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Publication Date

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Submitted to the Journal of Chemical Physics

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February 1982

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LBL-13696

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n-H₂, p-H₂, HD, AND D₂

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This work is supported by the Director, Office of Energy Research,
Office of Basic Energy Sciences, Chemical Sciences Division of the
U. S. Department of Energy under Contract No. W-7405-ENG-48.

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ABSTRACT

The 584Å photoelectron spectra of n-H₂, p-H₂, HD, and D₂ were recorded at a resolution of 11 meV FWHM using a supersonic molecular beam source. Spectra were taken at several stagnation temperatures and pressures in order to vary the rotational population distribution in the beam with a corresponding variation in the relative intensities of the rotational transitions. Many of the Q branch components were resolved for the first time. $\Delta G(v+1/2)$ and B_v values were measured for all observed vibrational states of H₂⁺, HD⁺, and D₂⁺ and were used to determine the ionic vibrational and rotational constants: ω_e , $\omega_e x_e$, $\omega_e y_e$, $\omega_e z_e$, B_e , and α_e . The results represent a substantial improvement over previous experimental determinations and were found to be consistent with the available theoretical rotation-vibration energy levels. The measurement of the intensity distribution of photoelectrons as a function of vibrational state yielded photoionization cross sections which were in good agreement with the theoretical values calculated by ONeil and Reinhardt.

I. INTRODUCTION

The photoelectron spectra of H_2 , HD, and D_2 can in principle provide a determination of the spectroscopic constants of the H_2^+ , HD^+ , and D_2^+ molecular ions and the relative photoionization cross sections for transitions to the various ionic rotation-vibration energy levels. Although several measurements of these spectra have been reported,¹⁻⁵ there still exists a need for data of higher resolution and signal-to-background ratio, particularly for the upper vibrational states which are usually obscured by the background of stray electrons. The Doppler broadening in the photoelectron spectra of these light molecules is relatively large and has limited the resolution obtained in previous experiments. The Doppler linewidth at room temperature for H_2^+ ($v = 0$) with 584Å (HeI α) light amounts to 20 meV, which is several times larger than the best attainable instrumental resolution. Åsbrink¹ used a Ne(I) light source (736Å, 744Å) to reduce the Doppler broadening and obtained a rotationally-resolved spectrum of H_2^+ ($v = 0$ to 5), but the positions of only a few of the rotational lines could be determined accurately because of the overlapping peaks from the two Ne(I) photon energies.

High quality photoelectron spectra would provide a considerable improvement in our experimental knowledge of the rotation-vibration energy levels of H_2^+ , HD^+ , and D_2^+ . The positions of the few lowest energy levels are known from the extrapolation of Rydberg series.⁶ Conventional absorption or emission spectra from a gaseous discharge have not been observed for these ions in the visible or UV regions

because all of the excited electronic states are repulsive in the vertical region of the ground state. Furthermore, the triatomic species (e.g. H_3^+) becomes the predominant molecular ion in the discharge before the number density of the diatomic ion is high enough for infrared measurements.⁷ The experimental situation has improved considerably in recent years for HD^+ , which, because of its dipole moment and the near coincidence of its vibrational frequency with those of certain CO and CO_2 laser transitions, can be observed in absorption by ion-beam-infrared-laser-resonance techniques.⁷⁻⁹ The accuracy of these measurements is very high ($\pm 0.002 \text{ cm}^{-1}$), but only a small number of rotation-vibration transitions have been observed.

Because the hydrogen molecular ions are composed of just three particles, theory provides a much more complete description of the rotation-vibration energy levels than has been available from experiment. Extensive tabulations exist for the bound state levels calculated in the Born-Oppenheimer and adiabatic approximations.¹⁰⁻¹² Calculations have also been reported which include relativistic, radiative, and non-adiabatic effects for many energy levels of HD^+ ^{13,14} and for a few low-lying levels of the other isotopes.^{15,16}

The relative intensities of transitions to the different ionic vibrational states at 584\AA have been measured for H_2^+ , HD^+ , and D_2^+ by Berkowitz and Spohr² and for H_2^+ by Gardner and Samson.⁴ On the theoretical side, the photoionization cross section as a function of v-state has been calculated at various levels of sophistication by Villarejo,¹⁷ by Itikawa,¹⁸⁻²¹ by Lee and Rabalais,³ by Ford, Docken, and

Dalgarno,²² and by O'Neil and Reinhardt.²³ The agreement between experiment and theory has been satisfactory in general, but a detailed comparison has awaited higher quality spectra, particularly for the upper v -states for which the limited sensitivity and unresolved rotational structure in previous experiments contribute to the uncertainty in the measured values.

We have recorded the 584Å photoelectron spectra of n -H₂, p -H₂, HD, and D₂ with an apparatus which uses a supersonic molecular beam source to remove Doppler broadening. The spectra reveal considerably more rotational structure than was observed in earlier experiments, and, because of the very low spectrometer background, transitions are observed for states up to one or two vibrational quanta from the dissociation limit. The rotational population distribution of the molecules in the beam can be varied significantly by adjusting the stagnation temperature and pressure, and this provides a useful tool for enhancing or reducing transitions from rotationally-excited states of the neutrals. We report values for the rotational and vibrational constants of H₂⁺, HD⁺, and D₂⁺, as well as the photoionization cross sections for all observed vibrational states.

II. EXPERIMENTAL

The apparatus has received a detailed description elsewhere,²⁴ so its characteristics will only be outlined here. Fig. 1 shows a schematic diagram of the experimental set-up. Hydrogen was expanded through a 70- μm -diam nozzle located 6.4 mm from the tip of a 0.66-mm-diam x 6.4-mm-tall skimmer. After entering the main chamber the beam of hydrogen was crossed with the photon beam from a helium resonance lamp, and a fraction ($\sim 10^{-4}$) of the resulting photoelectrons passed through the entrance aperture and was transported by a series of lenses to a 90° spherical sector pre-analyzer. From this point the electrons were decelerated into the main analyzer, a 10.16 cm mean radius hemispherical deflector, and were dispersed across a position-sensitive multichannel detector. The principal advantages of this analyzer design are 1) the reduction of background provided by the pre-analyzer, and 2) the enhanced collection efficiency through the use of multichannel detection. For these experiments the analyzer was operated at a constant pass energy of 1.0 eV which gave a resolution of 11 meV FWHM as observed for the Ar 3p doublet with 584Å light. All spectra were taken with the light source at the 90° geometry; that is, with the nominally unpolarized photon beam orthogonal to the electron trajectory.

Each spectrum was accumulated in a single scan of the kinetic energy lasting two to four hours. Data acquisition and storage were controlled by an LSI-11/2 microcomputer. To eliminate the nonuniformity in the response of the multichannel detector the "dithering" procedure was used, wherein each channel of the spectral array received

counts from every position on the detector for an equal length of time. The scan width was determined by measuring the voltage of the power supply controlling the kinetic energy with a computer-interfaced precision digital voltmeter (Dana 5900) at four points during the scan. The calibration of the scan width in the region of importance for hydrogen was checked by measuring the spectrum of nitrogen and determining the $N_2^+ X \ 2\Sigma_g^+$ ($v = 0$) to $B \ 2\Sigma_u^+$ ($v = 0$) splitting, which is accurately known from emission spectra ($25566.0 \text{ cm}^{-1} = 3.16981 \text{ eV}$).²⁵ This splitting was reproducible to within $\pm 0.001 \text{ eV}$ ($\pm 8 \text{ cm}^{-1}$) with this apparatus.

The n- H_2 and D_2 samples were obtained commercially, the H_2 being UHP grade (99.999%), and the D_2 being CP grade (99.5%) which nevertheless had a noticeable HD impurity that appears in some of our D_2 spectra. The p- H_2 sample was obtained by transferring a quantity of liquid p- H_2 from a hydrogen liquefier into a standard aluminum gas cylinder. The purity of the p- H_2 gas was approximately 90-95% initially, and the observed half-life for conversion to n- H_2 was 3 to 4 weeks at a pressure of 70 psig. HD was prepared²⁶ by the reaction of $LiAlH_4$ with D_2O , and the gas was compressed to several hundred psi and stored in an aluminum cylinder. Impurities of H_2 and D_2 amounted to about 1% each in the HD sample.

The quadrupole mass filter was not in the chamber during these experiments, but the fraction of clusters in the molecular beam was expected to be negligible. Even at a stagnation temperature of 77K the backing pressure we used (200 Torr) was an order of magnitude below that needed for significant dimerization.²⁷

III. RESULTS AND DISCUSSION

A. Spectra

The 584Å spectra of n-H₂, p-H₂, HD, and D₂ expanded from about one atmosphere at room temperature (297K) are shown in Figs. 2 and 3 with the ionic vibrational states indicated and the Q branch ($J' = J''$) rotational quantum numbers labeled for a typical vibrational band. The lower vibrational levels of H₂⁺ also exhibit partially resolved S branches ($J' = J'' + 2$) which are labeled as such. In most cases a separate scan with better statistics for the higher vibrational levels is also presented in the figure. Small discontinuities in the spectra at kinetic energies of 5.28 and 5.46 eV are due to Ar calibration peaks which have been subtracted out. These hydrogen spectra represent a considerable improvement over previously published results in both the resolution and the signal-to-background ratio (typically 200-300 near the strongest transitions). Even so, the Q branches are not totally resolved, and as a consequence the spectral analysis must rely heavily on deconvolution techniques, limiting the accuracy of the resulting spectroscopic constants. This limitation can be largely overcome by adjusting the nozzle temperature so as to change the rotational population distribution of the molecules in the beam. When hydrogen at 77K undergoes a supersonic expansion the molecules are left almost entirely in their lowest accessible rotational states. For p-H₂ and HD this is the $J'' = 0$ level, but for n-H₂ there is a 1:3 mixture of $J'' = 0$ and $J'' = 1$, and for n-D₂ a 2:1 mixture of $J'' = 0$ and $J'' = 1$. Thus the 77K spectra of p-H₂ and HD in Fig. 4 consist primarily of vibrational bands

involving only the Q(0) rotationless transitions. The 77K spectrum of D_2 in Fig. 4 is similar in appearance to a rotationless spectrum despite the $\sim 33\%$ Q(1) component because the splitting between the Q(0) and Q(1) transitions is only 4–6 meV and is not resolved. The 77K spectra give us the best data on the vibrational properties of H_2^+ , HD^+ , and D_2^+ , namely the ΔG values and photoionization cross sections. We can also produce a rotationally relaxed hydrogen beam starting from room temperature by running with a smaller nozzle at much higher backing pressure (e.g., 40- μ m-diam and 100 psi), but the cooling is not as effective as with the nozzle held at 77K. On the other hand the rotationally excited transitions can be enhanced by heating the nozzle, as was done for the high temperature spectra which are shown in Fig. 5. These spectra allow us to determine the rotational constants with better accuracy than is possible with the room temperature spectra because the Q branch extends to higher J-states. It was not possible to generate a satisfactory spectrum of HD while heating the nozzle because the sample rapidly converted to a mixture of HD, H_2 , and D_2 . The spectrum of HD with transitions out to Q(5) in Fig. 5 was taken with the nozzle at room temperature and a very low backing pressure (50 Torr), for which the degree of rotational relaxation was significantly less than for the HD scan at 600 Torr backing pressure shown in Fig. 3. A number of discontinuities are evident in the 50 Torr spectrum of HD, which are due to an air impurity that has been subtracted out. A scan of p- H_2 with the heated nozzle was not attempted because the conversion to n- H_2 was expected to be rapid.

