

Rotational-Resolved Pulsed Field Ionization Photoelectron Bands for $\text{H}_2^+(X^2\Sigma_g^+, v^+=0, 2, 9 \text{ and } 11)$

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INTRODUCTION

We have obtained the rotational-resolved pulsed field ionization photoelectron (PFI-PE) spectrum for H_2 at a resolution of 7 cm^{-1} (full-width-at-half-maximum) in the photon energy range of 15.30-18.10 eV. We present here the assignment and simulation of rotational transitions for the $\text{H}_2^+(X^2\Sigma_g^+, v^+=0, 2, 9, \text{ and } 11)$ vibronic bands using the Buckingham-Orr-Sichel (BOS) model.¹ The BOS simulation shows that perturbation of PFI-PE rotational line intensities due to near-resonance autoionization decreases as v^+ increases. Experimental rotational constants for $\text{H}_2^+(X^2\Sigma_g^+, v^+=0, 2, 9, \text{ and } 11)$ are determined with higher accuracy than those obtained in previous HeI and NeI photoelectron studies. In agreement with previous experimental and theoretical investigations, only the $\Delta N = 0$ and ± 2 rotational branches are observed in the PFI-PE spectrum for H_2 .

EXPERIMENT

The design and performance of the Chemical Dynamics Beamline at the ALS has been described previously.²⁻⁵ Briefly, the major components for the high-resolution photoionization facility at this beamline include a 10 cm period undulator, a gas harmonic filter; a 6.65m off plane Eagle mounted monochromator, and a photoion-photoelectron apparatus. The fundamental light from the undulator is then directed into the 6.65 m monochromator and dispersed by an Os coated 4800 l/mm grating (dispersion = $0.32 \text{ \AA}/\text{mm}$) before entering the experimental apparatus. A continuous molecular beam of pure H_2 was produced by supersonic expansion through a stainless steel nozzle (diameter = 0.127 mm) at a stagnation pressure of 330 Torr and a nozzle temperature of 298 K. The molecular beam was then skimmed by a circular skimmer (diameter = 1 mm) before intersecting the monochromatic VUV light beam 7 cm downstream in the photoionization region. The present experiment is performed in the multibunch mode with 304 bunches in the synchrotron orbit, corresponding to a repetition rate of 464 MHz. A pulsed electric field (height = 0.67 V/cm, width = 40 ns) was applied to the repeller at the photoionization/photoexcitation region to field ionize high-n Rydberg states and extract photoelectrons toward the detector, and was applied every 2 (1.31 μs) ring periods. The monochromator entrance/exit slits used are 150/150 μm , corresponding to a wavelength resolution of 0.048 \AA (or 0.9 meV at 800 \AA) (FWHM).

RESULTS

The rotational-resolved PFI-PE bands for $\text{H}_2^+(X^2\Sigma_g^+, v^+=0, 2, 9, \text{ and } 11)$ are shown in Figs. 1-4, respectively. The assignment of the rovibronic lines are based on the theoretical calculations of Hunter, Yau, and Prichard (HYP). Photoelectron peaks in Figs. 1-4, which are not assigned to (N^+, J'') ionization thresholds, can be partly attributed to prompt electron background features from autoionizing Rydberg levels of H_2 . The contamination by prompt electron peaks is expected to be less serious at higher v^+ states because strong autoionizing Rydberg states are mostly concentrated in the energy range (≈ 15.3 - 16.5 eV) covering the lower v^+ (<5) states. This expectation is confirmed by the PFI-PE spectra of Figs. 1-4. The $v^+=0$ and 2 PFI-PE bands exhibit many strong near-resonance autoionization peaks unassignable to rotational transitions, whereas the PFI-PE bands for $v^+=9$ and 11 are nearly free from such autoionization features.

