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PROTON AFFINITIES OF HYDROGEN HALIDES DETERMINED BY THE MOLECULAR BEAM - PHOTOIONIZATION METHOD

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ABSTRACT

Gas-phase proton affinities of HF (95.5 ± 1.4 kcal/mol), HCl (135 ± 1 kcal/mol), and HBr (141 ± 1 kcal/mol) have been measured along with the HX^+-HX binding energies for the HCl and HBr systems (20 ± 2 and 23 ± 2 kcal/mol, respectively) by photoionization of van der Waals molecules produced in a supersonic expansion. A detailed discussion of the potentialities and limitations of the method is presented.

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INTRODUCTION

When proton affinities obtained in gas phase experiments became available, many processes in solution involving proton transfer could be rationalized, because the effect of the solvent in altering the intrinsic properties of the reactants could then be assessed. Gas phase results of molecular properties also allowed direct comparisons with ever improving theoretical calculations, usually carried out on isolated molecules.

Very accurate relative proton affinities, to better than 0.2 kcal/mole, have been determined by the ion-molecule equilibrium method, using trapped ion cyclotron resonance mass spectrometry,[1-3] high pressure mass spectrometry,[4] and flowing afterglow techniques.[5] The equilibrium constant for the process of interest is evaluated by measuring the ratio of the number densities of the two protonated species in equilibrium for given pressures of the neutral molecules involved. The change of free energy for the proton transfer process is calculated from the measured equilibrium constant and, from a series of overlapping measurements, a relative scale of gas phase basicities is obtained. However, from a thermochemical point of view a relative scale of proton affinities is more useful, requiring the calculation of the enthalpy change for the process. This involves estimating the entropy change, which has sometimes been neglected[1] or taken into account approximately by considering it being due only to changes in rotational symmetry numbers.[6] Some experimental arrangements allow the sample temperature to be varied and ΔH is obtained from van't Hoff plots.[7,8]

In order to place the scale of relative proton affinities on an absolute basis it is necessary to have at least one reference compound of known proton affinity. The absolute proton affinity of a molecule can be obtained through threshold experiments, in which one directly determines the minimum energy necessary to form the protonated ion from a neutral species, thus obtaining the heat of formation of the ion. However, frequently it is not easy to find an appropriate neutral precursor for the ion of interest. The most frequently used reference base was isobutene, the proton affinity of which was based on the heat of formation of the tert-butyl cation ($\Delta H_f(t\text{-}C_4H_9^+) = 169$ kcal/mol).[9] Recently[10,11] this value has been redetermined and found to be 5 kcal/mol lower; this shifts the whole scale of proton affinities referenced to the proton affinity of isobutene to values 5 kcal/mol higher. In a few cases other reference compounds have been used. One example is formaldehyde,[5] whose proton affinity was derived from the appearance potential of H_2COH^+ from methanol.[12]

It is of course desirable to have a large number of absolute proton affinity measurements, preferably obtained by a variety of different methods, so as to better localize the relative proton affinity scale on an absolute energy scale. A novel method devised in our laboratories[13,14] involves the photoionization of a van der Waals dimer of the hydrogen containing molecule whose proton affinity is to be measured. The van der Waals dimers of the molecules under investigation are formed in a supersonic expansion. They are used in this method as precursors for protonated species. In the photoionization of van der Waals dimers, the maximum level of vibrational excitation of the ionic dimer produced can be controlled with the energy of the ionizing photons, since some of the ionic dimers retain most of the excess energy as vibrational excitation. As the photon energy increases, the vibrational excitation becomes higher and eventually excited ionic dimers fragment unimolecularly through a proton transfer reaction, yielding the protonated molecule under consideration. From the threshold energy for this fragmentation process and other known thermodynamic data the proton affinity can be calculated.

The series of the common hydrogen halides seem to be ideally suited for assessing the potentialities and limitations of this new method. The proton affinities of these compounds have been measured by the ion-molecule equilibrium method[15,16] so that the results of these two different methods can be compared.

EXPERIMENTAL

The photoionization apparatus has been described in detail previously.[17-19] Essentially it consists of a differentially pumped molecular beam source, a vacuum ultra-violet lamp, a McPherson 225 one meter near-normal incidence monochromator, a quadrupole mass spectrometer and an ion counting system. The windowless photon source consists of a quartz capillary discharge tube, the radiation being either the helium Hopfield continuum or the hydrogen many-line pseudo-continuum, depending on the wavelength region required.

