Bound-Free Ultraviolet Emission from Triatomic Hydrogen

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We report the first observation of an ultraviolet emission continuum attributed to transitions originating in bound Rydberg states of H_3 and terminating on the repulsive ground state.

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Observations by Herzberg and collaborators[1–3] of visible radiation resulting from transitions between bound Rydberg levels in H_3 have stimulated a number of theoretical[4,5] and experimental[6–8] investigations of the excited states of this molecule. Since H_3 is unstable in its electronic ground state with respect to H_2+H, Rydberg levels cannot be accessed by absorption from that state and emissions from transitions terminating in the ground state have not yet been reported. Figger *et al.*[8,9] have observed the visible emission bands of H_3 near 560 and 710 nm following an electron transfer process $H_3^+ + M(g) \rightarrow H_3^* + M^+$ (M denotes an alkali metal), but did not report examination of the vacuum-ultraviolet (vuv) region. In the experiments reported here we have used our ion-beam–luminescence apparatus to examine both visible and vuv emissions from H_3^*. We report the first observations of a uv continuum attributed to bound-free transitions in the H_3 molecule. We also show that vibrationally cool H_3^+ ions are essential precursors for the production of radiating states of H_3^*.

The crossed-beam apparatus used in these experiments has been described elsewhere.[10] H_3^+ were produced by H_2^+-H_2 collisions in an electron-impact source and focused into a beam with a set of electrostatic lenses. Control over the internal energy state distribution of the ion beam was accomplished by variation of the hydrogen gas pressure in the source and the temperature of the source. For some experiments buffer gas, usually nitrogen, was added to the source to reduce further the excited-state composition of the ion beam. After mass selection the beam was accelerated to 3 keV, focused into a collision cell, and collected on a Faraday cup. An atomic-beam oven beneath the cell produced a beam of potassium atoms with a density of $\sim 10^{11}$ cm^{-3} that intersected the ion beam in the center of the collision cell. Two monochromators, one covering the wavelength range 2000–8000 Å and the other an evacuated instrument for the vuv, located on opposite sides of the plane defined by the two beams were used for dispersal of radiation resulting from the decay of excited products of the ion-atom collisions. The spectra were obtained by our scanning the monochromators stepwise through the wavelength regions of interest and recording photon counts for a preset time period at each setting.

Emission spectra following charge transfer to D_3^+ were obtained in the wavelength regions 550–580 and 700–750 nm. We also observed a previously unreported continuum between 190 and 280 nm with $\lambda_{max} \approx 230$ nm and a much weaker Ly-α emission. Similar spectra were also recorded from H_3^+-K collisions, but in all cases spectral intensities were weaker. Emission intensities decreased sharply for all band systems when the hydrogen source pressure was reduced in the absence of a moderating gas. These spectra and the pressure dependences are shown in Fig. 1. A similar pressure dependence was also observed by the authors of Refs. 8 and 9 in their studies of visible H_3^* emissions.[11] To check possible interference from the uv continuum of D_2 produced by collisional dissociation of D_3, spectra were also recorded from D_2^+-K collisions with both moderated and unmoderated

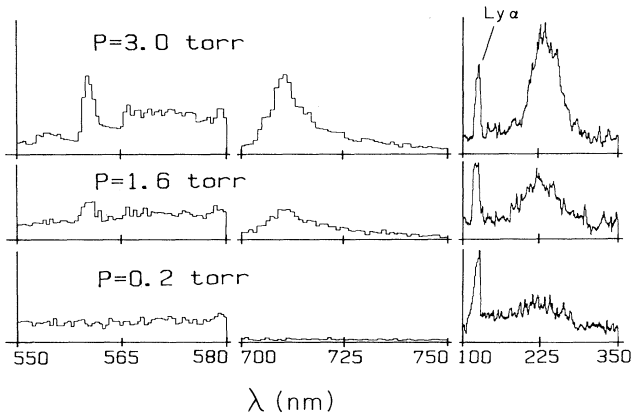

FIG. 1. Visible bands at 560 and 710 nm and vacuum-ultraviolet spectra resulting from 3-keV D_3^+-K collisions. Data are shown for three different ion-source D_2 pressures; the source was cooled with liquid nitrogen, but no moderating gas was used.

source conditions. Comparison of these continua with that produced by D_3^+-K collisions is illustrated in Fig. 2.