B. Energy Scale

The quantity measured in the photoelectron spectrum is the electron energy distribution in the laboratory frame, and to convert this to the kinetic energy distribution in the center-of-mass frame we must account for the recoil energy of the ion as given by conservation of momentum. This is particularly simple when the electrons are sampled perpendicular to a collimated molecular beam, because we may assume that the molecule initially has zero velocity along the detection direction. For a measured laboratory energy E_{lab} , the ionization energy E_I (equals photon energy minus kinetic energy) is given by

$$E_I = h\nu - (1 + m_e/m_+) E_{lab} \quad (1)$$

where $h\nu = 17119.148 \text{ cm}^{-1}$,²⁸ and $1 + m_e/m_+$ has the values 1.0002722 for H_2^+ , 1.0001816 for HD^+ , and 1.0001362 for D_2^+ . To convert the kinetic energy from electron volts to wave numbers we have used the factor $1.2398520 \times 10^{-4} \text{ eV/cm}^{-1}$ given by Cohen and Taylor.²⁹ The absolute ionization energy determined in this experiment is subject to an uncertainty of about $10\text{--}20 \text{ cm}^{-1}$ because of drift in the spectrometer offset due to changing contact potentials. However the present spectroscopic analyses rely only on relative ionization energies (peak splittings) for which the uncertainty is much less.

C. Vibrational Energy Levels

The 77K spectra of $p\text{-H}_2$, HD, and D_2 in Fig. 4 were used to determine the pure vibrational level energies of H_2^+ , HD^+ , and D_2^+ .

Since all transitions originate from the $v = 0$ level of the neutral

hydrogen molecule, the vibrational differences of the molecular ion, $\Delta G(v + 1/2) = G(v + 1) - G(v)$, are obtained directly from the successive vibrational splittings in the photoelectron spectra. The individual vibrational peaks exhibited a FWHM of 90–100 cm^{-1} , and the centers of the transitions could be located visually to an accuracy of about 5 cm^{-1} by plotting the spectrum on an expanded scale. We have been able to reduce considerably the random error inherent in the visual peak-finding process by a least-squares fitting procedure using an empirically derived lineshape function. The response function of the instrument was assumed to be represented by the 584Å spectrum of $\text{Ar}^+ 2p_{3/2}$ taken on the same occasion as a given hydrogen spectrum. The Ar^+ peak, which had a FWHM of 85–95 cm^{-1} , was both broadened by 2–3 cm^{-1} and smoothed via convolution with a 16 cm^{-1} FWHM Gaussian function in order to represent the residual Doppler-broadening in the hydrogen lineshape. The empirical lineshape was similar in appearance near its mean to a Gaussian, with the addition of a small exponential tail on the high kinetic energy side and a larger tail on the low energy side. The function was stored numerically with the area and mean as adjustable parameters and was evaluated along with the necessary partial derivatives for the least-squares procedure by a quadratic interpolation over the stored values. The fitting of the hydrogen peaks was performed interactively using a derivative least-squares fitting routine. An example of this procedure is illustrated in Fig. 6 which shows the $v = 2$ transition in $p\text{-H}_2$ at 77K with the decomposition into the four rotational components making up this peak. The $o\text{-H}_2$

impurity, as revealed by the Q(1) transition, contributes about 10% of the total area, and the S branch (primarily the $J' = 2 \leftarrow J'' = 0$ transition) contributes about 6%. Because of the limited resolution, it proved to be impractical to obtain a fit without constraining the relative positions of the rotational components in a given vibrational transition. These rotational splittings were calculated using the B_e and α_e values determined from the higher temperature photoelectron spectra as described in Section III.E. Thus the free parameters in the fitting of the 77K vibrational peaks were the position of the Q(0) transition, the areas of the rotational components, and the value of the background function which was assumed to be a constant. The least-squares fitting located the vibrational origins to within standard deviations of 1 cm^{-1} or better for p-H₂ and HD, and 2 cm^{-1} or better for D₂. Based on these results we have assigned a statistical uncertainty ($\pm 2\sigma$) for the measured $\Delta G(v + 1/2)$ values of $\pm 2 \text{ cm}^{-1}$ for H₂⁺ and HD⁺, and $\pm 5 \text{ cm}^{-1}$ for D₂⁺. The principal source of systematic error is the drift in the kinetic energy offset during the course of the scan, and its magnitude can be gauged from the reproducibility of the N₂⁺ X-B splitting ($25566 \pm 8 \text{ cm}^{-1}$) discussed in Section II. Since the $\Delta G(v + 1/2)$ values are 2200 cm^{-1} or less, we obtain a corresponding systematic error of $\pm 0.7 \text{ cm}^{-1}$ or less.

The experimental $\Delta G(v + 1/2)$ values for H₂⁺, HD⁺, and D₂⁺ are listed in column 2 of Tables I, II, and III, respectively. Column 3 lists the theoretical values of Hunter, Yau, and Pritchard¹² (HYP) for H₂⁺ and D₂⁺, and of Wolniewicz and Poll¹³ (WP) for HD⁺. Column

4 contains the available values from Rydberg series limits tabulated by Huber and Herzberg.⁶ The agreement between experiment and theory is generally quite good. The number of cases for which the theoretical $\Delta G(v + 1/2)$ falls within our statistical uncertainty is 14 out of 17 for H_2^+ , 19 out of 20 for HD^+ , and 21 out of 23 for D_2^+ . The stated accuracy of the HYP calculations performed in the adiabatic approximation is 0.1-0.2 cm^{-1} for H_2^+ and D_2^+ , whereas for HD^+ the WP calculations include relativistic, radiative, and nonadiabatic corrections and are expected to be accurate to 0.001 cm^{-1} . The precision of our results is best in the case of HD^+ for which the $Q(0)$ transitions contribute about 90% of the intensity in each vibrational peak and worst in the case of D_2^+ where the $Q(0)$ components are less than 67% of the total intensity.

The vibrational constants are defined by the expression

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3 + \omega_e z_e(v + 1/2)^4 + \dots \quad (2)$$

and can be evaluated by fitting $\Delta G(v + 1/2)$ to a power series in $v + 1/2$. In Fig. 7 are shown the experimental $\Delta G(v + 1/2)$ curves for the three ions. They are similar in shape to the corresponding curve for the $X \ ^1\Sigma_g^+$ ground state of H_2 obtained by Herzberg and Howe³⁰ from the analysis of the H_2 Lyman bands. The curvature is positive for low $v + 1/2$ with a point of inflection at 7-1/2, 9-1/2, and 10-1/2 for H_2^+ , HD^+ , and D_2^+ respectively, followed by a region of negative curvature as the dissociation limit is approached. This shape is made more

apparent by removing a linear term from the $\Delta G(v + 1/2)$ curve, an example of which is shown in Fig. 8 for the case of H_2^+ . Although Herzberg and Howe found that the full accuracy of their ΔG values ($\pm 0.05 \text{ cm}^{-1}$) could not be represented by a single power series expansion, we have been able to represent our data adequately within the statistical uncertainty by least-squares fitting to four-term formulas. The coefficients and the corresponding vibrational constants are presented in Tables IV and V. We have also fitted in the same manner the HYP and WP theoretical energy levels, and although they are not an exact representation of the theoretical energies the resulting vibrational constants are listed for comparison in Table V. It is seen that agreement to within our statistical uncertainty is achieved for all the constants of HD^+ and D_2^+ , and that the theoretical constants of H_2^+ are slightly larger in magnitude than our measured values. Because of the inadequacy of the four-term formula in fitting the theoretical energies, it is more meaningful to make a direct comparison of the $\Delta G(v+1/2)$ values to establish the consistency between theory and experiment.

An additional quantity of interest is the dissociation energy, D_0^0 , which we have evaluated by integrating $\Delta G(v+1/2)$ from $v+1/2=0$ to the intercept using the parameters given in Table IV. These results are listed together with other experimental and theoretical values in Table VI. Considering the possible inaccuracies in this method of evaluation, the agreement reached is reassuring and constitutes a useful check on the accuracy of the present vibrational constants.

D. Vibrational Cross Sections

The 77K spectra of p-H₂, HD, and D₂ in Fig. 4 were used to determine the vibrational intensity distributions, because of the absence of complications arising from rotational structure apparent in the higher temperature spectra. The areas of all observed peaks were determined from the peak-fitting procedure described in the previous section. To convert these areas into photoionization cross sections we must consider the effects of 1) the angular distribution of photoelectrons, and 2) the transmission of the analyzer as a function of kinetic energy.

Because the electrons were sampled at an angle of 90° from the photon propagation direction (rather than at the "magic" angle of 54.7°) the observed peak areas must be corrected to obtain the relative cross sections if the asymmetry parameter, β , varies as a function of vibrational state. The predominant rotational transitions in these spectra are $J'=0 \leftarrow J''=0$, for which Dill³¹ has shown that β equals 2.0 independent of the photon energy and v -state. The higher rotational components of the Q branch (mainly Q(1)) appearing in the 77K spectra are predicted by Itikawa²¹ and Dill³¹ to have β -values close to 2.0 which change only slightly with v -state. The precision of the experiment does not warrant a correction for this smaller effect. A more appreciable angular distribution effect results from the presence of the S branch (mainly $J'=2 \leftarrow J''=0$) seen as a shoulder on the first few v -states of p-H₂ in Fig. 5. For the S branch β is significantly less than 2.0, and we find that the S branch intensity decreases rapidly

relative to the Q branch with increasing v -state. Since the β -value for the S branch is in some dispute (see Itikawa²¹), we have measured the rotationally-resolved angular distribution of the H_2^+ ($v=0$) state using two lamps oriented at 90° and 54.7° from the electron trajectory. This measurement will be described fully in a future publication, but for the purpose of correcting the present H_2^+ vibrational intensity distribution we have used the values $\beta_Q = 2.0$ and $\beta_S = 1.0$ for all v -states. The correction turns out to be less than 0.5% of the area of the peak for all the transitions of H_2^+ , which is less than the statistical uncertainty in the areas. No attempt was made to correct the HD^+ and D_2^+ intensities for the angular distribution effect because the S branch contributions to the areas could not be determined accurately, and the magnitude of the correction would be quite small in any case.

The transmission of the analyzer as a function of kinetic energy provides the principal source of error in the vibrational cross sections. This aspect of the analyzer performance was discussed in a previous publication.²⁴ The spectra of N_2 and CO at 584\AA were recorded during the course of the present experiments, and the observed intensities were compared with those measured by Gardner and Samson³² using a calibrated analyzer of moderate resolution (45 meV). The resulting transmission curve for our spectrometer exhibits a decrease of about 20% across the kinetic energy range covered by the hydrogen scans. However, there is considerable scatter in the results despite the likelihood that the actual transmission is a smooth function of kinetic energy.

The discrepancies might arise from errors in the vibrationally-resolved β -values for H_2 and CO ,³³ or more probably from the fact that with our higher resolution and sensitivity the spectra take on a rather different appearance, and a direct comparison with Gardner and Samson may not be appropriate. For the case of the hydrogen vibrational cross sections we present both the uncorrected data and the data corrected with a transmission function derived by fitting a linear function to the results from N_2 and CO . In most cases the two sets of cross sections differ by less than 10%, and this provides a reasonable estimate of the maximum systematic error in the results. By comparison the statistical error is always much smaller, being about 1% or less for H_2 and HD .

