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Measurement of the ionization potential of triatomic hydrogen

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The *d* Rydberg series of H_3 converging to the lowest rotational level of *ortho*-$H_3{}^+$ has been detected for *n* values ranging from 27 to 100 using field ionization. The Rydberg molecules are prepared by photoexcitation from the long-lived species, H_3 $\tilde{B}(2p\,^2A_2'', N=K=0)$, in its lowest vibrational level. Extrapolation of the Rydberg series yields an ionization potential of $29\,562.6\pm0.5$ cm^{-1}. The amplitudes of the excitation spectra reveal the interaction between the $H_3{}^+$ cores with $N^+=1$ and 3 via *l* uncoupling of the *d* electron, as well as window resonances from interlopers belonging to vibrationally excited $H_3{}^+$ cores.

INTRODUCTION

The molecular ion $H_3{}^+$ has been among the first species known to mass spectroscopists,[1] but it was not until 1966 that the first observation of a neutral triatomic hydrogen species was reported.[2] Since then, long-lived triatomic hydrogen molecules have been observed in a variety of experiments.[3–11] Only after Herzberg[12] discovered emission spectra from neutral H_3 in 1979 was it realized why long-lived H_3 molecules could exist.[5] The known emission spectra[12–16] of H_3 arise from transitions between the lowest members of Rydberg states formed by attaching $n=2$ and 3 electrons to the stable ground-state $H_3{}^+$ core. The energy positions of some of these levels are shown in Fig. 1. The absolute energy of the Rydberg states with respect to the lowest dissociation limit has been established from dissociative charge transfer[17,18] and in a recent photofragment spectroscopy study.[19] The excited states of H_3 are adiabatically stable with respect to their dissociation limits $H(nl)+H_2(X)$, all of which lie above the ionization limit, $H_3{}^+ + e$.

The bound Rydberg states are imbedded in the continuum of the repulsive ground state of H_3 $\tilde{X}(1sa_1)^2 2pe'$. Allowed optical transitions connect the excited electronic states of symmetry A_1', E', and E'' with the ground state. In addition, pathways for predissociation into the continuum ground state exist for all electronic states of H_3. The electronic states A_1' and E' are opened through vibronic coupling, whereas rotational coupling connects all excited states with $\tilde{X}$. Both radiation[20] and predissociation[13,16,19] from $n=3$ and 2 states into the ground state have been studied experimentally.

The measurements reported here hinge on the existence of a single long-lived rotational level in the $\tilde{B}$ $2p\,^2A_2''$ state. In Herzberg's emission studies the linewidth for optical transitions terminating in the $\tilde{B}$ state was[13,16] observed to increase linearly with the quantity $N(N+1)-K^2$, the squared angular momentum of the molecule about an axis in the molecular plane. The tumbling motion of the core provides the Coriolis force required for rotational predissociation of the $\tilde{B}$ $2pA_2''$ state into the $\tilde{X}$ $2pE'$ continuum (see Fig. 1). This observation provided a first spectroscopic explanation for long-lived species of H_3: these could now be attributed[5] to H_3 molecules in the $\tilde{B}$ state in its lowest rotational level, $N=K=0$, for which this rotational coupling path is inactive. The expected dominant decay channel for this level of the $\tilde{B}$ state is the slow infrared transition to the rapidly predissociated[13] $2sA_1'$ state.

