STUDIES OF PHOTODISSOCIATION OF MOLECULAR IONS

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Preliminary results are reported on the measurement of the photodissociation cross section of $H_2^+$. Measurements have been made at a number of wavelengths between 3000 Å and 9000 Å, and a comparison is made with available theory. Disagreement of the measurements with theory suggest that improvement of the theory is justified for detailed comparisons with experiment.

A linear decrease with ion source pressure of the photodissociation cross section at 5500 Å is observed. This dependence yields a lower limit of $10^{-15}$ cm$^8$ on the collision cross section for depopulating vibrational states of $H_2^+$ participating in photodissociation at 5500 Å.

White light was also used to observe photodissociation of $H_2^+$ and $N_2^+$, and an average cross section was calculated from the data and the spectral distribution of the lamp used.

An effort to observe photodissociation of $H_2^+$ yielded no results except to place an upper limit of $10^{-26}$ cm$^8$ on the average cross section.

1. Introduction

The hydrogen molecular ion, as the simplest of all molecules, has been extensively investigated theoretically$^1$. In the approximation of stationary nuclei the Schrödinger equation is exactly soluble for the wave functions and electronic energy eigenvalues. The availability of wave functions and the relative simplicity of the system then invite using it as a prototype in calculations of important molecular collisions. Calculations have been made of cross sections for dissociation by electron and proton impact$^2$, $^3$, dissociative recombination$^4$, and photoionization$^5$ and photodissociation$^6$.

It is the last of these processes which is to be discussed here. Linlor and Barnett$^7$ previously observed this process, but did no radiometry on their photon beam. Jefferts and Demehlt$^8$ have done an elegant experiment in which they made use of the photodissociation of $H_2^+$ to selectively align a trapped sample of $H_2^+$. Here, again, no cross sections were measured.

2. The problem

Figure 1 shows relevant potential energy curves of $H_2$ and $H_2^+$ and shows the relative probabilities of forming $H_2^+$ in different vibrational states. (The
relative heights of the probability curves for the $\Sigma^+_g$ and $\Sigma^+_u$ is not significant.) These vibrational probabilities are determined by the Franck-Condon rule, that is, the transition matrix element between the electronic states should not depend very rapidly on $R$, the internuclear separation, over the range of $R$ for which the ground state vibrational wave function is appreciable, so that the relative populations of final vibrational states is determined solely by the overlap integrals of the initial and final vibrational wave functions.

The validity of the above assumptions when forming $H_2^+$ in the $^4\Sigma_u^+$ state has recently been demonstrated by Dunn and Keiffer, and these results are shown in figures 2 and 3.

Fig. 1. Electronic energy level diagram of $H_2$ and $H_2^+$, showing how the Franck-Condon principle determines the distribution of final vibrational states of $H_2^+$ when $H_2$ is ionized by electron impact.

Fig. 2. Experimental measurement showing validity of Franck-Condon rule in determining final "vibrational" states of $H_2^+$ in the $^2\Sigma_u^+$ electronic state.
It is not unreasonable to extrapolate this confirmation of the Franck-Condon principle to formation of \( \text{H}_2^+ \) in the bound \( ^2\Sigma_g^+ \) state. In addition one has the direct evidence of Marmet and Kerwin \(^{10}\) that the first three vibrational levels of \( \text{H}^+(^2\Sigma_g^+) \) are populated in accordance with the Franck-Condon rule.

![Diagram](image)

**Fig. 3.** Energy of peak of proton energy distribution from dissociative ionization of \( \text{H}_2 \) as a function of electron energy. This shows that past about 100 eV electron energy the distribution of final vibrational states of \( \text{H}_2^+(^2\Sigma_g^+) \) is independent of electron energy.

Radiative transitions between the vibrational levels of \( \text{H}_2^+ \) are forbidden, and the state distribution defined by the Franck-Condon rule will be maintained unless collisions with the gas de-excite or excite the vibration of the ion.

Figure 4 shows the states of \( \text{H}_2^+ \) in more detail and indicates the nature of some of the vibrational wave functions. One notes from the energy scale that photodissociation is energetically possible from the vacuum ultraviolet through the infrared, if all vibrational states are populated.

The cross section for photodissociation is proportional to the square of the matrix element

\[
\int \chi_\alpha^*(R) Q(R) X_\nu(R) \, dR,
\]

where \( \chi_\alpha(R) \) and \( X_\nu(R) \) are the vibrational wave functions of the \( ^2\Sigma_u^+ \) and \( ^2\Sigma_g^+ \) states respectively, \( Q(R) \) is the electronic dipole moment, and \( R \) is the internuclear separation.
Gibson\textsuperscript{5} has approximated the calculation of this matrix element by assuming that $Q(R)$ may be replaced by an average value and taken out of the integral (Franck-Condon rule) and by approximating the $\chi_\nu(R)$ with $\delta$ functions at the classical turning points (reflection approximation). Bates\textsuperscript{11} has calculated $Q(R)$ using exact wave functions and shown that it varies rapidly with $R$ for $R > 1$. One also notes that replacing $\chi_\nu$ with a $\delta$ function will probably be a succeeding worse approximation as $R_0$, the classical turning point becomes larger. It would seem then that both of these approximations are questionable when the higher lying vibrational levels of $\text{H}_2^+$ are involved.

This is the calculation with which comparison of experiment will be made, however, since the calculation has not been performed using the exact quantities.