The present spectra show the vibrational states with a good signal-to-background ratio out to quite near the dissociation limit, thus permitting us to place the vibrational cross sections on an absolute scale by summing the peak areas and equating the sum to the total ionization cross section (less the dissociative ionization cross section). We have taken a weighted average of the values determined by Bennet, et al.³⁴ (6.51 ± 0.33 Mb), Starr and Lowenstein³⁵ (6.19 ± 0.31 Mb), and Brolley, et al.³⁶ (6.48 ± 0.17 Mb) to obtain the value of 6.41 Mb for the 584Å photoionization cross section of H_2 . The HD and D_2 cross sections are expected to be equal to that of H_2 at 21.2 eV, since the excitation energy is well above all bound ionic states. The assumption has been verified by Lee, Carlson, and Judge³⁷ who measured essentially identical absorption cross sections for H_2 and D_2 in

the 21 eV region using synchrotron radiation. The fraction of dissociative ionization at 584Å has been measured for H₂ ($H^+/H_2^+ = 0.0205$) and D₂ ($D^+/D_2^+ = 0.0080$) by Browning and Fryar,³⁸ and for HD we have used the theoretical value ($H^+(D^+)/HD^+ = 0.013$) of Ford, Docken, and Dalgarno²² which is expected to be accurate in light of the good agreement between theory and experiment for H₂ and D₂. (It should also be possible to determine the fraction of dissociative ionization from the ratio of the continuum intensity to the bound state intensity in the 584Å photoelectron spectra. From the p-H₂ spectrum at 77K we arrive at a value of 0.01 to 0.04 depending on how the continuum intensity is extrapolated to zero kinetic energy.) The bound state photoionization cross sections at 584Å are thus 6.28 Mb, 6.33 Mb, and 6.36 Mb for H₂, HD, and D₂, respectively.

Tables VII, VIII, and IX list the measured vibrational cross sections together with the theoretical values which are available in the case of H₂ and D₂. The results are plotted in Fig. 9. The correction for the analyzer transmission is seen to be fairly small relative to the overall variation in the cross section by two orders of magnitude. Probably of greatest interest here are the cross sections for the higher v-states, many of which are reported for the first time. The relative intensities for states with v greater than 9 are rather insensitive to transmission effects because the variation in kinetic energy is less than 1 eV over this portion of the spectrum. Whether one chooses to compare the corrected or the uncorrected results with the theoretical values of O'Neil and Reinhardt,²³ the agreement between

experiment and theory is quite good for all v -states. The approach of O'Neil and Reinhardt uses the molecular frame, Hund's case b description of photoionization, where both the initial and final states are described by high quality CI wave functions, and the angular momentum of the outgoing wave is not specified. The transition moment, which depends explicitly on the internuclear distance and the photoelectron energy, is calculated using the moment-imaging technique to extract the continuum oscillator strength. The vibrational cross sections are then obtained by numerical integration of the transition moment over the initial and final state vibrational wave functions. The effect of rotation-vibration interaction is neglected, but a direct comparison with the present results is still appropriate, because the spectra are nearly rotationless, and rotational coupling effects have been predicted to be rather small.¹⁷

The theoretical cross sections of Itikawa²⁰ which were calculated using a single ($\ell = 1$) partial wave are seen to be in good agreement with experiment for the higher v -states but are systematically low for v less than 9. This situation is not changed significantly by the inclusion of higher partial waves,²¹ and O'Neil and Reinhardt²³ point out that the discrepancy at the lower v -states is due to error in Itikawa's transition moment. The results of Ford, Docken, and Dalgarno²² rely on a more approximate theory but nevertheless agree fairly well with experiment for v greater than 4.

The present cross sections may be compared with previously reported relative photoelectron intensities by an appropriate scaling of the data, and we find that the agreement is fairly good (within 5 - 10%) for the results of Berkowitz and Spohr² on H_2^+ , HD^+ , and D_2^+ ($v = 0$ to 9 or 10) and of Gardner and Samson⁴ on H_2^+ ($v = 0$ to 9). However, Gardner and Samson give intensities significantly lower than ours for $v = 10$ to 15. The source of the discrepancy is most likely the noticeable background and unresolved rotational components falling between the predominant Q(1) transitions in their room temperature spectrum of $n-H_2$ (see Fig. 2 of this paper for comparison). This led Gardner and Samson to conclude that Itikawa's cross sections¹⁷ were too high at the upper v -states, whereas our data support a different conclusion, namely that Itikawa's results are accurate for high v but too low for v less than 9. The good agreement between the present values and those of O'Neil and Reinhardt indicates that the vibrational photoionization cross sections of hydrogen have now been both measured experimentally and understood theoretically in a very satisfactory manner.

E. Rotational Energy Levels

The rotational constants of H_2^+ , HD^+ , and D_2^+ were determined from the higher temperature spectra shown in Fig. 5. In the case of H_2^+ the room temperature spectrum of $p-H_2$ was also used. The peaks were located visually to an accuracy of 5 to 10 cm^{-1} , because the incomplete resolution made it impractical to use a fitting procedure. The Q branch transitions were analyzed by least-squares fitting to the formula

$$v = v_0 + (B_V' - B_0'') J(J+1) - (D_V' - D_0'') J^2(J+1)^2 \quad (3)$$

where the second order term was used only in the case of H_2^+ for which it was justified by the precision of the data. From Huber and Herzberg⁶ we obtained the B_0'' values of 59.336, 44.670, and 29.907 cm^{-1} for H_2 , HD, and D_2 and the D_0'' value of 0.046 cm^{-1} for H_2 . The ionic rotational constants are listed in Table X and are plotted in Figs. 10 and 11. The B_V' curves were least-squares fitted to the formula

$$B_V = B_e - \alpha_e(v + 1/2) \quad (4)$$

and the resulting equilibrium rotational constants and internuclear distances are presented in Table XI. The values for B_e and r_e are in agreement with the Rydberg series results to within our statistical uncertainty, but the present α_e values are consistently lower than those measured previously. This is a consequence of the fact that the B_V curves initially have a slight positive curvature, so that the slope is steeper over the region observed in Rydberg series than it is for the higher v -states. Also shown in Fig. 10 is the theoretical B_V curve of H_2^+ obtained by Beckel, Hansen, and Peek¹¹ by fitting a fourth order polynomial in $J(J+1)$ to their calculated rotational energies (which were essentially identical to the rotational energies of HYP). In general the theoretical curve falls within our error limits, although the measured values seem to be systematically higher than the theoretical ones, a trend which is also apparent in the photoelectron-derived data of Morioka, Hara, and Nakamura.⁵

IV. SUMMARY

The high resolution 584Å photoelectron spectra of n-H₂, p-H₂, HD, and D₂ were measured in a molecular beam experiment to obtain improved spectroscopic constants for H₂⁺, HD⁺, and D₂⁺, and to determine the photoionization cross sections as a function of ionic vibrational state. The vibrational differences, $\Delta G(v+1/2)$, for the ions were measured to an accuracy of about 2 cm⁻¹ for H₂⁺ and HD⁺ and about 5 cm⁻¹ for D₂⁺, and in nearly all cases these results were in agreement with the theoretical $\Delta G(v+1/2)$ values to within our expected accuracy. These experiments do not constitute a definitive test of the theory, because the calculated level energies should be considerably more accurate than our measured values, as has been confirmed for some levels of HD⁺ by infrared laser experiments.^{7,8} However, the present measurements do provide a valuable check on the correctness of the theory for many ionic levels that are likely to be very difficult to observe by optical techniques. The $\Delta G(v+1/2)$ curves were least-squares fitted to four-term formulas, thereby giving ω_e , $\omega_e x_e$, $\omega_e y_e$, and $\omega_e z_e$ for each of the three ions. D_0^0 , B_e , α_e , and r_e were also determined and found to be consistent with previous experimental and theoretical results.

The vibrational photoionization cross sections were measured for nearly all the bound states of H₂⁺, HD⁺, and D₂⁺ to an accuracy of 5-10%, with the transmission function of the analyzer being the principal source of uncertainty. The results were in very good agreement with the theoretical H₂⁺ and D₂⁺ cross sections of ONeil and Reinhardt,²³ calculated using the body-frame Hund's case b description and the

Stieltjes moment-imaging procedure. The discrepancy that existed in the literature between experiment and theory for the high v -states of H_2^+ has now been resolved.

We have not discussed the rotational intensity distributions in the photoelectron spectra of hydrogen, because this topic is closely related to the study of the rotational relaxation of the molecules in a supersonic expansion. We have performed measurements of the rotational populations as a function of stagnation temperature and pressure by photoelectron spectroscopy, and these results will be reported in a future publication.

ACKNOWLEDGMENTS

We wish to thank Mr. A. Wodtke and Mr. D. Neumark of LBL for the HD samples. We are also grateful to Dr. S. V. O'Neil and Prof. W. P. Reinhardt for providing us with their D_2 cross section results. This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. W-7405-ENG-48.

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Table I. Vibrational differences, $\Delta G(v+1/2)$, of the H_2^+ ground state $^2\Sigma_g^+$, in cm^{-1}

$v+1/2$	Present results	HYP theory ^a	Rydberg series ^b
.5	2190.9	2191.32	2191.2
1.5	2065.2	2064.09	2064.2
2.5	1941.8	1941.08	1940.8
3.5	1822.1	1821.64	
4.5	1706.2	1705.13	
5.5	1591.1	1590.90	
6.5	1477.7	1478.32	
7.5	1367.0	1366.75	
8.5	1257.8	1255.51	
9.5	1145.8	1143.88	
10.5	1031.9	1031.09	
11.5	913.3	916.31	
12.5	796.6	798.59	
13.5	676.4	676.86	
14.5	548.4	549.97	
15.5	415.4	416.62	
16.5	280.3	275.96	
17.5		131.26	

^aG. Hunter, A. W. Yau, and H. O. Pritchard, At. Data Nucl. Data Tables, 14, 11 (1974).

^bG. Herzberg and Ch. Jungen, J. Mol. Spectrosc., 41, 425 (1972).

Table II. Vibrational differences, $\Delta G(v+1/2)$, of the HD^+ ground state $^2\Sigma_g^+$, in cm^{-1}

$v+1/2$	Present results	WP theory ^a	Rydberg series ^b
.5	1913.1	1912.994	1913.1
1.5	1817.2	1816.862	1816.7
2.5	1722.7	1723.587	1723.7
3.5	1631.8	1632.799	
4.5	1543.0	1544.134	
5.5	1456.8	1457.231	
6.5	1372.0	1371.735	
7.5	1287.5	1287.287	
8.5	1201.7	1203.524	
9.5	1119.4	1120.066	
10.5	1035.2	1036.522	
11.5	951.3	952.469	
12.5	866.2	867.459	
13.5	779.8	781.002	
14.5	693.2	692.557	
15.5	600.6	601.522	
16.5	507.2	507.237	
17.5	409.0	408.975	
18.5	306.1	306.048	
19.5	203.0	198.460	
20.5		90.67	

^aL. Wolniewicz and J. D. Poll, J. Chem. Phys., 73, 6225 (1980).

^bK. P. Huber and G. Herzberg, Constants of Diatomic Molecules, Van Nostrand Reinhold, New York (1979).