The long lifetime associated with this infrared transition [87 μs (Ref. 5)] permits observation of "stable" H_3 species in beam experiments and formed the basis for our previous photoionization study[9] of H_3. In this previous study it was observed that long-lived species exist in the ground vibrational state, as well as in vibrationally excited states of the nonrotating $\tilde{B}$ state. Photoabsorption by these species was detected by monitoring $H_3{}^+$ ions formed in field ionization and autoionization. Due to the

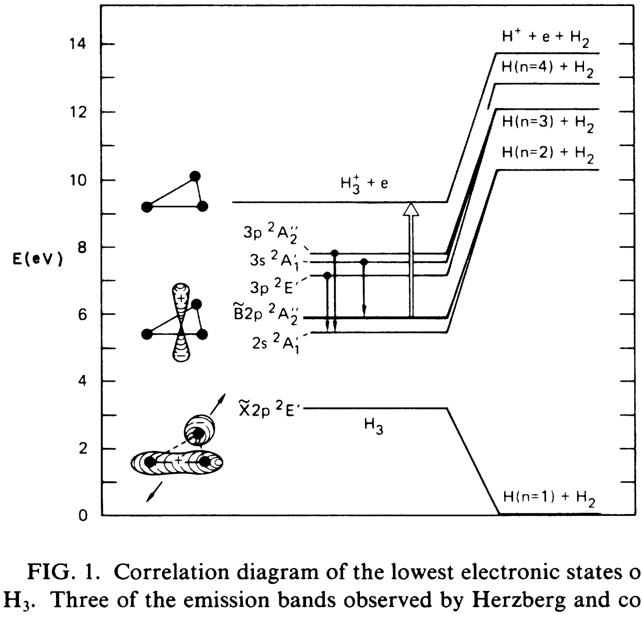

FIG. 1. Correlation diagram of the lowest electronic states of H_3. Three of the emission bands observed by Herzberg and coworkers (Refs. 12–16) are indicated. Schematic orbital representations are also given. The photoexcitation step studied here is indicated by the open arrow.

rather low concentration of H_3 molecules that could be prepared, the resolution and counting statistics was limited[9] by excessive measurement times. This difficulty is overcome in the present work, which employs a much more intense source of H_3 molecules.

Here we report a reinvestigation of the lowest *d*-electron Rydberg series. This series, labeled *A* in the previous study (see Fig. 3 of Ref. 9), is now observed over a much extended range of principal quantum numbers. This observation permits a precise definition of the ionization potential and of the quantum defect of the lowest *d* series.

EXPERIMENT

The photoexcitation study was carried out in the fast neutral beam photoionization spectrometer described recently.[9,10] H_3 molecules are formed by electron transfer from a cesium vapor target onto mass selected $H_3{}^+$ ions in a fast (1.5-keV) beam. The resulting neutral beam is purged of residual ions using small electric fields and enters a UHV chamber where it interacts with a copropagating or counterpropagating beam from a pulsed dye laser. Photoionization of the neutral molecules is detected by field ionization of the high Rydberg states at the end of the 120-cm-long photon-interaction region. A fixed field of 2.3 kV/cm was employed for ionization of the excited states. The resulting ions are mass selected to ensure that photoexcitation and subsequent field ionization involved neutral triatomic hydrogen rather than diatomic fragments that are copiously formed in dissociative charge transfer of $H_3{}^+$ in cesium.[5,21,22]

Two modifications of the experiment helped improve the counting statistics over that obtained in our earlier study, by a factor of >100. For one, an ion source was developed which is capable of delivering a highly stable beam of "cool" $H_3{}^+$ ions. The source is a hollow cathode glow discharge[23] operating around 1 torr between a cylindrical (5 cm diameter), cooled stainless-steel cathode and a cooled cylindrical anode made of copper. At 5–20 mA discharge current an ~1-cm-diam, bright negative glow develops along the axis of the 4-cm-long cathode. Ions are extracted from the negative glow, through a 300-μm hole in a stainless-steel electrode, opposite to the anode (see Fig. 3 of Ref. 23). The source delivers $H_3{}^+$ beams collimated to 1 mm diameter, 80 cm from the source of up to 8×10^{-7} A. At 1 Torr gas pressure, and using water cooling, the ratio $[H_3{}^+]/[H_2{}^+]$ is typically 5:1. This beam current is observed to be stable in continuous running over periods of weeks with drifts in the ion beam current being $<10\%$. The long-term stability was essential for the measurements described below. A second improvement was the use a high repetition rate pulsed dye laser with narrower bandwidth (0.4 cm^{-1}).