The apparatus has been modified in one respect, namely, the experiment is now under control of a microcomputer using the MCS-8080 microprocessor. Signal is accumulated at a selected wavelength for the appropriate length of time so as to maintain an approximately constant standard deviation at each experimental point; the photoionization efficiency is calculated and the monochromator wavelength setting is advanced. Time normalization of the data to account for long-term fluctuations in experimental conditions is accomplished by periodically measuring the signal at an arbitrary reference wavelength.

The compounds used in this experiment, HF, HCl, HBr, and HI were all from Matheson Gas Products. Hydrogen fluoride was cooled in a water-ice bath; this gave an HF vapor pressure and thus a stagnation pressure behind the nozzle of nearly 400 torr. In the case of hydrogen chloride and hydrogen bromide pressure regulators were used; most experiments were done at stagnation pressures of 1000 and 800 torr, respectively. Hydrogen iodide was again used without a regulator, the lecture bottle being cooled in a water-glycol slush so as to yield a pressure of 1000 torr.

The nozzle used in producing the supersonic beam was a 0.13 mm diameter orifice in a nickel plate.

RESULTS

The photoionization efficiency curves for HF^+, H_2F^+, $(HF)_2H^+$ and $(HF)_3H^+$ are shown in Fig. 1. The ionization potential of HF was found to be 15.98 ± 0.04 eV, in good agreement with previous measurements (16.007 ± 0.010 eV).[20] Ionized polymers $(HF)_n^+$ were not observed with dispersed light; however a very weak signal was detected with electron bombardment ionization. The appearance potential of H_2F^+ is 15.65 ± 0.04 eV. Previous evidence[13] leads to the conclusion that H_2F^+ is formed by dissociative ionization of $(HF)_2$. Using the dissociation energy of $(HF)_2$ into HF molecules (0.29 eV, 6.8 kcal/mol)[21] and the endoergicity of the dissociative ionization of HF to form H^+ and F (19.445 eV),[20] the proton affinity of HF is calculated as 4.09 ± 0.06 eV (94.3 ± 1.4 kcal/mol). This is illustrated in more detail in Fig. 2. The proton affinity can be considered as the solvation energy of a proton by one hydrogen fluoride molecule. Fig. 2 shows that successive proton solvation energies can be obtained from the ionization thresholds and the dissociation energies of larger clusters. It is seen that attachment of additional HF molecules to the proton lowers the energy of the system by successively smaller amounts. Thus, the solvation energy of a proton by one HF molecule is 4.09 ± 0.06 eV (94.3 ± 1.4 kcal/mol), by two HF molecules the solvation energy is 5.18 ± 0.13 eV (119 ± 3 kcal/mol), and by three molecules, 5.8 ± 0.2 eV (134 ± 5 kcal/mol).

In Fig. 3 the photoionization efficiency curves for HCl^+, H_2Cl^+, and $(HCl)_2^+$ are presented. The bottom curve shows that the threshold for HCl^+ production from HCl occurs at 97.5 ± 0.2 nm, which corresponds to an ionization potential of 12.72 ± 0.03 eV, in good agreement with the recommended literature value (12.74 ± 0.01 eV).[22] Protonated HCl, a fragment produced in the ionization of the HCl van der Waals dimer, appears at 100.6 ± 0.2 nm (12.32 ± 0.03 eV). The energy diagram in Fig. 4 indicates how the proton affinity of HCl can be calculated from this threshold, the known dissociative ionization threshold[22] of HCl and the binding energy between two neutral HCl molecules.[23] The value obtained is 5.81 ± 0.04 eV (134 ± 1 kcal/mol). Figure 3 shows that the ionization potential of the HCl van der Waals dimer is 11.91 ± 0.05 eV, which leads to an HCl^+-HCl binding energy of 0.87 ± 0.09 eV (20 ± 2 kcal/mol) as indicated in Fig. 4.

Analogous results were obtained for HBr. In Fig. 5 the photoionization efficiency curves for HBr^+, H_2Br^+, and $(HBr)_2^+$ are depicted. The ionization potential of HBr was measured as 11.66 ± 0.02 eV, again in very good agreement with literature values (11.677 ± 0.004 eV).[22] A diagram similar to the one in Fig. 4, with a 0.13 ± 0.04 eV (3 ± 1 kcal/mol) $(HBr)_2$ dissociation energy and a 7.356 eV (400.22 kcal/mol) HBr dissociative ionization energy[22] allows one to calculate the proton affinity of HBr and the HBr^+-HBr binding energy from the data in Fig. 5. Values of 6.07 ± 0.04 eV (140 ± 1 kcal/mol) and 1.00 ± 0.09 eV (23 ± 2 kcal/mol) have been obtained for these quantities, respectively.