3. Experimental

Figure 5 shows a schematic diagram of the experiment. Ions from the source are mass analyzed and focussed in the collision chamber. At this focus the ion beam is crossed with a photon beam modulated at 450 cps. Protons formed from photodissociation are separated from the $\text{H}_2^+$ ions with an electrostatic analyzer and focussed onto the cathode of an electron multiplier. The output current of the multiplier is then amplified and put
through a synchronous detector. The output of the synchronous detector is integrated with an operational amplifier for a preset time and its output is then punched in digital form onto paper tape. Also entered on the tape are a photon intensity monitoring signal, the primary $H^+_2$ beam, the wavelength and the phase of the synchronous detector.

![Schematic Diagram of Experiment]

Fig. 5. Schematic diagram of the photodissociation experiment.

The hot cathode ion source had the geometry of a Phillips discharge, but was run with regulated emission currents (about 1 mA) and with constant voltage (about 200 volts) across it. The $H_2$ pressure in the source was varied between 2 and 60 microns.

The beam traversed two differentially pumped regions prior to entering the collision chamber. When the ion source pressure ranged from 2 to 60 microns, the intermediate pressures ranged as follows: Region 1, $3-8 \times 10^{-6}$ Torr, Region 2, $2-7 \times 10^{-7}$ Torr, Collision region $0.5-1 \times 10^{-8}$ Torr.

The main source of noise in the experiment was protons from dissociation of $H^+_2$ on the background gas. The noise from these protons was about 30 times that expected from Schott noise.

The experiments performed were:

1. With a constant pressure in the ion source and a constant ion beam all the light from the high pressure xenon arc was focussed on the $H^+_2$ beam. To assure linearity of signals with light, the intensity was varied by varying the arc current and the intensity was measured with a calorimeter. Linearity with ion beam current was determined by varying the beam current.
2. With a constant pressure in the ion source and a constant ion beam monochromatic light (200 Å band width) from the monochromator was focussed on the ion beam. The wavelength was varied and the proton signal observed. This was repeated for two pressures in the ion source. Light intensities were measured with an Eppley thermopile.

3. With constant wavelength light (5500 Å) focussed on the ion beam the pressure in the ion source was varied with ion source current and voltage held constant. Data were obtained for four values of pressure.

4. Results

Fig. 6 shows the results of the measurement of cross section as a function of wavelength at 3 microns source pressure and at 58 microns source pressure. The solid curve is that calculated by Gibson\(^5\) decreased by a factor of 10 in order to plot it on the same scale.

![Graph showing cross section for photodissociation of H\(_2\) vs wavelength](image)

Fig. 6. Preliminary results showing photodissociation cross section in units of 10\(^{-18}\) cm\(^2\) as a function of wavelength. Data are shown for two values of H\(_2\) pressure in the ion source. The solid curve is that calculated by Gibson\(^5\) multiplied by 1/10.

The noise from background dissociation was extremely high, and each point is the average of about fifty measurements, each measurement being a signal integrated for 25 seconds. The data between 3500 Å and 6500 Å have a relative uncertainty of about 20%. Outside of these limits where the light intensity is down the uncertainty is proportionately higher.

In view of the large uncertainty one must accept these results as only
quite preliminary. There are some things which can be noted from the data, however:

1. There is evidence of structure presumably arising from vibrational overlaps.

2. The curves do not agree in either size or shape with the calculation by Gibson. This suggests that the theory should be done more thoroughly as well as further experimental work.

3. There is a definite dependence of the signal at these wavelengths on the ion source pressure.

The last of these facts was more thoroughly investigated, and fig. 7 shows the variation of photodissociation cross section at 5500 Å with ion source pressure.

![Relative cross section for photodissociation of H_2^+ by light of wavelength 5600 Å vs H_2 pressure in the ion source.](image)

Fig. 7. Relative photodissociation cross section at 5500 Å versus H_2 pressure in the ion source.

The linear decrease of this signal with pressure suggests that single collisions in the source are depopulating the vibrational levels responsible for the signal at 5500 Å. An estimate of the maximum path length of ions in the source and the slope of this curve combine to give a lower limit of $10^{-15}$ cm$^2$ on the cross section for depopulating these states. One sees that if he can extrapolate the straight line to zero pressure then the data at 3 microns should be nearly characteristic of the state distribution discussed earlier.

The integrated cross section over the entire spectral distribution of the xenon arc was measured for H_2^+ and N_2^+. The cross sections obtained were $\Sigma_{H_2^+} = 2.6 \times 10^{-19}$ cm$^2$ and $\Sigma_{N_2^+} = 1.7 \times 10^{-20}$ cm$^2$ where $\Sigma$ is defined by...
\[ \Sigma = \int \phi(\lambda) \sigma(\lambda) \lambda d\lambda / \int \phi(\lambda) \lambda d\lambda. \]

For the lamp used* \( \lambda = \int \phi(\lambda) \lambda d\lambda \) is about 7300 Å. The uncertainty in these values is judged to be about 50%.

An effort was made to observe photodissociation of \( \text{H}_2^+ \) using white light, but no signals were obtained. This indicates that \( \Sigma \) is less than \( 10^{-20} \text{ cm}^2 \) for this ion.

6. Conclusions

From the preliminary experimental results reported here it is concluded that further theoretical work on the process \( \text{H}_2^+ + h\nu \rightarrow \text{H}^+ + \text{H} \) is justified. It is concluded that very low ion source pressure must be used in further experimental work if a detailed comparison with theory is to be made.

With increased signal to noise ratio it is anticipated that detailed study of the structure in the photodissociation cross section and the variation of this structure with pressure will yield useful knowledge of vibrational energy transfer of \( \text{H}_2^+ \) by collision with \( \text{H}_2 \).

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