A typical wavelength spectrum is shown in Fig. 2. This spectrum was recorded in a continuous 14-h scan. The intensity scale refers to the number of $H_3{}^+$ ions detected in 512 laser shots. At the strongest transitions up to one ion is detected per shot. The excitation of the Rydberg series up to around $n=100$ is resolved with the broad-bandwidth laser. Several portions of the spectrum were recorded using an étalon to narrow the bandwidth of the laser to 0.05 cm^{-1}. At low laser powers (<1 μJ) this gave rise to transitions with widths of magnitude of the laser bandwidth, but no splitting was resolved nor was clear evidence found for two parallel series (*s* and *d*) as anticipated for excitation of the *p* orbital in the long-lived molecule.

Reference experiments were carried out to ensure that the observed spectrum is indeed associated with photoexcitation of the H_3 molecule. The most obvious question regards the HD^+ impurity in the mass-3-selected beam. HD^+ is known to produce metastable HD molecules in

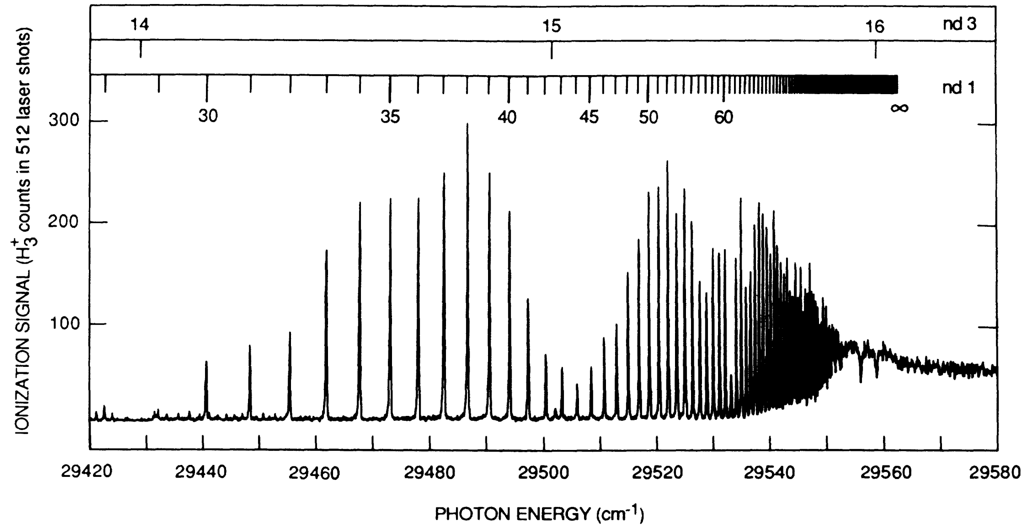

FIG. 2. Photoabsorption spectrum of the long-lived $N=K=0$ level of H_3 $\tilde{B}$ $^2A_2''$ in its lowest vibrational level. The series members belonging to the field-ionized *nd*1 series and the *nd*3 interlopers are marked at the top of the figure.

the $c\ ^3\Pi$ state in charge exchange with Cs.[24,25] Runs with pure HD samples were carried out and they revealed photoionization spectra very much more complex[26] than those shown here, and any contamination of the spectrum by HD molecules is therefore ruled out. An additional improvement over our previous experiment is that precise electronic gating of the ion detector with respect to the laser pulse eliminated interference events that arise from photoexcitation of the cesium charge transfer target. In the wavelength range under consideration here, excitation of the Cs atoms to the $11p$ states by the laser modifies the charge transfer characteristics of the target for molecules that arrive at the cell during or immediately after the laser pulse.[10] This is due to the fact that the laser runs coaxial with the neutral beam and hence passes through the charge exchange cell. Selective detection of excitation events of only those molecules that had passed the charge transfer cell prior to the laser pulse now completely eliminates this interference.