Attempts to measure the proton affinity of HI were unsuccessful because the H_2I^+ signal intensity was too low for any acceptable measurements to be done. The ionization potential of HI obtained (10.38 ± 0.02 eV) agrees very well with literature values (10.386 ± 0.001 eV).[24] $(HI)_2^+$ was not observed due to the limited mass range of our mass spectrometer.

DISCUSSION

Very high resolution photoionization spectra for HF^+ and HI^+ have been obtained previously (0.08 and 0.007 nm fwhm resolution, respectively)[20,24] and Rydberg series have been assigned to the observed transitions. In the present study, in order to obtain sufficient photon flux to observe the ionization of van der Waals molecules, the resolution was set at 0.25 nm fwhm so that the detailed structure of the spectra is not as well resolved as in the published ones, especially in the case of hydrogen iodide.[24] Thus no attempt was made to assign any transitions to the peaks observed in the HCl^+ and HBr^+ spectra. The measured thresholds however agree very well with the literature values, as pointed out above.

In order to compare the proton affinities obtained in this work with values obtained by the ion-molecule equilibrium method it is necessary to transform the former, which essentially correspond to 0 K values, to 298 K, the temperature at which most ion-molecule experiments were carried out. This was done by using the appropriate heat capacities (for those ions for which no heat capacities as a function of temperature were available, data for the corresponding isoelectronic neutral species were used)[25] and the following proton affinities corrected to 298 K were obtained: 4.14 ± 0.06 eV (95.5 ± 1.4 kcal/mol) for HF, 5.85 ± 0.04 eV (135 ± 1 kcal/mol) for HCl, and 6.11 ± 0.04 eV (141 ± 1 kcal/mol) for HBr. The proton affinities of HCl and HBr agree very well with published data: 135 ± 2 kcal/mol and 140 ± 1 kcal/mol, respectively.[16] However, the proton affinity of HF is substantially lower than the literature value: 112 ± 2 kcal/mol.[15] This will be consider in turn.

It is interesting to compare the behavior of all the common hydrogen halides with respect to photoionization. In the case of HF the H_2F^+ ion intensity is very high, but no $(HF)_2^+$ is observed. On the other extreme, in the case of HI, very little H_2I^+ is observed. HCl and HBr fall nicely in between, yielding both H_2X^+ and $(HX)_2^+$. Observation of the dimer ion is an important condition for obtaining reliable proton affinities. If $(HX)_2^+$ is observed below the ionization threshold of H_2X^+, then, as the photon energy is increased some $(HX)_2^+$ will have sufficient vibrational excitation to unimolecularly decompose into H_2X^+ and X. The threshold for H_2X^+ formation can be considered as the threshold for vibrational energy induced dissociation of $(HX)_2^+$, producing ground state H_2X^+. Consequently, if a stable dimer ion is not accessible, there is no assurance that the protonated molecule is formed in its ground state. Thus a larger appearance potential would be measured, leading to a lower proton affinity, which could only be considered a lower bound. Comparing the H_2F^+, H_2Cl^+ and H_2Br^+ photoionization efficiency curves (Figs. 1, 3, and 5) it is apparent that just above threshold the H_2F^+ curve displays extremely pronounced curvature. Curvature is usually interpreted[26,27] as the result of vertical transitions from the molecular ground state into closely spaced, higher energy levels of the ion, due to a dramatic change in the potential energy surface upon ionization. The well depth of the HX^+-HX pair is significantly larger than that of the HX-HX pair and the intermolecular distance is shorter, rendering an adiabatic transition unlikely. The H_2Cl^+ and H_2Br^+ ion current onsets are considerably sharper than that of H_2F^+, making it more likely that the ions are produced in their ground states.