Table III. Vibrational differences, $\Delta G(v+1/2)$, of the D_2^+
ground state $^2 \Sigma_g^+$, in cm^{-1}

$v+1/2$	Present results	HYP theory ^a	Rydberg series ^b
.5	1583.5	1577.15	1577.3
1.5	1510.0	1512.47	1512.1
2.5	1450.3	1449.40	
3.5	1388.4	1387.81	
4.5	1326.3	1327.51	
5.5	1271.0	1268.36	
6.5	1211.2	1210.18	
7.5	1157.3	1152.83	
8.5	1091.7	1096.13	
9.5	1044.7	1039.95	
10.5	985.8	984.10	
11.5	927.0	928.41	
12.5	872.7	872.73	
13.5	814.3	816.86	
14.5	759.3	760.60	
15.5	702.4	703.77	
16.5	644.7	646.12	
17.5	584.9	587.43	
18.5	523.9	527.43	
19.5	463.7	465.84	
20.5	399.6	402.35	
21.5	327.3	336.63	
22.5	271.0	268.41	
23.5		197.52	
24.5		124.61	
25.5		54.77	
26.5		11.07	

^aG. Hunter, A. W. Yau, and H. O. Pritchard, *At. Data Nucl. Data Tables*, 14, 11 (1974)

^bK. P. Huber and G. Herzberg, *Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York (1979).

Table IV. Least squares coefficients derived from fitting of the experimental data to the formula $\Delta G(v+1/2) = a_0 + a_1(v+1/2) + a_2(v+1/2)^2 + a_3(v+1/2)^3$, in cm^{-1}

	H_2^+	HD^+	D_2^+
a_0	2257.5	1963.8	1612.7
a_1	-132.80	-100.85	-67.11
a_2	2.815	1.951	1.017
a_3	-0.1232	-0.0724	-0.0308

Table V. Hydrogen molecular ion vibrational constants, in cm^{-1} . Stated error limits are statistical uncertainties ($\pm 2\sigma$) from the least-squares fit. Theoretical constants were obtained by fitting to published energy levels.

	H_2^+		HD^+		D_2^+	
	Present results	HYP theory ^a	Present results	MP theory ^b	Present results	HYP theory ^a
ω_e	2324.4 ± 2.6	2326.6	2014.6 ± 1.8	2015.2	1646.4 ± 5.2	1645.2
ω_e^x	67.84 ± 0.64	68.71	51.42 ± 0.39	51.58	34.07 ± 0.96	34.20
ω_e^y	1.000 ± 0.059	1.085	0.687 ± 0.030	0.709	0.354 ± 0.065	0.371
ω_e^z	-0.0308 ± 0.0017	-0.0332	-0.0181 ± 0.0007	-0.0188	-0.0077 ± 0.0014	-0.0080

^aG. Hunter, A. W. Yau, and H. O. Pritchard, At. Data Nucl. Data Tables, 14, 11 (1974).

^bL. Wolniewicz and J. D. Poll, J. Chem. Phys., 73, 6225 (1980).

Table VI. Hydrogen molecular ion dissociation energies, D_0^0 ,
in cm^{-1} . The first two entries are experimental;
the remainder are theoretical.

	H_2^+	HD^+	D_2^+
Present results	21375	21515	21687
Huber and Herzberg ^a	21379.8	21516.4	21711.9
HYP ^b	21379.17	21515.91	21711.47
Bishop ^c	21379.39	21515.99	21711.51
WP ^d		21516.073	

^aK. P. Huber and G. Herzberg, Constants of Diatomic Molecules, Van Nostrand Reinhold, New York (1979).

^bG. Hunter, A. W. Yau, and H. O. Pritchard, At. Data Nucl. Data Tables, 14, 11 (1974).

^cD. M. Bishop, Mol. Phys., 28, 1397 (1974).

^dL. Wolniewicz and J. D. Pott, J. Chem. Phys. 73, 6225 (1980).

Table VII. Photoionization cross sections (in Mb) for $H_2X^2\Sigma_g^+(v') \leftarrow H_2X^1\Sigma_g^+(v''=0)$ at 584Å. Error limits are the statistical uncertainties ($\pm 2\sigma$). Experimental values have been corrected for β . Columns 2 and 3 are the results uncorrected and corrected for analyzer transmission. Columns 4, 5, and 6 are theoretical values.

v'	Uncorrected	Corrected	ONeil and Reinhardt ^a	Itikawa ($\ell = 1$) ^b	Ford, et al. ^c
0	.447±.006	.477±.006	.4533	.3879	.53
1	.868±.008	.907±.008	.8639	.7428	1.00
2	1.021±.008	1.048±.008	1.0036	.8722	1.15
3	.966±.007	.975±.007	.9313	.8206	1.05
4	.799±.006	.793±.006	.7656	.6845	.85
5	.611±.005	.598±.005	.5866	.5332	.65
6	.462±.004	.446±.004	.4315	.3971	.47
7	.329±.004	.315±.004	.3105	.2893	.33
8	.236±.003	.223±.003	.2211	.2082	.24
9	.168±.003	.157±.003	.1568	.1493	.16
10	.1183±.0007	.1095±.0007	.1113	.1069	.12
11	.0842±.0006	.0773±.0005	.07927	.0769	.08
12	.0596±.0006	.0543±.0005	.05659	.0554	.06
13	.0416±.0012	.0377±.0011	.04038	.0396	
14	.0293±.0003	.0264±.0003	.02856	.0282	
15	.0199±.0002	.0179±.0002	.01969	.0197	
16	.0124±.0002	.0111±.0002	.01273	.0128	
17	.0077±.0002	.0068±.0002	.006933	.0069	
18			.002162	.0021	
19			.000098		
Sum	6.280	6.280	6.083	5.434	6.69

^aS. V. ONeil and W. P. Reinhardt, J. Chem. Phys., 69, 2126 (1978).

^bY. Itikawa, Chem. Phys., 30, 109 (1978).

^cA. L. Ford, K. K. Docken, and A. Dalgarno, Astrophys. J., 195, 819 (1975).

Table VIII. Photoionization cross sections (in Mb) for
 $\text{HD}^+ \chi^2 \Sigma_g^+ (v')$ \leftarrow $\text{HD} \chi^1 \Sigma_g^+ (v''=0)$ at 584Å. Error limits are
the statistical uncertainties ($\pm 2\sigma$). Columns 2 and 3 are the
results uncorrected and corrected for analyzer transmission.

v'	Uncorrected	Corrected
0	.283±.006	.302±.007
1	.635±.008	.667±.008
2	.877±.009	.907±.009
3	.895±.008	.912±.008
4	.809±.007	.813±.007
5	.685±.006	.679±.006
6	.552±.005	.541±.005
7	.419±.004	.406±.004
8	.321±.004	.307±.004
9	.241±.003	.229±.003
10	.172±.003	.162±.003
11	.128±.002	.119±.002
12	.0918±.0016	.0849±.0015
13	.0662±.0014	.0608±.0013
14	.0485±.0012	.0443±.0011
15	.0354±.0010	.0321±.0009
16	.0260±.0007	.0235±.0006
17	.0185±.0006	.0167±.0005
18	.0125±.0005	.0112±.0004
19	.0084±.0004	.0075±.0004
20	.0057±.0004	.0051±.0003
Sum	6.330	6.330

Table IX. Photoionization cross sections (in Mb) for
 $D_2^+ X^2 \Sigma_g^+(v')$ \leftarrow $D_2 X^1 \Sigma_g^+(v''=0)$ at 584Å. Error limits
 are the statistical uncertainties ($\pm 2\sigma$). Columns 2 and 3 are the
 results uncorrected and corrected for analyzer transmission.
 Column 4 lists the theoretical values.

v'	Uncorrected	Corrected	O'Neil and Reinhardt ^a
0	.171±.031	.182±.033	.1744
1	.452±.016	.475±.017	.4597
2	.702±.035	.728±.037	.7008
3	.826±.031	.846±.032	.8160
4	.821±.030	.831±.030	.8097
5	.738±.027	.739±.027	.7247
6	.631±.024	.625±.024	.6054
7	.503±.022	.493±.021	.4825
8	.386±.016	.374±.016	.3725
9	.294±.013	.283±.012	.2815
10	.218±.012	.208±.012	.2099
11	.161±.010	.153±.009	.1553
12	.123±.009	.115±.008	.1145
13	.0913±.0027	.0851±.0025	.08435
14	.0663±.0021	.0614±.0019	.06227
15	.0491±.0018	.0452±.0016	.04614
16	.0363±.0015	.0332±.0014	.03433
17	.0276±.0013	.0251±.0012	.02566
18	.0204±.0011	.0185±.0010	.01925
19	.0155±.0010	.0140±.0009	.01447
20	.0109±.0009	.0098±.0008	.01087
21	.0083±.0007	.0074±.0006	.008101
22	.0051±.0005	.0046±.0004	.005925
23	.0037±.0005	.0033±.0005	.004164
24			.002680
25			.001411
26			.000339
27			.000048
Sum	6.360	6.360	6.227

^aS. V. O'Neil and W. P. Reinhardt, private communication.

Table X. Hydrogen molecular ion rotational constants, in cm^{-1} .
 Stated error limits are statistical uncertainties ($\pm 2\sigma$)
 from the least-squares fit.

v	B_v	H_2^+ D_v	HD^+ B_v	D_2^+ B_v
0	29.6±2.5	.03±.08	22.6±1.7	14.9±0.2
1	28.1±1.1	.04±.04	21.5±1.0	14.0±0.4
2	26.4±1.1	.03±.03	20.3±1.1	13.6±0.5
3	24.8±0.5	.02±.02	19.8±1.2	13.1±0.5
4	23.6±1.1	.03±.04	18.7±0.9	13.2±0.6
5	22.3±0.4	.03±.01	18.0±0.4	12.4±0.1
6	21.0±1.3	.02±.04	16.9±0.6	11.8±0.2
7	19.0±0.3	.00±.01	16.6±0.5	11.2±0.2
8	18.3±0.5	.04±.03	15.6±0.3	10.7±0.2
9	17.2±0.6	.05±.03	14.0±0.4	10.3±0.4
10	15.0±0.8	.00±.04	14.0±0.5	9.8±0.4
11	14.5±0.5		14.4±1.6	9.8±0.4
12	12.8±0.6		11.4±0.5	9.0±0.3
13	11.1±0.5		11.9±0.8	8.4±0.4
14	9.9±1.4		9.5±0.7	8.4±0.7
15	8.3±1.0		9.9±1.3	7.6±0.6
16			7.5±1.0	7.2±1.0
17			6.1±1.0	6.4±0.3
18			6.1±1.0	5.4±0.1
19				6.4±0.1

Table XI. Hydrogen molecular ion rotational constants and internuclear distances. Stated error limits are statistical uncertainties ($\pm 2\sigma$) from the least-squares fit.

	H_2^+		HD^+		D_2^+	
	Present results	Rydberg series ^a	Present results	Rydberg series ^a	Present results	Rydberg series ^a
$B_e(\text{cm}^{-1})$	29.99 \pm .30	30.2 ₁	23.03 \pm .63	22.45 ₂	14.89 \pm .28	15.016
$\alpha_e(\text{cm}^{-1})$	1.388 \pm .033	1.68 ₅	0.901 \pm .057	1.00 ₁	0.471 \pm .024	0.560
$r_e(\text{\AA})$	1.056 \pm .005	1.052	1.044 \pm .014	1.057	1.060 \pm .005	1.0559

^aK. P. Huber and G. Herzberg, Constants of Diatomic Molecules, Van Nostrand Reinhold, New York (1979).

