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ROTATIONALLY-RESOLVED PHOTOELECTRON ANGULAR DISTRIBUTIONS
FOR H₂ (v' = 0) AT λ=584 Å AND 736Å

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ABSTRACT

The photoelectron asymmetry parameter for H$_2^+$ (v' = 0) was measured for the S rotational branch at $\lambda$=584Å and 736Å using a supersonic beam of n-H$_2$. Comparison with the theoretical $\beta$-values of Itikawa demonstrates the importance of coupling between the p and f photoelectron waves at higher photon energy.
I. INTRODUCTION

The measurement of photoelectron angular distributions for selected rotational transitions of molecules should be a valuable probe of the dynamics of the photoionization process as well as a very sensitive test of the theoretical description of the behavior of photoelectrons in the continuum. The only case for which this measurement is feasible with present experimental techniques is the photoionization of the hydrogen molecule

\[ \text{H}_2 (X^1\Sigma_g^+, v'', J'') + h\nu \rightarrow \text{H}_2 (X^2\Sigma_g^+, v', J') + e^- (E_k, \ell) \]  

In the photoelectron spectrum of H\(_2\) the rotational structure of each vibrational band can be partially resolved if the experimental arrangement allows the energy resolution to be on the order of 10 meV. The rotational selection rules for this process were shown to be \( J' = J'' \) (Q branch) and \( J' = J'' + 2 \) (S and O branches) by Sichel [1], by Dixon, et al. [2], and by Dill [3]. The photoelectron asymmetry parameter \( \beta \), which characterizes the angular distribution, is defined by the expression for the differential cross section in the electric dipole approximation

\[ \frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left( 1 - \frac{\beta}{4} (3 \cos^2 \vartheta - 1) \right) \]  

where the light is assumed to be unpolarized, and \( \vartheta \) is the angle between the photon propagation vector and the direction of electron collection. \( \beta \) has been determined theoretically for specific
rotational transitions by Dill [3], by Ritchie and Tambe [4], by Chandra [5], and by Itikawa [6-8]. The essential conclusions to be drawn from these calculations are 1) that $\beta_Q(J'=J')$ has a value close to 2.0 and is rather insensitive to which theoretical method is used, and 2) that $\beta_S(J'-J''\neq 2)$ has a value much less than 2.0 and depends strongly on the method of coupling the $p(\ell=1)$ and $f(\ell=3)$ photoelectron partial waves.

Rotationally-resolved photoelectron spectra of $\text{H}_2$ have been observed by Åsbrink [9], by Niehaus and Ruf [10], and by Pollard, et al. [11]. In accordance with the selection rules, the predominant rotational transition is observed to be the $Q$ branch, with the $S$ branch intensity being lower by at least a factor of 10. Niehaus and Ruf [10] made the only previous angular distribution measurement for specific rotational transitions, reporting values for the asymmetry parameters of $\beta_Q = 1.95 \pm 0.03$ and $\beta_S = 0.85 \pm 0.14$ for $\text{H}_2^+ (v'=1)$ at $\lambda=736\text{Å}$. Chang [12] has questioned the method used by Niehaus and Ruf in the analysis of their data and has published revised values of $\beta_Q = 1.95 \pm 0.01$ and $\beta_S = 0.45 \pm 0.87$ based on his re-analysis.

In this letter we report values for $\beta_S$ at 584Å and 736Å for $\text{H}_2^+ (v'=0)$, measured with a high resolution photoelectron spectrometer which uses a collimated supersonic beam of hydrogen to remove Doppler broadening. The results provide evidence for the importance of coupling between the $p$ and $f$ waves at the higher photon energy.
II. EXPERIMENTAL

The apparatus has been described in detail elsewhere [13]. A supersonic beam of n-H₂ (99.999% purity) was expanded through a 70-μm-diam nozzle at a stagnation pressure of 200 Torr and temperature of 77K, and was crossed with the photon beam from a resonance lamp operating at the HeIα (584 Å, 21.22 eV) and NeIα (736 Å, 16.85 eV) lines. The electron kinetic energy spectra were measured with an analyzer consisting of a double electrostatic deflector with multi-channel detection. The analyzer was operated at a resolution of 11 meV FWHM (for Ar) and an angular acceptance of ±1.8° (assuming a point source). The angular distributions were measured by orienting the unpolarized photon beam at two angles with respect to the analyzer, which remained in a fixed position. One lamp was placed so that the photon beam was orthogonal to both the molecular beam axis and the direction of electron collection. A second lamp was oriented such that the photon beam was at an angle of approximately 53° with respect to both the molecular beam axis and the direction of electron collection. The experiment consisted of measuring the Q-to-S branch intensity ratio for H₂⁺ (v' = 0) at the two angles. The spectra were accumulated by taking a series of 1-hour-long scans of the v' = 0 transition (2-3 scans at 90° and 10-11 scans at 53°) and summing the scans together after shifting the peaks as necessary to account for the drift in the kinetic energy offset. The angle of the off-normal lamp was subsequently measured to be 52.6° ± 1°.
III. RESULTS AND DISCUSSION