Thus the production of H_2F^+ at the threshold may occur through a direct ionization process of $(HF)_2$ yielding a vibrationally excited ion. In the case of $(HF)_2$ as with $(H_2)_2$[28] predissociation may compete effectively with vibrational autoionization of the $HF^{*}\cdot$ HF complex initially formed by adsorption of a photon thus preventing the formation of the $(HF)_2^+$ parent ion and its subsequent fragmentation to ground state H_2F^+. Although no $(HF)_2^+$ was observed in the photoionization experiment, it was detected by electron bombardment in a 0.1% quantity in the beam, indicating that the $(HF)_2^+$ species is stable relative to its fragment H_2F^+. A lower bound to the binding energy of $(HF)_2^+$ can then be calculated as 33 kcal/mol using 112 kcal/mol as the HF proton affinity.[15] The discrepancy between the proton affinity of HF obtained in the present photoionization work and in ion-molecule equilibrium experiments[15] could be due to the production of vibrationally excited

H_2F^+ at the threshold of H_2F^+ production from $(HF)_2$. In light of this the proton solvation energies by more than one HF molecule, as presented in the results section, are also likely to be too low.

Another point that has to be considered is the contribution of larger van der Waals clusters to the ion current of smaller fragments. The appearance potential of an ion, however, is not affected by the presence of larger clusters. Since $(HX)_{n+1}$ is more stable than $(HX)_n$ + HX the ionization threshold of $(HX)_{n-1}H^+$ from $(HX)_{n+1}$ should be higher than the ionization threshold of $(HX)_{n-1}H^+$ from $(HX)_n$ by the binding energy of $(HX)_n$ and HX. Thus, the presence of higher clusters is manifested at some energy above the threshold in accordance with previous findings.[14]

The method of measuring proton affinities through photoionization of van der Waals dimers in a supersonic molecular beam is thus reliable as long as the ionic dimer is observed. Of course, the protonated molecule has to be observed and this is not always possible; in the case of HI for instance, no H_2I^+ was detected, although this species is readily formed in ion-molecule reactions.[24] Another apparent limitation is that the molecule has to contain hydrogen, but this can be circumvented by preparing mixed van der Waals dimers of the molecule of interest and hydrogen molecules or hydrogen containing molecules.

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FIGURE CAPTIONS

Fig. 1. Photoionization efficiency curves for HF^+, H_2F^+, $(HF)_2H^+$ and $(HF)_3H^+$.

Fig. 2. Energy diagram for the HF system upon photoionization.

Fig. 3. Photoionization efficiency curves for HCl^+, H_2Cl^+ and $(HCl)_2^+$.

Fig. 4. Energy diagram for the HCl system upon photoionization (energies in eV).

Fig. 5. Photoionization efficiency curves for HBr^+, H_2Br^+ and $(HBr)_2^+$.