FIGURE CAPTIONS

Fig. 1. Schematic top view of the apparatus: (1) beam source, (2) beam catcher; (3) pass energy selector lens, (4) field lens, (5) kinetic energy scan lens, (6) deflectors, (7) 90° spherical sector pre-analyzer, (8) conductance barrier, (9) 8:1 decelerator lens, (10) hemispherical analyzer, (11) multichannel detector, (12) ion extraction lenses, (13) quadrupole mass filter, (14) differential pumping. The photon sources are located above the plane of the drawing. Not shown are two layers of mumetal surrounding the electron flight path.

Fig. 2. The 584Å photoelectron spectrum of n-H₂ expanded from 800 Torr at 297K. The ionic vibrational states and the rotational quantum numbers of a typical Q branch are indicated in the figure. The S branch is also labeled for the first three v-states.

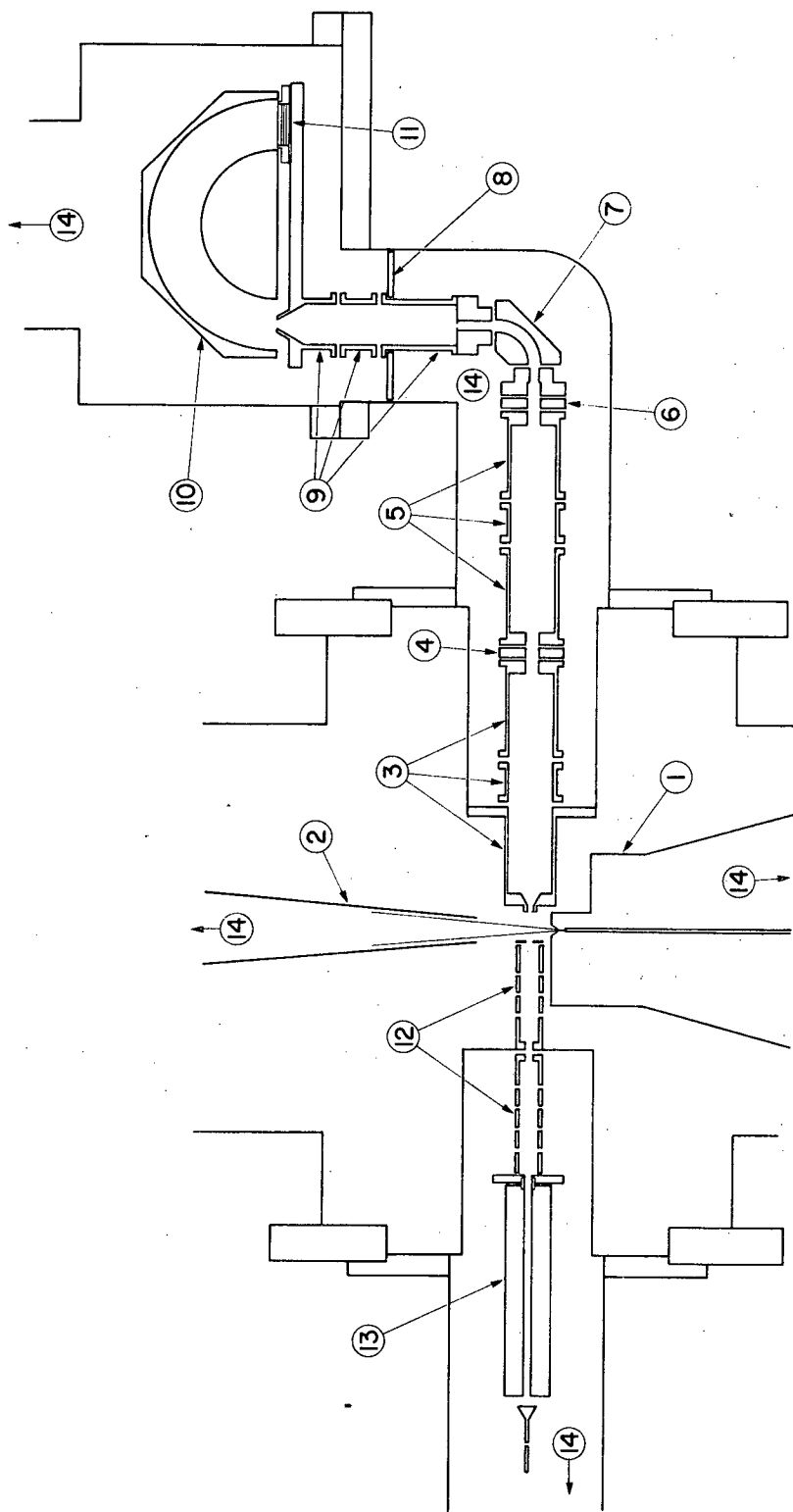
Fig. 3. The 584Å photoelectron spectra of p-H₂, HD, and D₂ expanded from 800, 600, and 1000 Torr, respectively, at 297K.

Fig. 4. The 584Å photoelectron spectra of p-H₂, HD, and D₂ expanded from 200 Torr at 77K.

Fig. 5. The 584Å photoelectron spectra of n-H₂, HD, and D₂ expanded from 600 Torr at 473K, 50 Torr at 297K, and 400 Torr at 403K, respectively.

Fig. 6. The H₂⁺(v=2) transition from the spectrum of p-H₂ expanded from 77K. (a) Experimental points with the line representing the least-squares fit. (b) Experimental points with the decomposition into the four rotational components.

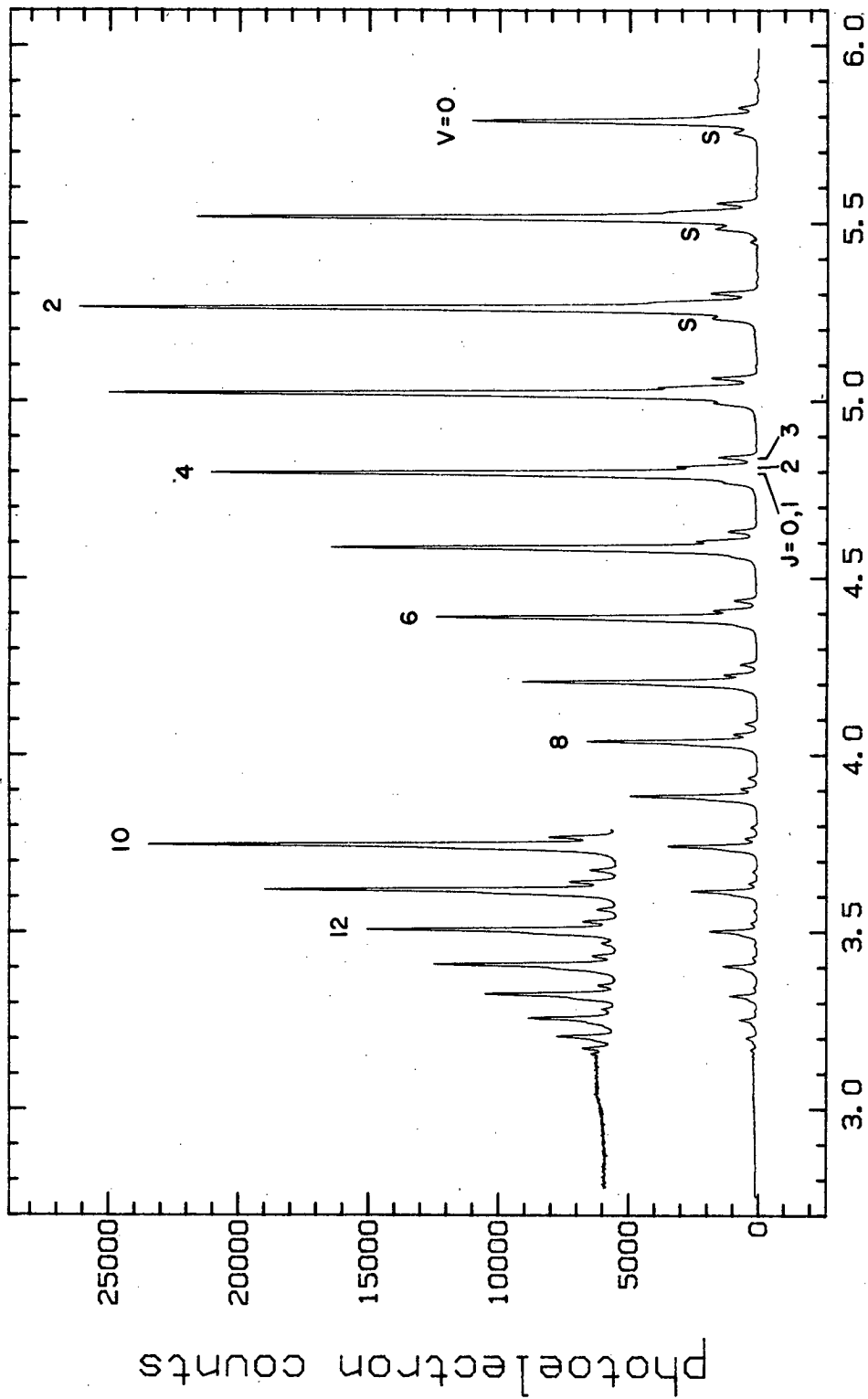
- Fig. 7. The vibrational differences of H_2^+ , HD^+ , and D_2^+ determined from photoelectron spectra of p- H_2 , HD, and D_2 at 77K shown in Fig. 4.
- Fig. 8. The vibrational differences of H_2^+ as in Fig. 7, but with a linear term, $2242.6 - 116.93 (v + 1/2)$, subtracted.
- Fig. 9. The vibrational photoionization cross sections of H_2 , HD, and D_2 determined from the 584Å photoelectron spectra at 77K shown in Fig. 4. Theoretical values are from ONeil and Reinhardt (Ref. 23).
- Fig. 10. The rotational constants of H_2^+ determined from the spectra of n- H_2 at 473K shown in Fig. 5 and p- H_2 at 297K shown in Fig. 3. Error bars are statistical uncertainties ($\pm 2\sigma$) from the least-squares fit to Eq. (3). The solid line gives the theoretical B_v values of Beckel, Hansen, and Peek (Ref. 11).
- Fig. 11. The rotational constants of HD^+ and D_2^+ determined from the spectra of HD and D_2 shown in Fig. 5. Error bars are statistical uncertainties ($\pm 2\sigma$) from the least-squares fit to Eq. (3) omitting the second order term.