Finally, checks were made to ensure that the intense discrete peaks in the spectrum shown in Fig. 2 are indeed a result of field ionization. To this end a weak magnetic field was applied to the beam path close to the field-ionization region. H_3^+ ions formed by direct ionization (and autoionization) are thereby eliminated from the beam. It was found that the intense peaks under the Rydberg series markers shown in the top of the figure originated from field ionization. The weaker spectral features at the red end of the scan and the small peak between $n=42$ and 43 are formed in autoionization processes. These peaks arise from excitation of vibrationally excited species in the $\tilde{B}$ state but they will not be considered in this paper. We note that in this new source the relative abundance of molecules in the lowest vibrational level greatly exceeds that of vibrationally excited species.

DISCUSSION

The identification of the Rydberg series in Fig. 2 is based on the following arguments: A single rotational level of H_3 is expected[5] to be long lived. This molecule, characterized by the quantum numbers $N=K=0$, may be thought of as consisting of a $2p$ electron attached to the lowest rotational level of H_3^+. In Hund's case (d) the core is labeled by the quantum numbers $N^+=1$, $K^+=0$, the angular momentum of the p electron and the core rotation balancing each other to form neutral triatomic hydrogen with overall angular momentum of zero (neglecting the electron spin). The core configuration, $N^+=1$, $K^+=0$ is the lowest *ortho*-level[27,28] of H_3^+.

In the absence of degenerate vibration, three allowed dipole transitions exist from this long-lived rotational level for each principal quantum number n. Two of these involve excitation of the p orbital into s- and d-type Rydberg states of electronic symmetry $ns\,^2A_1'$ and $nd\,^2A_1'$ built on the $N^+=1$, $K^+=0$ ionic core. For $n=3$ these upper states have been resolved in emission,[13,16] in photodissociation,[19] as well as in two-photon ionization[29] studies. A third allowed transition[16] connects to the $nd\,^2E''$ states which converge in the ionization limit to the $N^+=3$, $K^+=0$ core. However, at large values of n excitation of this state is weak, owing to the required change in core rotation. The three allowed transitions from the long-lived level belong to R branches and they populate $N=1$ states.

Based on the similarity of nuclear configurations of the Rydberg species and the H_3^+ core[30–32] we expect that Franck-Condon factors strongly favor diagonal transitions. As a consequence, excitation of the nonvibrating $\tilde{B}$ state will access predominantly the series converging to the lowest vibrational level of the ion. This series always lies below the ionization threshold of *ortho*-trihydrogen. Since field ionization is required for the detection of our spectra we conclude that the series shown in Fig. 3 does indeed converge to the lowest vibrational level of H_3^+.

The two expected series, s and d, which converge to $N^+=1$, $K^+=0$ for $N=1$, are predicted to have transition moments[32] differing by about a factor of 15. Since we observe only a single series, we attribute it to the stronger d component, the s component either being blended with the d members or else being too weak at the high-n values studied here to be detected. The line positions for the observed series were fitted to the Rydberg formula

$$\nu = E_{\text{lim}} - \mathcal{R}/(n-\delta)^2 \ . \tag{1}$$

Using as the value of the Rydberg constant, $\mathcal{R}=109\,717.40\ \text{cm}^{-1}$, an optimal fit was obtained with $E_{\text{lim}}=29\,562.58\pm0.014\ \text{cm}^{-1}$ and $\delta=0.0189\pm0.0053$. The uncertainties quoted reflect two standard deviations. The deviation of measured line positions from those predicted in Eq. (1) is plotted in Fig. 3. The deviation falls well within the estimated $0.2\ \text{cm}^{-1}$ precision of our wavelength scale. The scale was calibrated using an optogalvanic neon spectrum. To convert the laser wavelength to the moving frame of the absorbing molecule, the transla-