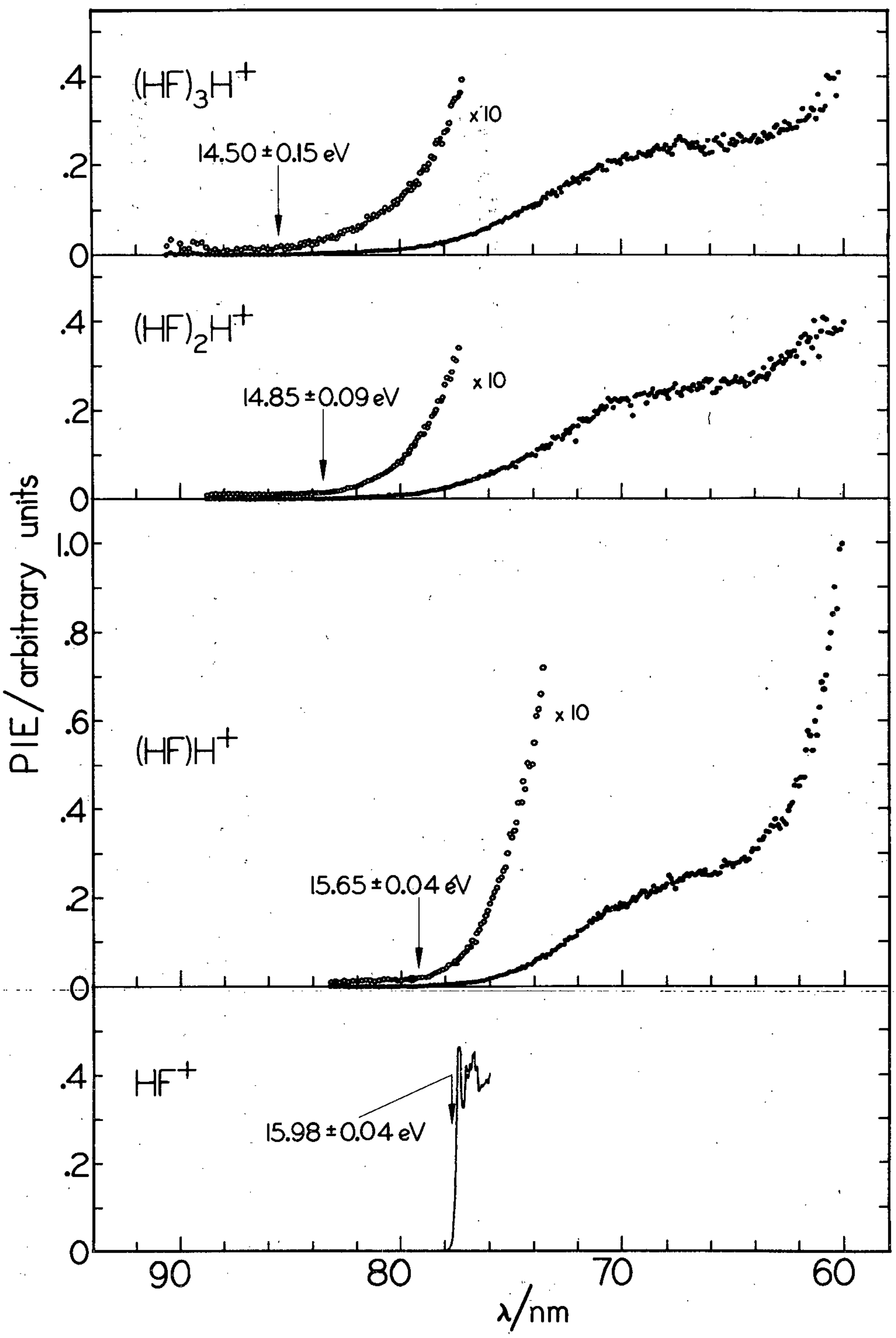

Fig. 1

