowitz and Spohr recorded their data 3 peaks at a time, introducing subsequent normalization errors when the peaks were combined to give the total intensity distribution.

Also included in Table 1 are the intensity distributions predicted by Franck-Condon factors from the $v = 0$ level of the neutral ground state and by the calculations of Itikawa. The Franck-Condon factors were calculated by numerically integrating

the Schrodinger equation using the potential energy curves tabulated by Sharp,¹² and evaluating the overlap of the vibrational wavefunctions. The resulting numbers agree with those of Peek, for $v = 0$ to 10 .¹³ Franck-Condon factors ignore the electronic part of the wavefunction. Itikawa included the electronic transition moment in his calculation, allowing for dependence on both the internuclear separation and the energy of the departing electron. The two values quoted in Table 1 represent different fields for the ejected electron; case B values were calculated with a modified two center Coulomb field and case C with the true electrostatic potential.

The ratio of the measured intensity to the calculated values is plotted in Fig. 2 for the various levels, normalized to unity at $v = 2$. A smooth curve is drawn for each comparison, although in general this curve does not fall within the statistical error bars (omitted for clarity) on the data at the lower vibrational levels. The Franck-Condon distribution clearly does not provide a good representation of the measured distribution, as noted previously.³ The best agreement with the theory of Itikawa occurs with his case B, which is surprising as the case C calculation uses a better approximation for the electronic wavefunction. However, both case B and C disagree significantly with the measured data for levels above $v = 9$, predicting intensities higher than those observed.

Some systematic error could be present in our data above about $v = 12$ because of the proximity of the rotational

transitions for the different H_2^+ vibrational levels. This would lower the observed intensity from the true value, with an estimated 20% possible error at $v = 14$. However this systematic error would still not explain all the discrepancy between experiment and theory.

The rotational coupling effects calculated by Villarejo⁵ are also too weak to explain the observed discrepancy. His data show $\approx 1\%$ variation for the Q branch ($N' = N''$) and $\approx 15\%$ for the O and S branches ($|N' - N''| = 2$); these latter branches occur with only $\sim 10\%$ of the intensity of the Q branch⁸ and thus the overall effect is too weak to explain the effect seen.

TABLE 1. Observed and Calculated Vibrational Distributions

v ¹	Present		Itikawa Theory	
	Expt	FCF	Case B	Case C
0	44.8±0.9	52.1	46.8	44.6
1	92.2±0.7	91.8	87.4	85.3
2	100.0±1.1	100.0	100.0	100.0
3	96.9±1.2	87.9	91.8	94.0
4	71.3±0.9	68.9	74.8	78.3
5	57.2±0.8	50.8	56.9	60.8
6	42.3±0.5	36.1	41.6	45.4
7	30.8±0.5	25.3	29.8	33.0
8	20.8±0.4	17.6	21.2	23.8
9	13.2±0.3	12.2	15.0	17.0
10	8.9±0.2	8.5	10.6	12.2
11	5.8±0.1	6.0	--	--
12	3.9±0.1	4.2	5.4	6.3
13	2.4±0.1	3.0	--	--
14	1.5±0.1	2.1	2.7	3.2
15	0.5±0.1	1.4	--	--