XBL 813-8421

Figure 1

$n\text{-H}_2$ 297 K



kinetic energy (eV)

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Figure 2

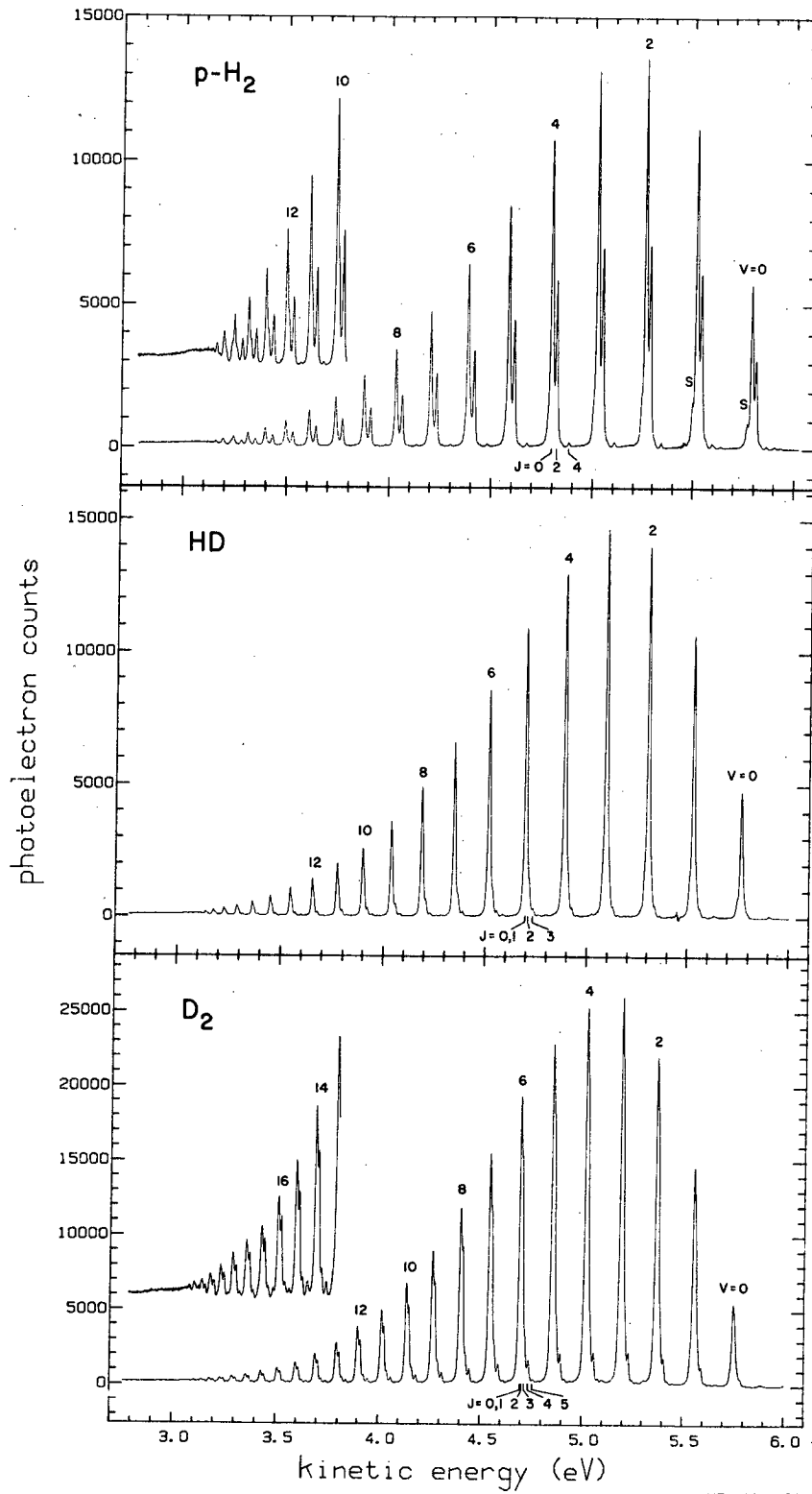


Figure 3

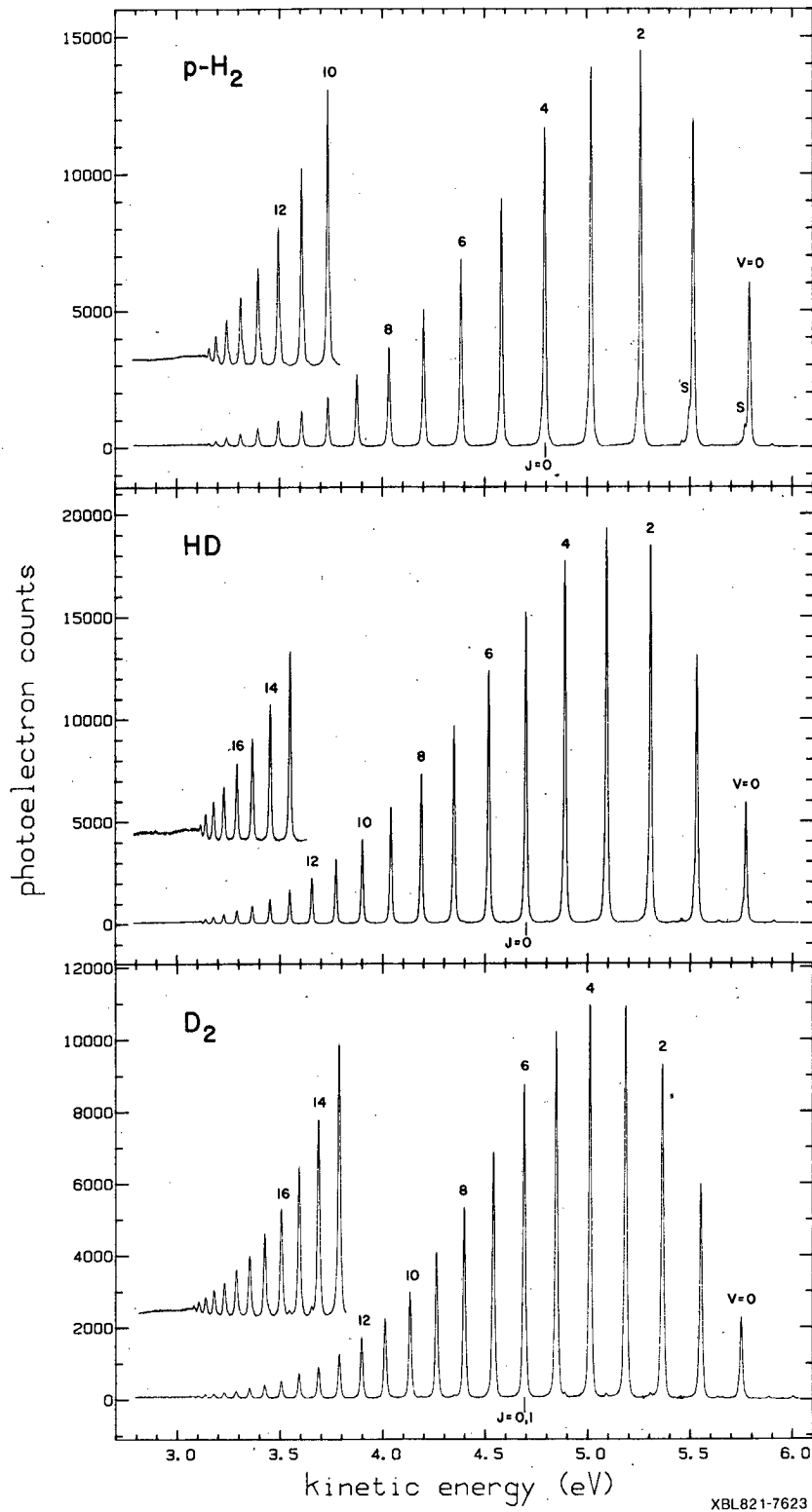


Figure 4

XBL821-7623

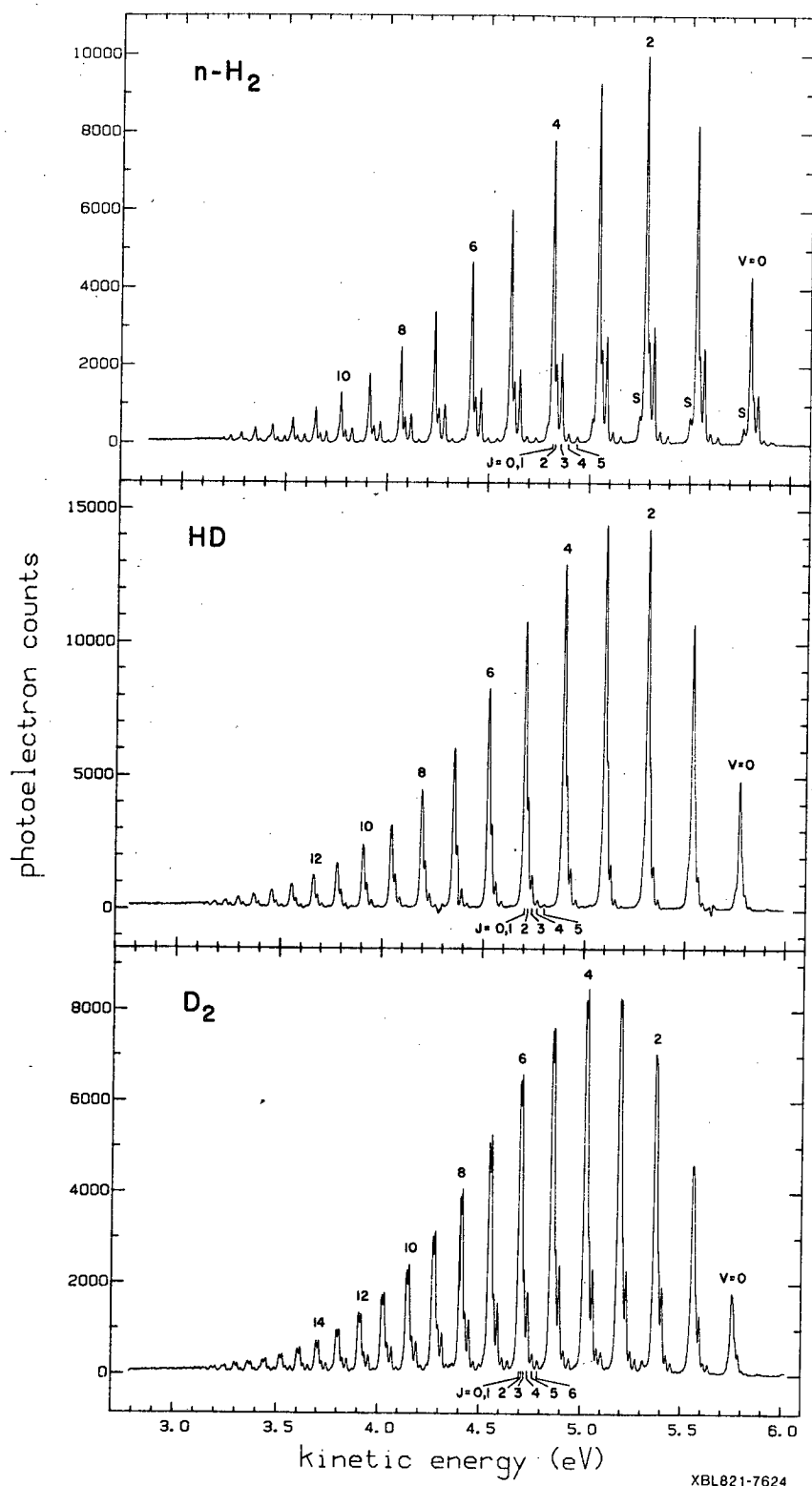
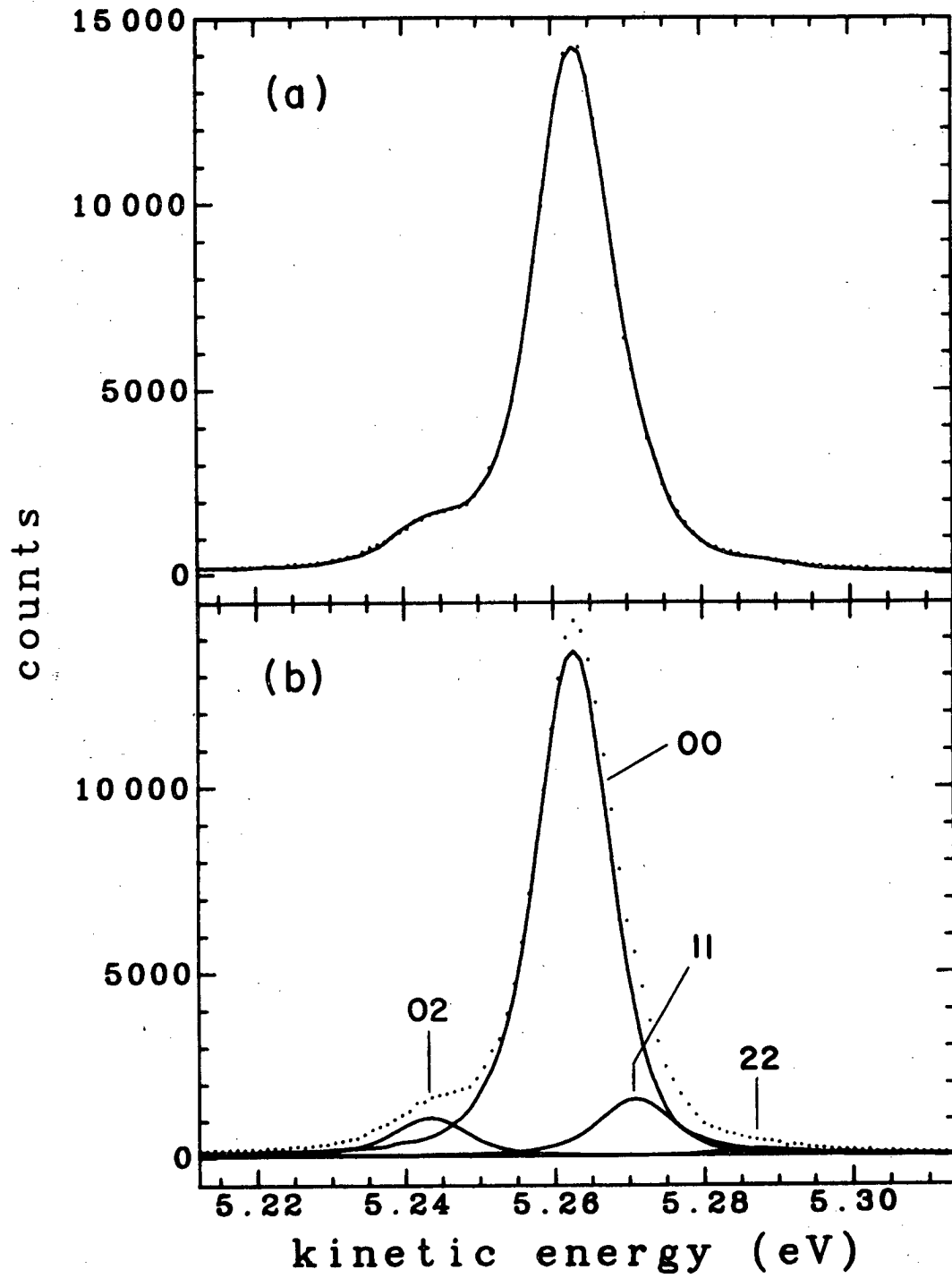