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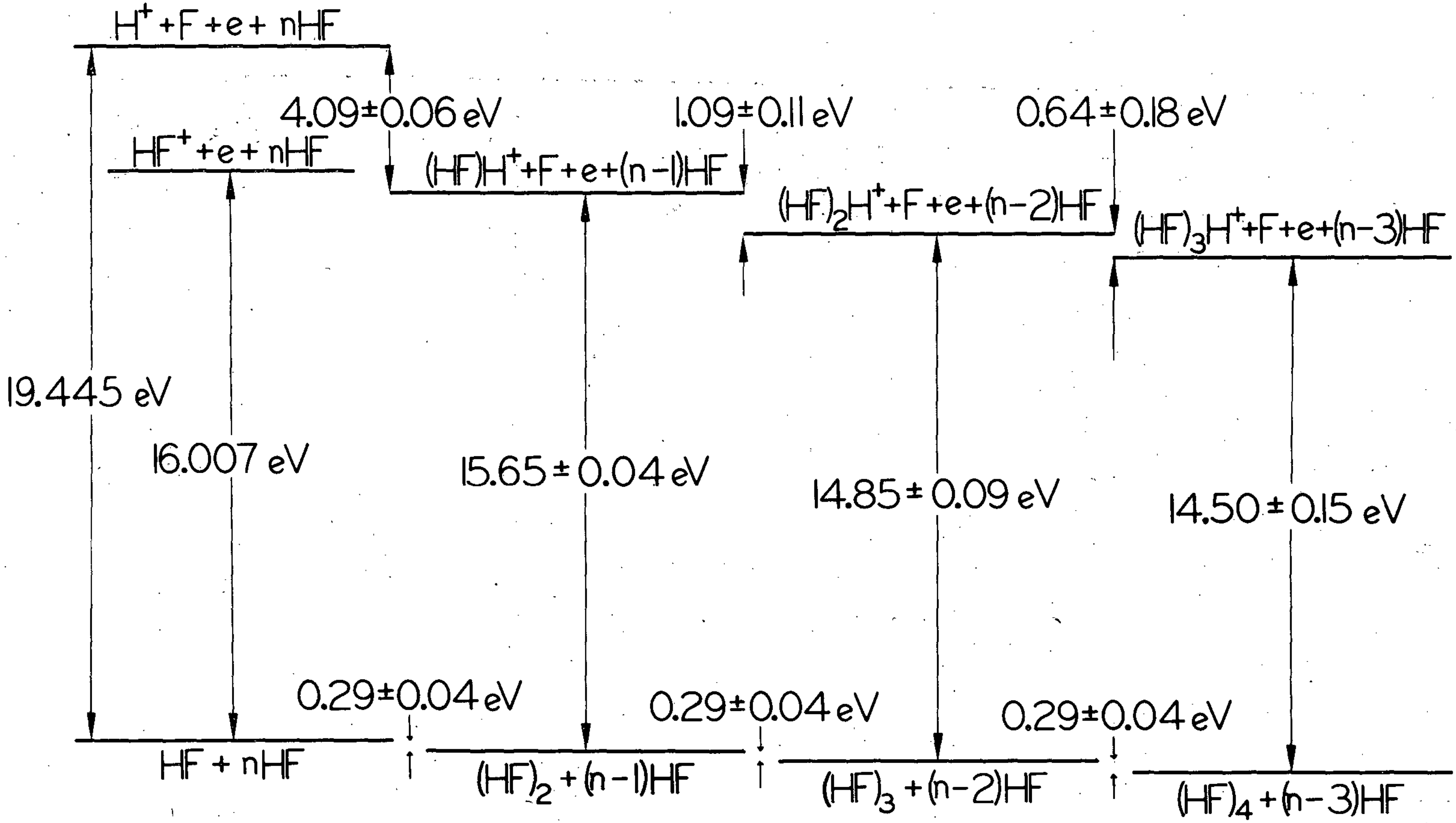