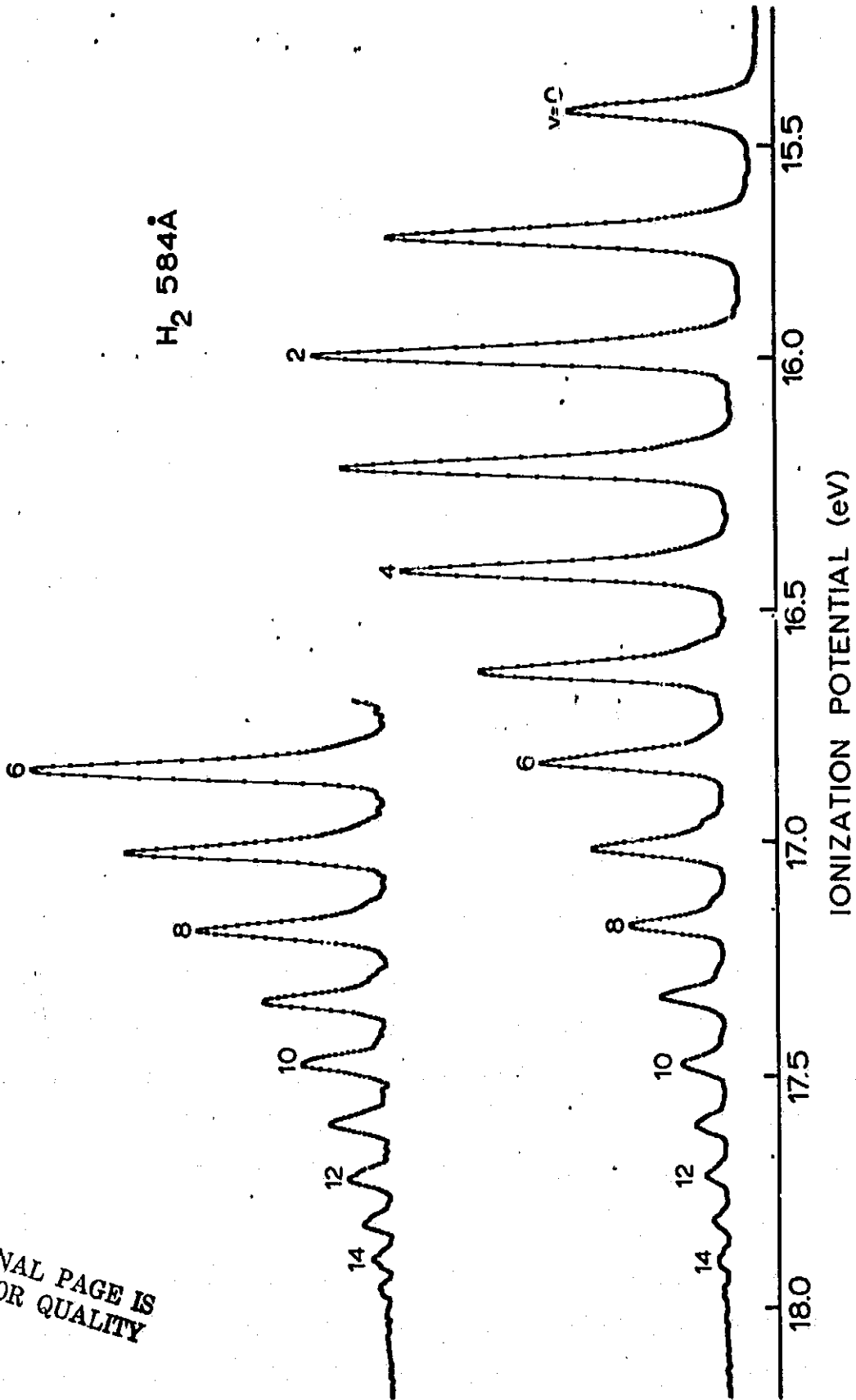
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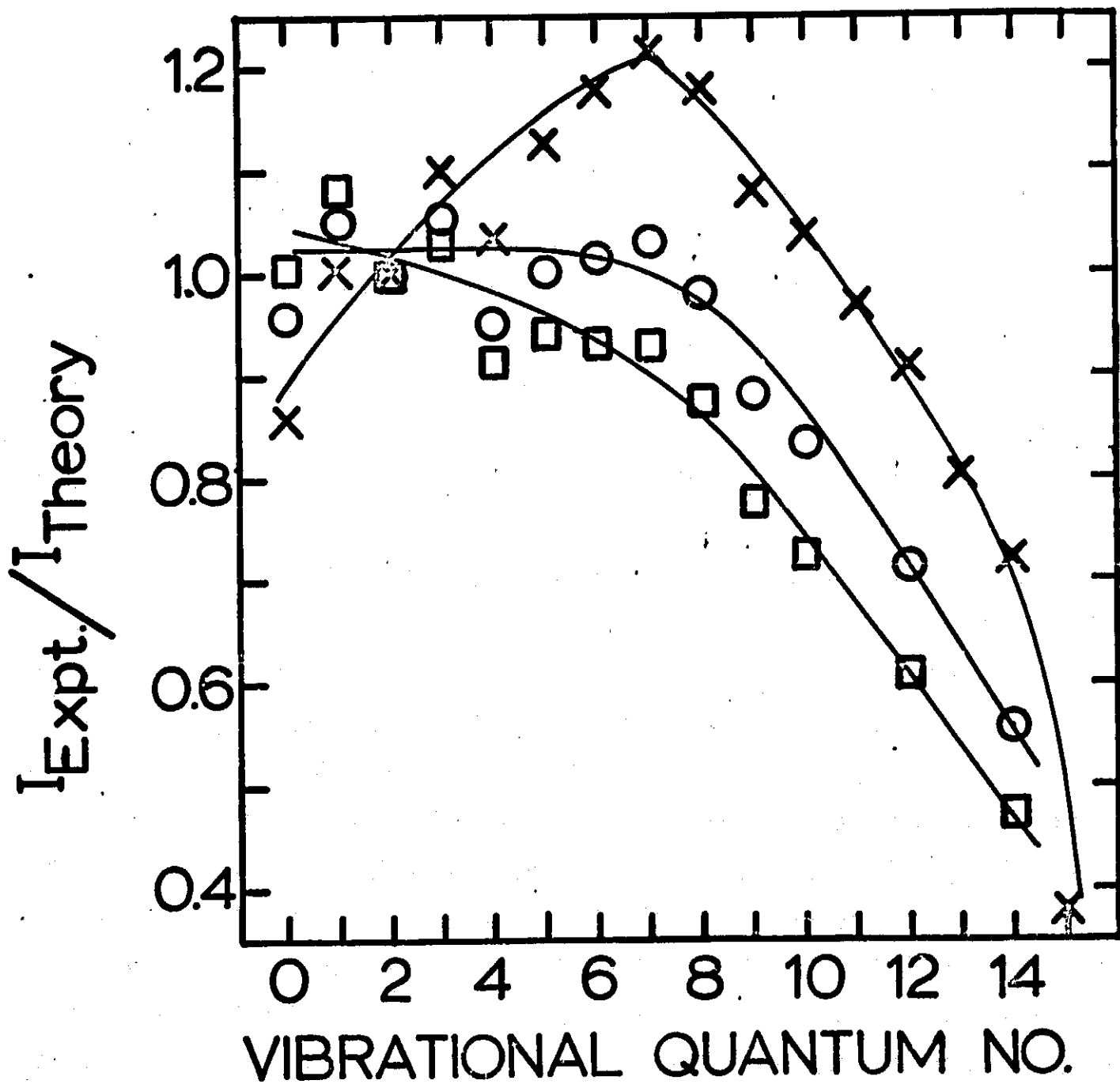
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FIGURE CAPTIONS

1. Hydrogen photoelectron spectra recorded at a wavelength of 584 \AA , corrected for the analyzer response. Lower trace: complete spectrum recorded with 30 meV resolution. Upper trace: spectrum for levels $v = 6$ and higher at a resolution of 15 meV.
2. Ratio of measured vibrational intensity to calculated values.
x - Franck-Condon factors; o - Itikawa case B; π - Itikawa, case C.

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