In accordance with the selection rule due to nuclear spin statistics, only the $\Delta N = N^+ - J'' = \text{even}$, i.e., $0, \pm 2, \pm 4, \dots$, transitions are allowed. As shown in Figs. 1-4, the dominant rotational transitions for $v^+=0, 2, 9, \text{ and } 11$ are $\Delta N = 0$, i.e., $(0, 0), (1, 1), (2, 2), \text{ and } (3, 3)$. In general, the PFI-PE intensity for $(1, 1)$ is higher than that for $(0, 0)$ within a given vibrational band. This observation and the low PFI-PE intensities for transitions involving $J'' \geq 4$ are in general accord with the thermal distribution of J'' for H_2 . Weak transitions attributable to $\Delta N = \pm 2$, i.e., $(2, 0), (3, 1), (0, 2), (4, 2), (1, 3), \text{ and } (5, 3)$ are also observed. The dominance of the rotational transitions with $\Delta N = 0$ over that with $\Delta N = \pm 2$ is consistent with the results of previous experiments and theoretical predictions. Here, we present the simulation of the relative rotational intensities observed in the PFI-PE bands for $\text{H}_2^+(X^2\Sigma_g^+, v^+=0, 2, 9, \text{ and } 11)$ using the BOS model. This model was derived to predict rotational line strengths observed in one photon ionization of diatomic molecules. Basically, the rotational line strength is separated into two factors. The factor C_λ is associated with the electronic transition