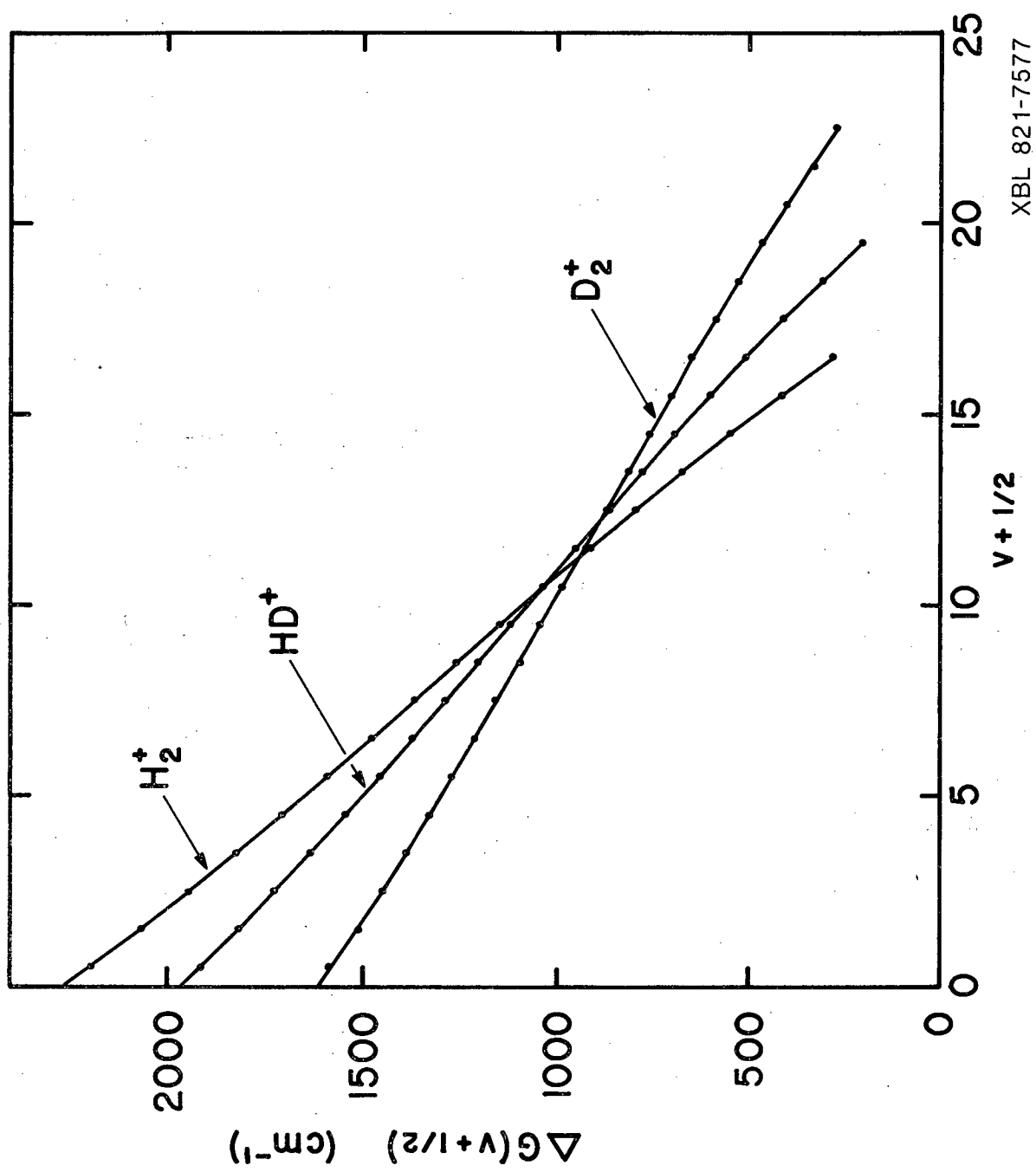
Figure 5

p-H₂ v' = 2 77K



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Figure 6



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Figure 7

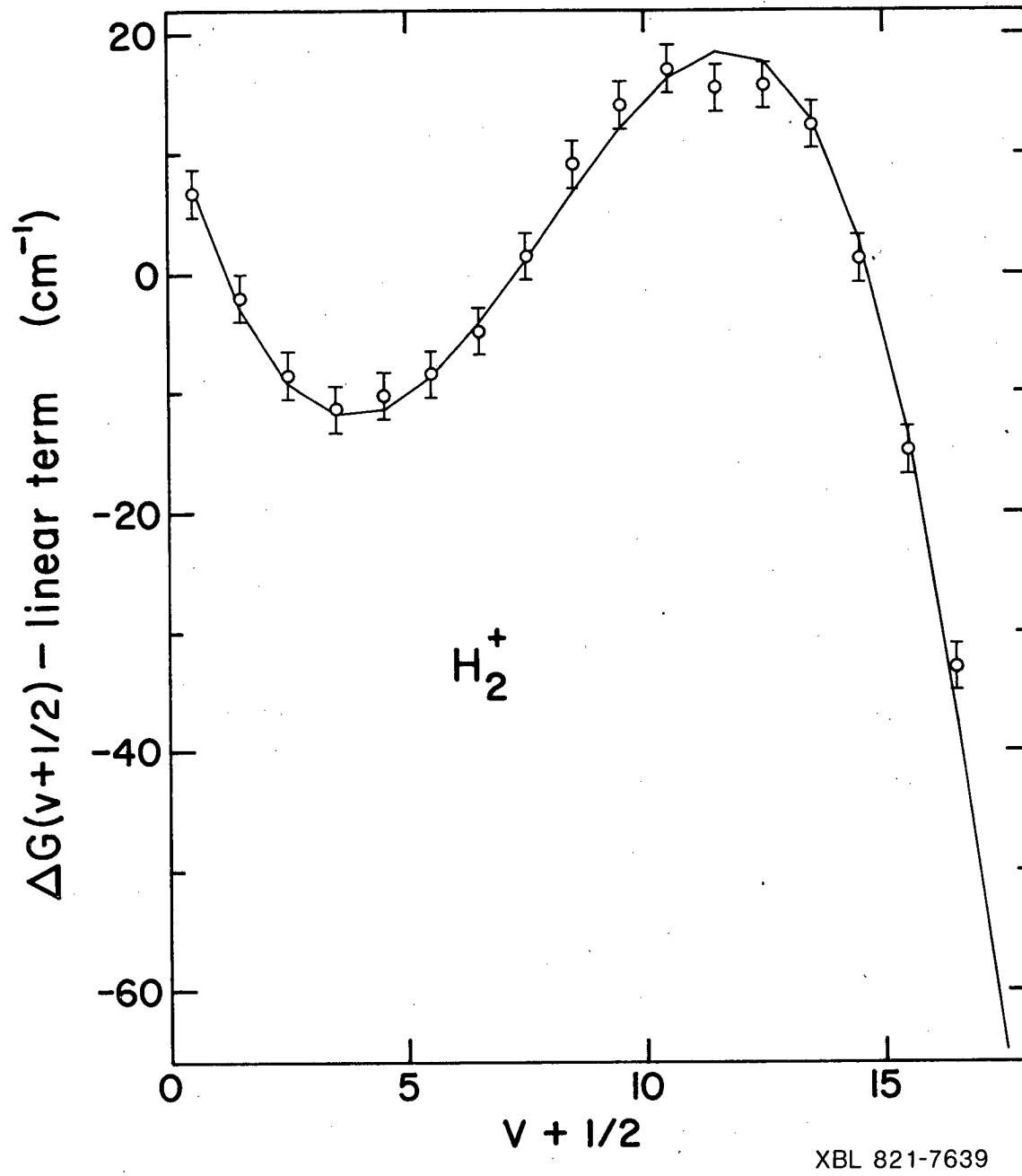