Figure 3 is an energy-level diagram for H_3 scaled to the ground state of H_2+H. The H_3 molecule has D_{3h} symmetry and its levels are designated by united-atom group-theoretical symbols. The repulsive $2p,{}^2E'$ and predissociative $2s,{}^2A_1'$ states are positioned in the diagram from H_3 fragmentation energies measured in beam scattering experiments.[6] The upper levels are fixed relative to the $2s,{}^2A_1'$ state. The highest continuum level of the $2p,{}^2E'$ state corresponds[12] to an H_3 molecular configuration with the ground-state geometry of H_3^+. The bands at 560 and 710 nm correspond to the $3p,{}^2A_2'' \rightarrow 2s,{}^2A_1'$ and $3p,{}^2E' \rightarrow 2s,{}^2A_1'$ transitions analyzed by Herzberg and collaborators. Both bands involve transitions between the lowest vibrational levels of the electronic states involved. Very recently Ketterle, Figger, and Walther[13] observed weak transitions originating in the first excited vibrational levels of the upper electronic states; however, the lower electronic state undergoes efficient heterogeneous predissociation into the repulsive ground state. Rotational analyses[2,3] of the upper Rydberg levels show that they have very similar geometries, with the H-H bond distance close to that[12] in H_3^+. The fall-off in intensities of the visible bands with increasing vibrational excitation of the D_3^+ (source-pressure effect, Fig. 1) can be understood as a consequence of the vibrational energy tranferred in a vertical process; that is, $D_3^+(v>0)+K \rightarrow D_3^*(v>0)+K^+$ is followed by rapid predissociation of the vibrationally excited D_3^*. However, vibrationally cool D_3^+ leads to $D_3^*(v=0)$ which undergoes radiative transitions. It is unrealistic to assume as an alternative that the cross section for electron capture to excited D_3^+ drops abruptly.

This mechanism is consistent with previous studies

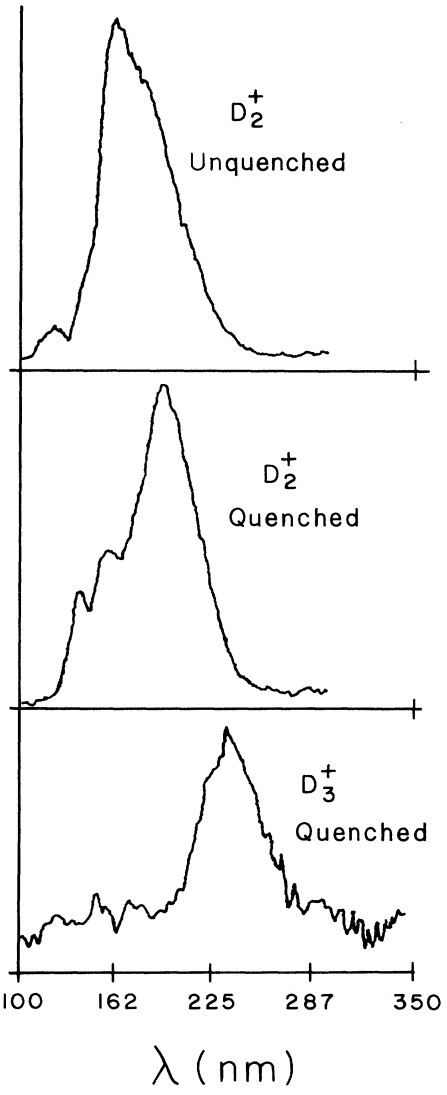

FIG. 2. Vacuum-ultraviolet spectra resulting from 3-keV D_2^+-K and D_3^+-K collisions. The unquenched D_2^+ was produced with low D_2 pressure in the ion source. Both quenched spectra were acquired with ions formed with moderating nitrogen gas in a liquid-nitrogen–cooled source. The spectrum obtained with quenched D_2^+ shows both the $a \rightarrow b$ D_2 continuum and, at shorter wavelengths, bands of the $B \rightarrow X$ Lyman system of D_2.

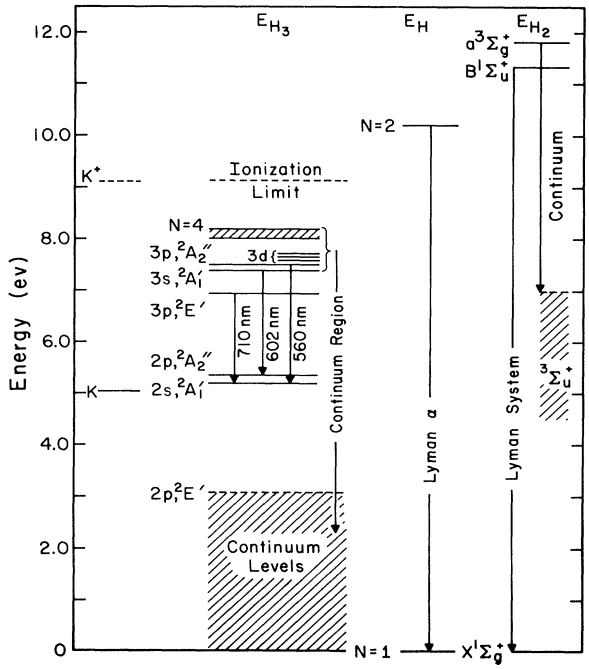

FIG. 3. Energy-level diagram for H_3 showing the spectral region of the ultraviolet continuum. The energy separation between the $N=4$ and $N=3$ levels in H_3 is known only theoretically (Ref. 4).