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Fig. 2

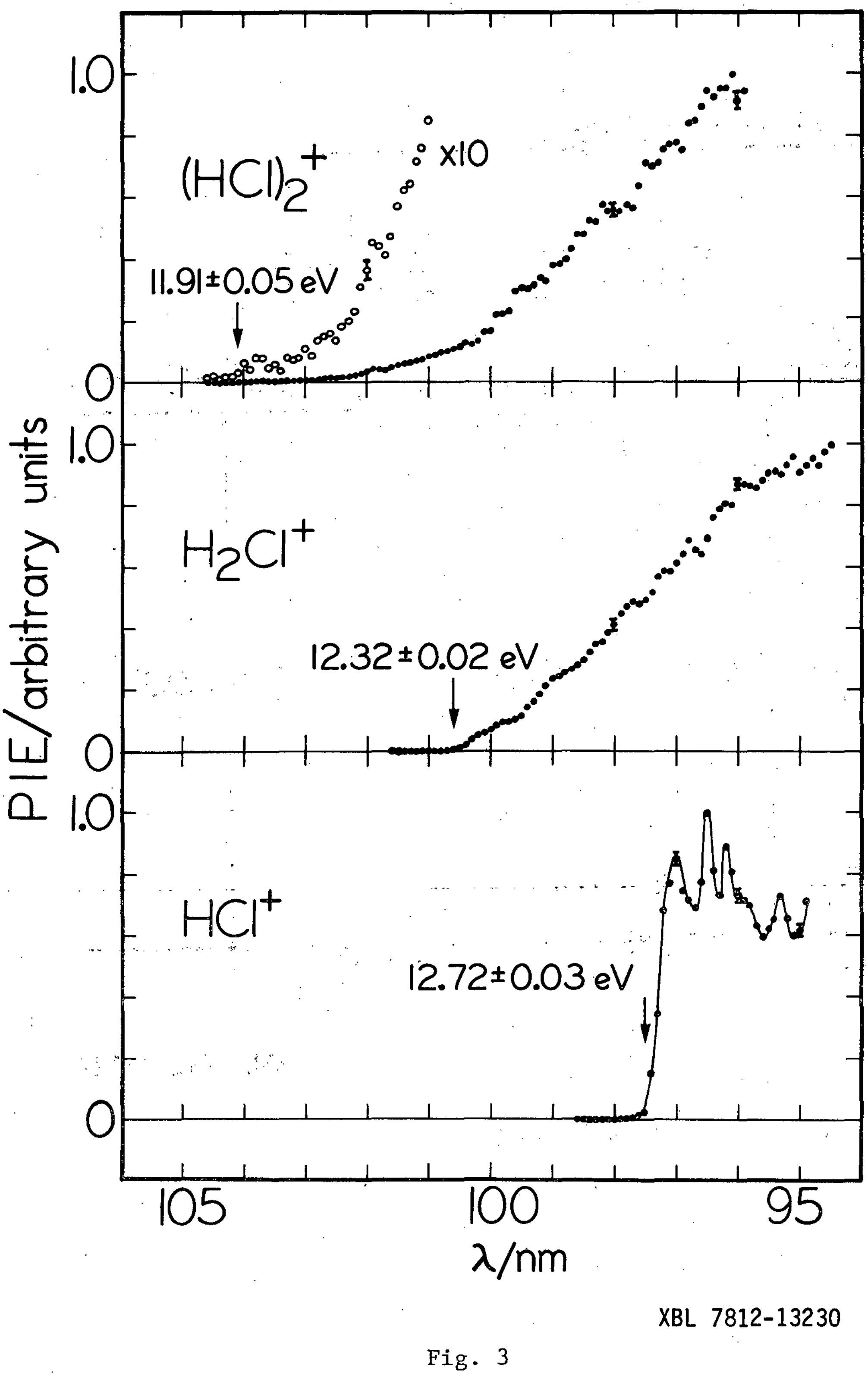

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Fig. 3

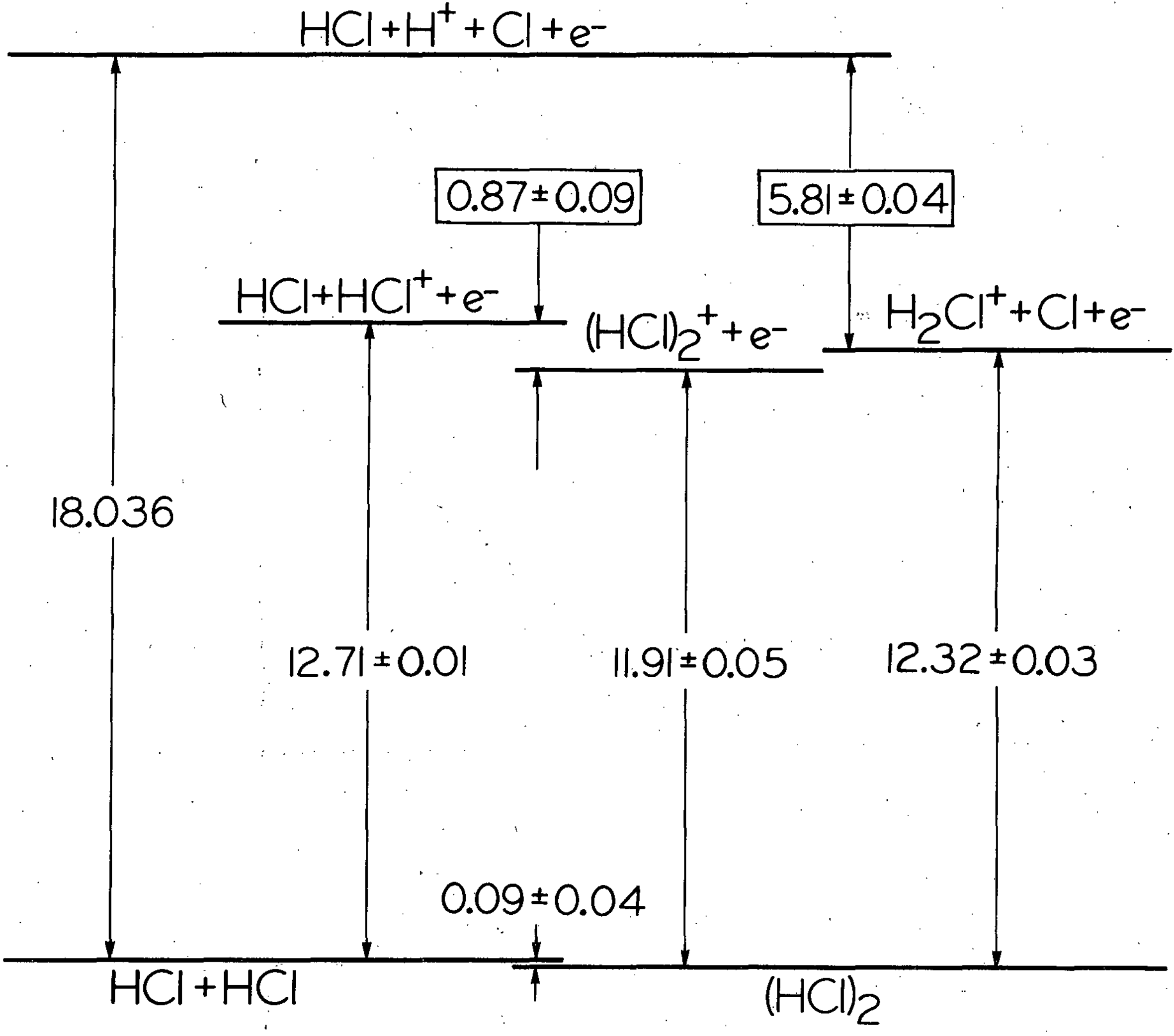