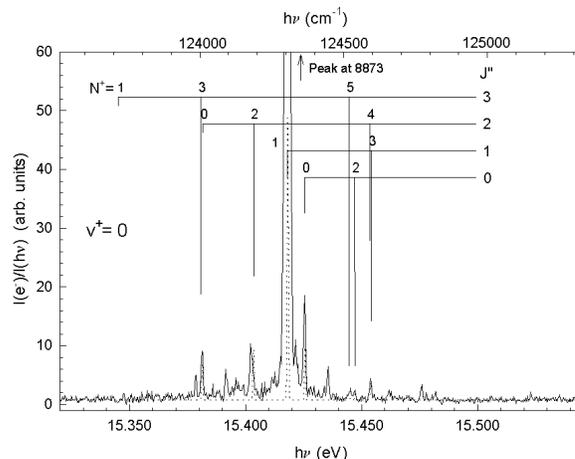


Figure 1. $\text{H}_2^+ X^2\Sigma_g^+, v^+=0$

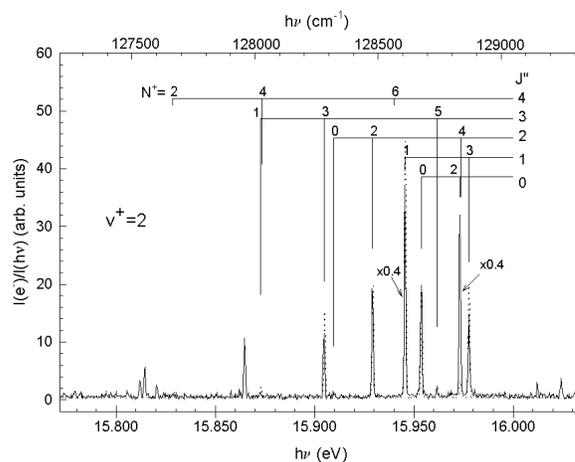


Figure 2. $\text{H}_2^+ X^2\Sigma_g^+, v^+=2$

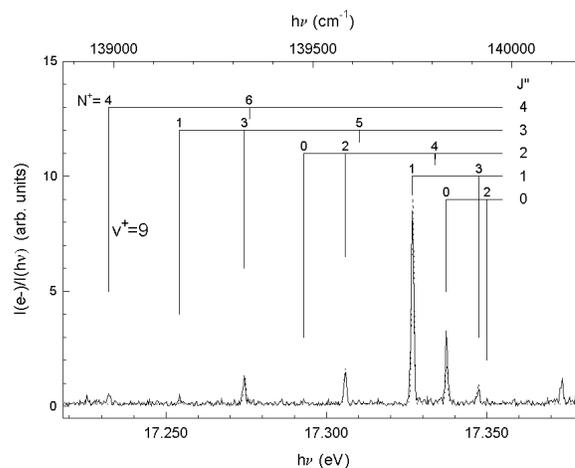


Figure 3. $\text{H}_2^+ X^2\Sigma_g^+, v^+=9$

moments, which is the linear combination of electron transition amplitudes for the possible angular momenta ℓ of the ejected electron. The general interpretation of λ is that of the angular momentum transfer in the photoionization process. The other factor is determined by the standard angular momentum coupling constants (Clebsch Gordon Coefficients), which were calculated using the formula for a Hund's case (b) to (b) transition in the present study. The known spectroscopic constants for the $H_2(X^1\Sigma_g^+, v'' = 0)$ were used. The best fits for the PFI-PE bands for $H_2^+(X^2\Sigma_g^+, v^+ = 0, 2, 9, \text{ and } 11)$ are depicted as dashed curves in Figs. 1-4. The fact that only the

$\Delta N = -2, 0, \text{ and } +2$ rotational branches are observed implies that only the BOS coefficients C_0 and C_2 are nonzero. The C_0 and C_2 values for the simulated spectra shown in Figs. 1-4 are listed in Table I. The dominance of the $\Delta N = 0$ or Q-branch observed in the experimental spectra is consistent with the significantly higher C_0 values than the corresponding C_2 values. As expected, the BOS simulation, which has not taken into account the effect of near-resonance autoionization, cannot account for the

overwhelming intensity for the (1, 1) transition observed in the $v^+=0$ PFI-PE band. Surprisingly, general agreement is found between the experimental spectra and the BOS simulation of the PFI-PE bands for $v^+ \geq 1$ states. In general, the agreement becomes better for higher v^+ . Disregarding the C_0 and C_2 values for the $v^+=0$ band, we find that the C_0 value generally increases compared to the C_2 value as v^+ is increased. Such a trend is consistent with the observation that the $\Delta N = \pm 2$ rotational branch diminishes as v^+ is increased.

In addition, we have obtained the rotational constants B_{v^+} and D_{v^+} for $H_2^+(X^2\Sigma_g^+, v^+ = 0, 2, 9, \text{ and } 11)$ by fitting the rotational structures resolved in Figs. 1-4. These values are compared with those reported in the previous HeI photoelectron study of Pollard *et al.*⁶ and theoretical predictions.⁷ The B_{v^+} and D_{v^+} values obtained in the present experiment are more accurate than previous results of Pollard *et al.* As expected, the results of the present experiment and the theoretical predictions are in excellent agreement.

CONCLUSIONS

We present here rotationally resolved PFI-PE data for the formation of $H_2^+(X^2\Sigma_g^+, v^+ = 0, 2, 9, \text{ and } 11)$. The analysis of these data has provided rotational constants B_{v^+} and D_{v^+} for these states with higher accuracy compared to those reported in previous experimental studies. The simulated photoelectron bands based on the BOS model are in good agreement with PFI-PE bands of higher v^+ states, indicating that the strong perturbation of the relative intensities for rotational transitions occurs mostly at lower $v^+ (\leq 5)$ states.

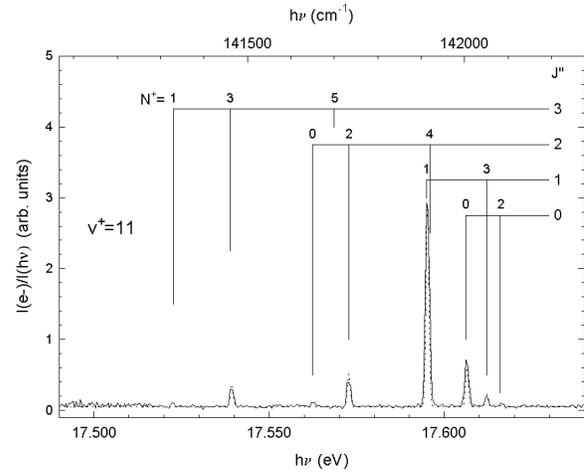


Figure 4. $H_2^+ X^2\Sigma_g^+, v^+=11$

Table I.

v^+	BOS Coefficients	
	C_0	C_2
0	90	10
2	75	25
9	85	15
11	90	10

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