of H_3^+ formed by H_2^+-H_2 collisions in an electron-impact ion source since it has been established[14,15] that collisional energy transfer is an efficient mechanism for the cooling of nascent H_3^+ or D_3^+. This is also consistent with the observation of greater light yields from D_3^+-K charge transfer than from H_3^+-K charge transfer. Because the vibrational levels of the light isotope are more widely spaced, V-T (vibrational to kinetic) quenching in the source will be less efficient for H_3^+ than for D_3^+, leading to the observed isotope effect. Also contributing is the fact that predissociation of the upper electronic state,[5] which competes with radiative decay, will be faster for H_3^* than for D_3^*.

From Fig. 2 we note that the D_2^+-K continuum has the predicted shifts toward longer wavelength when the D_2^+ ion beam is quenched.[16] Under that condition both the $B\,^1\Sigma_u^+ \rightarrow X\,^1\Sigma_g^+$ Lyman bands and the $a\,^3\Sigma_g^+ \rightarrow b^3\Sigma_u^+$ continuum from D_2 are clearly evident. The D_3^+-K continuum, which lies in the same region as the D_2 continuum, was found to parallel the decrease in intensity of the visible bands as the source pressure was reduced (Fig. 2), but λ_{max} is shifted only slightly. At total disappearance of the D_3^+-K continuum only the Lyman line of D was present, but under no set of conditions were the Lyman bands from D_2 observed. When the D_3^+ beam was further relaxed Lyman-α emission disappeared (Fig. 2).

We believe that the correlation between the pressure dependences of the uv and visible spectra (Fig. 1), together with the observed isotopic differences (H_3^+ vs D_3^+) and the dissimilarities between D_2^+-K and D_3^+-K spectra, rule out $D_2(a\,^3\Sigma_g^+)$ as the emitting species in the D_3^+-K continuum, which leaves D_3 as the only possible source of radiation. This conclusion is supported by our observation that, unlike the case for H_3^+ and D_3^+, H_2^+ and D_2^+ formed under similar source conditions produce nearly identical spectra and emission intensities in collisions with K atoms.

Because we are dealing with an essentially structureless emission continuum (structureless at least under our present resolution) it is not possible to determine *unequivocally* the source of radiation. We believe that the evidence presented above provides a compelling case for D_3; however, the possibility of dissociative processes leading to radiating D_2 exists. However, spin-rule considerations cannot preclude production of either singlet or triplet states of D_2 in such collisions, and there is no reason to presume that one would be favored over the other. Since absence of the Lyman bands in the D_3^+-K continuum establishes that $D_2(B\,^1\Sigma_u^+)$ is not formed, it therefore seems unlikely that $D_2(a\,^3\Sigma_g^+)$ is produced. Furthermore, it may be seen in Fig. 3 that the $N=2$ level of D is energetically more accessible by collision of D_3^+ with K than are the a and B states of D_2. The populations of both of these states are more likely to be enhanced, not diminished, by collisional dissociation if the D_3^+ reactant ions are vibrationally excited.

King and Morokuma[4] calculated transition moments for a number of transitions originating in excited Rydberg levels of H_3 and terminating in the $2p,\,^2E'$ ground state. Transitions with $3s$ and $3d$ upper states are both allowed and expected to be strong in the united-atom approximation. The strongest transition is predicted to occur from the $3d,\,^2E'$ upper state. From Fig. 3 we estimate that for a strictly vertical transition between $3d,\,^2E'$ and $2p,\,^2E'$ radiation would occur near 280 nm. However, the intensity distribution of a continuum terminating on the ground state will depend on the shape of its potential surface near the D_{3h} saddle point. The expected effect of Jahn-Teller distortion[4,17] will be to shift λ_{max} to the blue. Furthermore, under our resolution the uv continuum has only one obvious maximum, but until high-resolution spectra are recorded we cannot be certain that only one upper state is involved in the transition. Transitions from $4s$ and $4d$ upper levels are also allowed, and any radiative contribution from these transitions would of course further shift the continuum to wavelengths shorter than 280 nm.

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