Fig. 4

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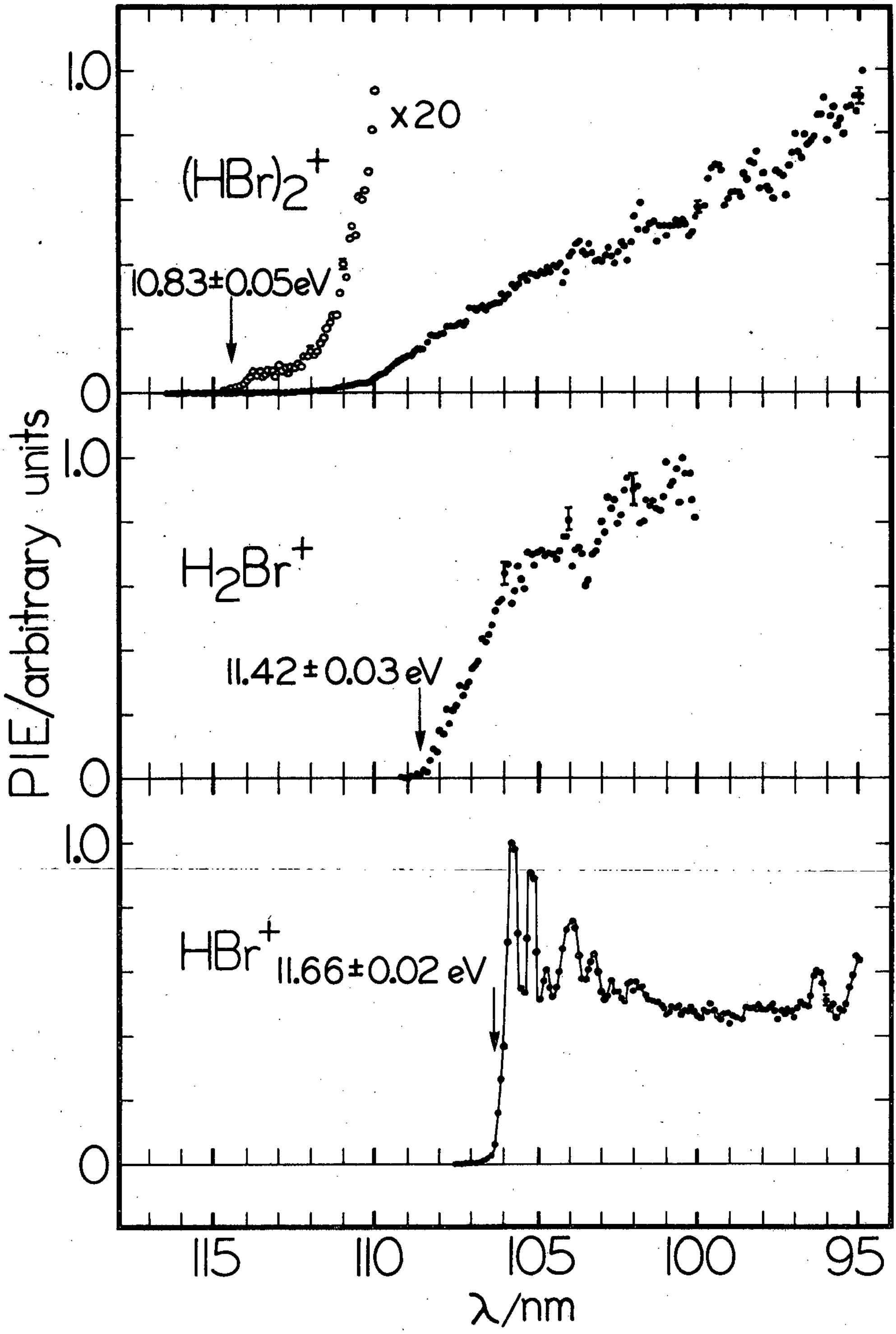

Fig. 5

XBL 7812-13231

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