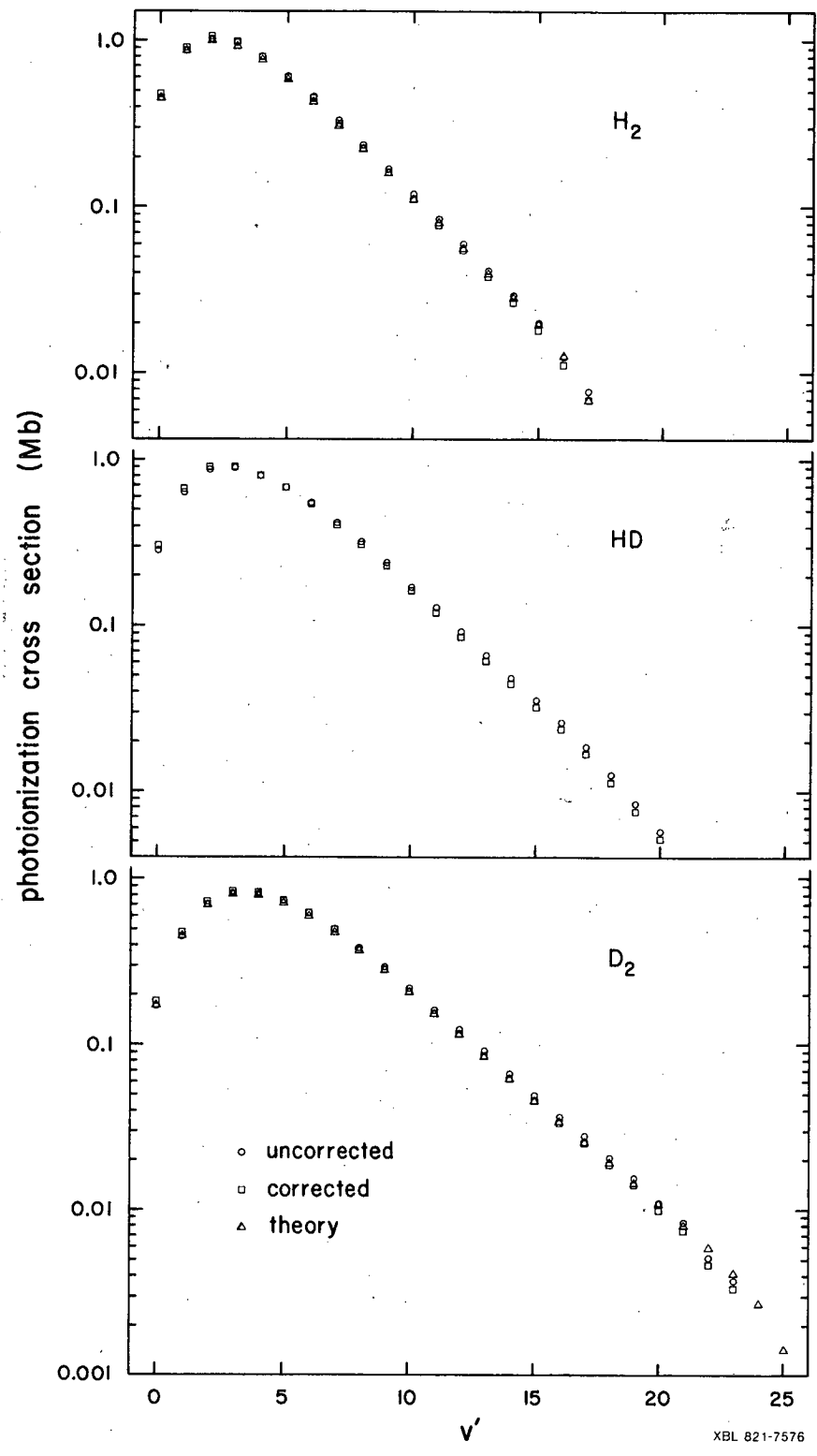
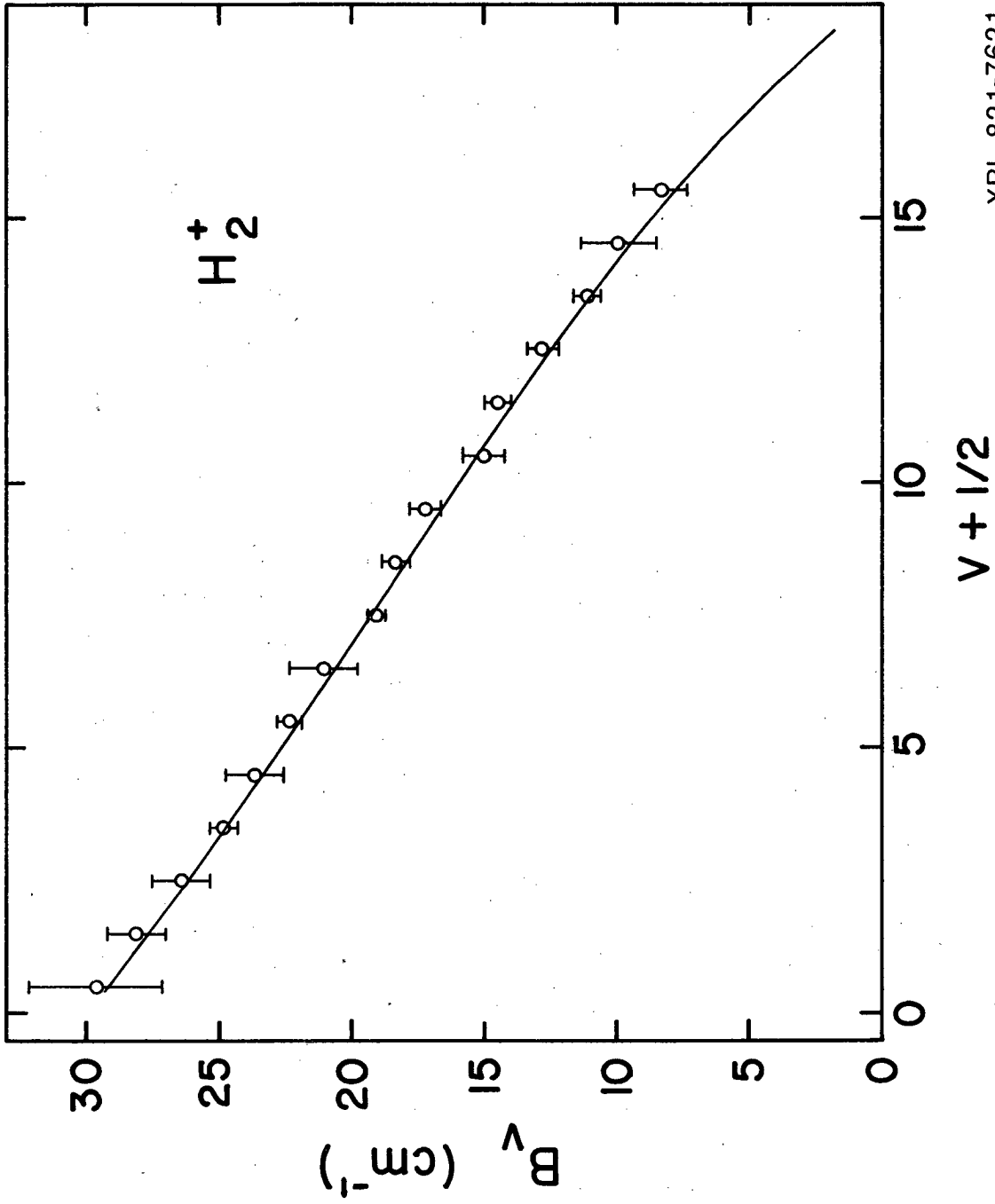


Figure 8



XBL 821-7576

Figure 9



XBL 821-7621

Figure 10

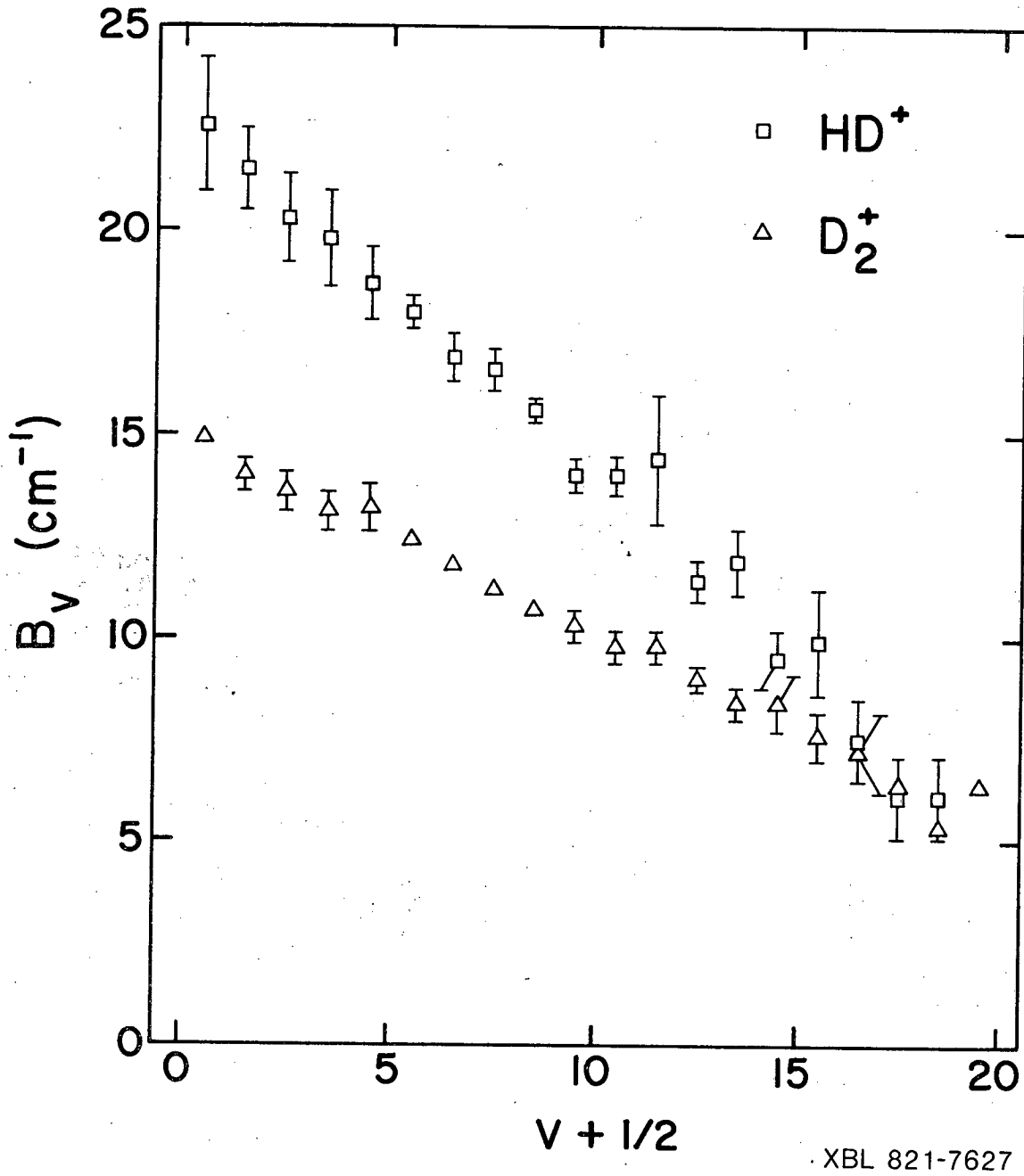


Figure 11

XBL 821-7627

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