The complete spectrum of n-H$_2$ recorded with the 90° lamp under the conditions used in the present angular distribution study is shown in Fig. 1. The hydrogen molecules in the beam consist of a 1:3 mixture of the J"=0 and J"=1 rotational states with the fraction of J"=2 less than 0.5%, so that the Q branch has contributions from the (J'=0 \leftrightarrow J''=0) and (J'=1 \leftrightarrow J''=1) components and the S branch has contributions from (J'=2 \leftrightarrow J''=0) and (J'=3 \leftrightarrow J''=1). The simplification of the rotational structure achieved by running at 77K is advantageous for the purpose of determining the Q-to-S branch intensity ratio.

The areas of the rotational components of the v'=0 transition were determined by least-squares fitting using an empirically-derived line-shape function as we have described elsewhere [11]. The spectra at 584Å and 736Å at the two angular geometries are shown in Figs. 2 and 3. The background is higher for the 53° spectra than for the 90° spectra, because the 53° photons strike the inside of the vacuum chamber (after crossing the molecular beam) at a point which is undesirably close to the entrance aperture of the analyzer. This background is especially bad at 736Å where the v'=0 peak is at a low kinetic energy (1.4 eV). The Q-to-S intensity ratios are listed in Table I. To obtain the asymmetry parameters we use the formula for the differential cross section given in Eq. 2. Putting in the values $\theta = 90°$ and $\phi = 52.6° \pm 1°$ we obtain an expression for the ratio of the photo-electron intensities at the two angles,
\[ \frac{I_{90}}{I_{53}} = \frac{(1 + \beta/4)}{(1 + \epsilon \beta/4)} \]  \hspace{1cm} (3)

where \( \epsilon \) would equal zero if the off-normal lamp were at \( \theta = 54.7^\circ \) but in the present case has the value \( \epsilon = -0.104 \pm 0.050 \). Eq. 3 leads to the expression relating the intensity ratios at the two angles to the \( Q \) and \( S \) branch asymmetry parameters,

\[ \left( \frac{I_{90}(Q)}{I_{90}(S)} \right) \left( \frac{I_{53}(S)}{I_{53}(Q)} \right) = \left( \frac{1+\beta_Q/4}{1+\epsilon \beta_Q/4} \right) \left( \frac{1+\epsilon \beta_S/4}{1+\beta_S/4} \right) \]  \hspace{1cm} (4)

Although we apparently cannot determine \( \beta_Q \) and \( \beta_S \) independently based on the present data, it is possible to make a reasonable estimate of the value of \( \beta_Q \) and thereby obtain a value for the more interesting quantity \( \beta_S \). For the \( (J' = 0 \leftarrow J'' = 0) \) transition, which contributes 25\% of the intensity to the \( Q \) branch, Dill [3] and Itikawa [6] have shown that \( \beta \) equals 2.0 for all \( v \)-states. The \( (J' = 1 \leftarrow J'' = 1) \) transition, which contributes the remaining 75\%, has been predicted to have a \( \beta \) close to 1.9 by Itikawa [8] for both 584Å and 736Å. The previous experimental value of \( \beta_Q(v' = 1, 736Å) = 1.95 \) [10, 12] is consistent with our expectations from theory. We have adopted the value \( \beta_Q(v' = 0) = 1.90 \pm 0.10 \) and used it to calculate \( \beta_S \) for both photon energies.

There is a rather wide variation represented in the available experimental and theoretical values for \( \beta_S \) which are listed in Table II. The present result at 584Å is the only experimental value available, and it is in good agreement with the theoretical value calculated by Itikawa [8] using coupled p and f partial waves. Our value at 736Å
is the lowest of any tabulated and is actually in better agreement with the theories which do not include the f wave. Nevertheless, the substantial increase in $\beta_S$ as the photoelectron energy varies from 1.4 eV (at 736Å) to 5.8 eV (at 584Å) is well represented by Itikawa's coupled wave $\beta$-values. The source of the increase is clearly the enhancement of the f wave at the higher energy, because the effect is not predicted by the theories that use only the p wave.