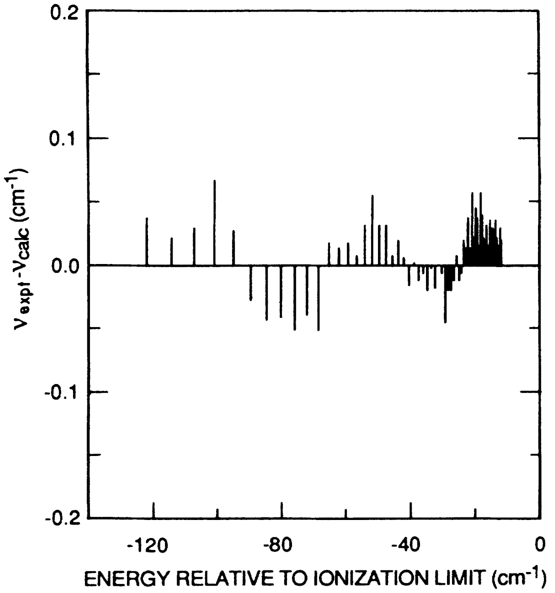

FIG. 3. Deviation of measured line positions of the $nd1$ Rydberg series from the Rydberg formula [Eq. (1)]. The energy scale is referenced to the ionization limit, $29\,562.58\ \text{cm}^{-1}$.

tional energy of the beam was first determined by measuring several line positions with the laser propagating parallel and antiparallel to the fast beam, and using the relativistic Doppler-shift formula. The ionization potential quoted above is considered to be precise to within 0.5 cm^{-1}.

Six members of the Rydberg series shown in Fig. 2 have been identified in the previous study (see Fig. 3 of Ref. 9, series A). Extrapolation from these six members ($n=33$ to 39) had yielded 29 566 cm^{-1} as our previous estimate for the ionization potential.

An energy diagram of the threshold region of $H_3{}^+$ for $K^+=0$ is given in Fig. 4. The electronic d states in Hund's case (b) (appropriate at low principal quantum numbers) are of electronic symmetry A_1' and E''. At higher-n values a transition occurs towards Hund's case (d), and two series, $nd1$ and $nd3$, converging to $N^+=1$ and 3 emerge. The hypothetical rotational levels with $N^+=0$ and 2 are indicated by the dashed lines. These levels do not exist in H_3 as a consequence of the Pauli-principle requirement for the $H_3{}^+$ nuclei.[28]

Owing to the conservation in core rotation, excitation of the $nd1$ series is favored from the $N=K=0$ level of the $\tilde{B}$ state. Nevertheless, the l uncoupling from the core allows the two $N=1$ series to mix, and it is tempting to attribute the wide open intensity windows, which appear in the neighborhood of the $n=14$ and 15 members of the $d3$ series, to this mixing. The unfavored $nd3$ character, admixed to the $nd1$ series, may effectively drain transition strength from the Rydberg series in the vicinity of the $nd3$ resonances. However, it is found that a two-channel quantum-defect treatment[33] cannot adequately model the observed intensity modulation. The origin for this failure is likely to be connected with the appearance of additional interlopers: At least three other window resonances, near $n=61$, and at the unresolved positions $n=128$ and 168 appear in the spectrum (see Fig. 2). These additional interlopers cannot be attributed to any of the remaining d series which connect to the lowest vibrational level of $H_3{}^+$. Of the remaining six nd series[16] with $J=1$ only one exists for *ortho*-trihydrogen. This series converges to $N^+=3$, $K^+=3$ of the ion and has overall symmetry $\Gamma=A_2''$. In the absence of external fields it should not connect to the $\Gamma=A_2'$ species as represented by the $nd1$ and $nd3$ series observed here.