The fact that our measured $\beta_S$ is less than the predicted values at 736Å is conceivably a consequence of autoionization, which is not included in the theory. This effect was investigated by Raoult and Jungen [14] who calculated rotationally averaged $\beta$-values for $H_2$ from 790Å to 760Å, a spectral region with many strongly autoionizing transitions. The asymmetry parameter for each $v$-state undergoes large oscillations at resonances near the corresponding vibrational threshold, but the effect is largely damped out for $v'=0$ at wavelengths of 760Å or less. These authors also showed that the rotational branching ratio shifts dramatically at the resonances from the $J'=J''$ channel to the $J'=J''\pm2$ channel. We can use our measured intensities and $\beta$-values to determine this branching ratio with the results: $\sigma(S)/\sigma(Q) = 0.095 \pm 0.004$ (at 584Å) and $0.061 \pm 0.002$ (at 736Å). Clearly, at 736Å for the $v'=0$ channel there is no large resonance of the type considered by Raoult and Jungen, for which we would observe $\sigma(S)/\sigma(Q)$ to be much greater than 0.1. The high resolution photoionization spectrum of $H_2$ by Dehmer and Chupka [15] exhibits some weak structure near 736Å but does not provide evidence for a major effect from autoionization. Berkowitz
[16] also examined the photoionization spectrum in this region and reached the same conclusion. We should note that the present rotational branching ratios are significantly smaller than are predicted by Itikawa [8], whose theoretical cross sections lead to the values of \( \sigma(S)/\sigma(Q) = 0.157 \) (at 584Å) and 0.139 (at 736Å) for a 1:3 mixture of \( \text{H}_2(J=0) \) and \( \text{H}_2(J'=1) \).

The possibility exists that a systematic error could be present in our results due to a partial alignment of the rotational angular momentum vectors induced by the supersonic expansion. Such an alignment was observed in the case of sodium dimer, \( \text{Na}_2 \), by Sinha, Caldwell, and Zare [17]. These authors proposed a classical model to explain the effect, based on the exchange of angular momentum in an inelastic collision between a hard ellipsoid (the dimer) and a hard sphere (the monomer). We believe that there is no appreciable alignment in our hydrogen beam for at least two reasons. First, the hydrogen molecule is somewhat more spherical in shape that the sodium dimer, which means that collisions are less effective in causing alignment. Second, the rotational levels of hydrogen at 77K are almost fully relaxed behind the nozzle, so that there are few rotationally-inelastic collisions during the expansion.
IV. CONCLUSION

We have measured the photoelectron asymmetry parameter for the S branch of $H_2^+(v'=0)$ with the results: $\beta_S(584\text{Å}) = 0.87 \pm 0.19$ and $\beta_S(736\text{Å}) = 0.08 \pm 0.15$. The trend toward higher $\beta_S$ with increasing photon energy is well accounted for by the theory of Itikawa [8], and is a manifestation of coupling between the p and f photoelectron waves.
ACKNOWLEDGMENT

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REFERENCES

Table I. Intensity ratios for H$_2^+$ ($v'=0$). Stated error limits are statistical uncertainties ($\pm \sigma$) from the least-squares peak fitting.

<table>
<thead>
<tr>
<th></th>
<th>584Å</th>
<th>736Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{90}(Q)/I_{90}(S)$</td>
<td>12.79 ± 0.21</td>
<td>23.59 ± 0.29</td>
</tr>
<tr>
<td>$I_{53}(Q)/I_{53}(S)$</td>
<td>10.26 ± 0.24</td>
<td>15.55 ± 0.32</td>
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Table II. S branch asymmetry parameters, b₅, for H₂⁺ (v' = 0).

<table>
<thead>
<tr>
<th></th>
<th>584Å</th>
<th>736Å</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Present results</td>
<td>0.87 ± 0.19</td>
<td>0.08 ± 0.15</td>
</tr>
<tr>
<td>Niehaus and Ruf (v' = 1)ᵃ</td>
<td>0.85 ± 0.14</td>
<td></td>
</tr>
<tr>
<td>Chang (v' = 1)ᵇ</td>
<td>0.45 ± 0.87</td>
<td></td>
</tr>
<tr>
<td><strong>Theory:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dill (direct PI)ᶜ</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Ritchie and Tambeᵈ</td>
<td>1.215</td>
<td>0.740</td>
</tr>
<tr>
<td>Chandraᵉ</td>
<td></td>
<td>0.20 - 0.38</td>
</tr>
<tr>
<td>Itikawa (p wave)ᶠ</td>
<td>0.2338</td>
<td>0.2069</td>
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<tr>
<td>Itikawa (p+f waves)ᶠ</td>
<td>0.7494</td>
<td>0.3484</td>
</tr>
</tbody>
</table>

FIGURE CAPTIONS

Fig. 1. The 584Å photoelectron spectrum of n-H$_2$ expanded from 200 Torr at 77K.

Fig. 2. The H$_2^+(v'=0)$ transition at 584Å for two angular geometries. The curve is the least-squares fit, and the points are the data minus the fit (shifted upward for visibility.)

Fig. 3. The H$_2^+(v'=0)$ transition at 736Å for two angular geometries. The curve is the least squares fit, and the points are the data minus the fit (shifted upward for visibility.)
Figure 1
Figure 2
Figure 3
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