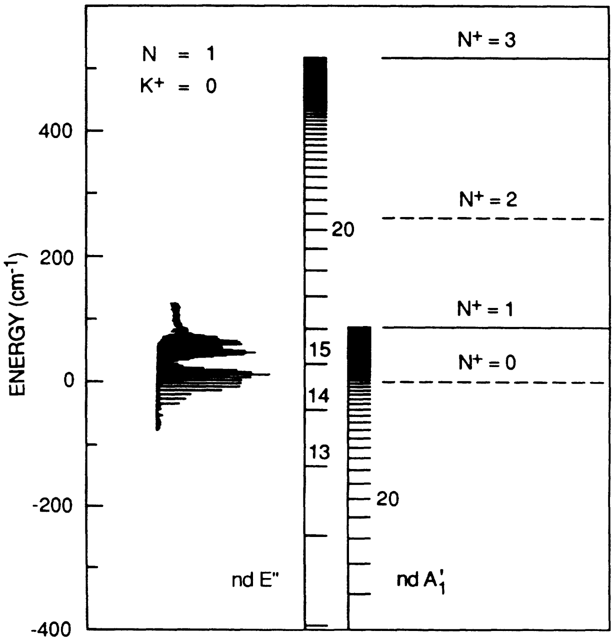

FIG. 4. Energy diagram of the threshold region of $H_3{}^+$, showing the two ($N=1$) d series which converge to the lowest levels of *ortho*-trihydrogen for $K^+=0$.

The additional interlopers which give rise to these window resonances are attributed to Rydbergs belonging to vibrationally excited cores. Assignment of the interlopers hinges on a more complete understanding of the Rydberg series that converge to vibrationally excited $H_3{}^+$. Current knowledge of these series is too limited[9] to permit definitive assignments. Work is currently underway to extend the previously covered spectral range for the vibrationally excited series, and it is hoped that a quantitative quantum-defect theory model can then be developed to explain the observed intensity modulation and window resonances.

Finally, mention should be made of the observed magnitude of the quantum defect found here. The value $\delta=0.0189$ is consistent with that obtained previously for the d states converging to vibrationally excited cores, $\delta=0.02$ and 0.022. As noted then,[9] a small discrepancy exists between the experimental quantum defects obtained for the high-n members and those predicted by theory for $n=3$ and 4. The calculations[30–32] predict the defect to be -0.006 and -0.01 for the $nd\,{}^2A_1'$ and $nd\,{}^2E''$, respectively. The smoothness with which the observed series follows the simple Rydberg formula (1) makes it unlikely that the discrepancy arises from the unaccounted interactions with other Rydberg series.

CONCLUSION

An extended photoabsorption spectrum for the lowest d-Rydberg series in the triatomic hydrogen molecule has been recorded. A precise value is obtained for the ionization potential of the long-lived $N=0$, $K=0$ level of the $\tilde{B}$ ${}^2A_2''$ state of H_3, and the quantum defect for the $N=1$ d series which converges to the lowest *ortho*-level of $H_3{}^+$, $N^+=1$, $K^+=0$ is determined. The $\tilde{B}$ ${}^2A_2''$ configuration is not the lowest bound state of H_3. The $N=K=0$ level of $\tilde{B}$ lies 898 cm^{-1} above the $N=1$, $K=0$ level of the $2s\,{}^2A_1'$ state.[13–16] The latter is, however, rapidly predissociated[14] with a natural width of 30 cm^{-1} (0.14 ps). It therefore appears appropriate to reference the ionization potential to the long-lived $N=K=0$ levels of the $\tilde{B}$ state.

The most fundamental triatomic molecule is long lived in only a single rotational level. Techniques for forming neutral molecules in fast beams by using electron transfer, developed 25 years ago,[34] allow us to synthesize copious quantities of this molecule. The molecule exhibits an atomiclike absorption spectrum and is a molecular analog to the lithium atom, but with a complex and well-defined[27] core. Thus detailed investigations of the fundamental $H+H_2$ interaction can be carried out with spectroscopic precision.

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