

Spectroscopy of Triatomic Hydrogen Molecules in a Beam

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The formation of beams of triatomic deuterium D_3 and the mixed isotopic molecule D_2H was optically observed for the first time when the corresponding ions were neutralized by charge exchange. The molecules were detected via the transitions between the Rydberg states $n = 3$ and $n = 2$. An assignment of the D_2H spectrum is given. The total lifetimes of rotational sublevels of different electronic states with $n = 3$ of D_3 were measured from the radiative decay of molecules along their path behind the charge-exchange region. Agreement with theory is satisfactory.

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H_3 , D_3 , and T_3 molecules as well as their mixed isotopes are the simplest neutral triatomic systems and therefore well suited to theoretical investigations. The existence of these fundamental molecules has been discussed for about sixty years.¹⁻³ Their electronic ground states are unstable, as many scattering experiments have exhibited in the past.⁴ Experimental indications of long-lived excited electronic states were obtained in neutralized-ion-beam experiments. In these experiments the existence of H_3 or D_3 in higher electronic states is confirmed by detection of the triatomic ions in a successive charge-exchange process (e.g., $H_3^+ \rightarrow H_3 \rightarrow H_3^+$)⁵⁻⁷ or from translational energy spectra of the fragments H_2 and H after the formation of H_3 .⁸ Optical spectra have not been obtained during these investigations. Most of the information on the structures of H_3 and D_3 has been obtained by Herzberg and co-workers^{9,10} since 1979 after the optical spectra of these molecules were discovered in hollow-cathode discharges in H_2 and D_2 , respectively. The interpretation of the spectra showed that H_3 and D_3 have to be considered as Rydberg molecules with one electron orbiting around a H_3^+ or D_3^+ core and with a dissociative ground state.

The purpose of our experiment was to investigate the formation of triatomic hydrogen molecules by charge transfer to H_3^+ and D_3^+ ions under single-collision conditions, in order to obtain a beam source of these molecules that is suitable for spectroscopy without the background of diatomic hydrogen molecules always present in a hollow-cathode discharge.¹¹ Such a source should be more ap-

propriate for laser spectroscopy, especially of highly excited states.

The experimental setup is shown in Fig. 1. For intensity reasons most of our experiments so far have been performed on D_3 . The D_3^+ ions for the charge exchange were generated in a hollow-cathode discharge in D_2 from which an ion beam was extracted by an acceleration voltage of 5 kV. A D_3^+ beam of $5 \mu A$ was separated by a homogeneous 90° magnetic field from other ions such as D^+ and D_2^+ also formed in the ion source. It was focused for charge exchange into a 1-cm-long cell filled with alkali-metal vapor. The ion beam passed through two holes of 3 mm diameter. In such a cell the alkali-metal dimer concentration is much lower than in an alkali-metal beam, which was used at the beginning of the experiments. With an alkali-metal vapor pressure of about 10^{-3} mbar 80% of the ions were neutralized. In the charge-exchange process

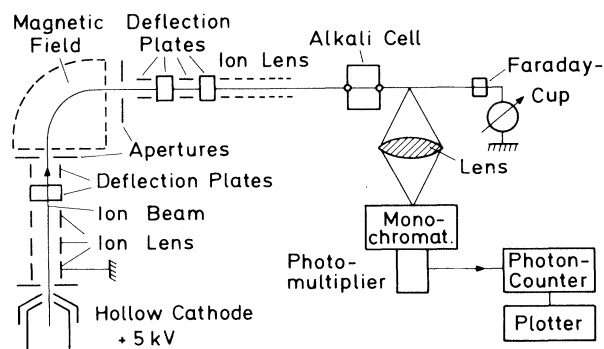


FIG. 1. Experimental setup for the neutralized-beam experiment.

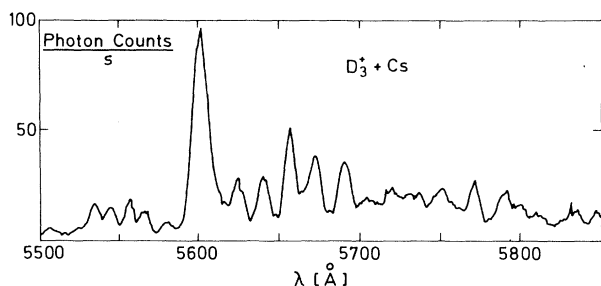
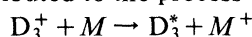


FIG. 2. Emission signal recorded from the D_3 molecular beam behind the charge-exchange region around 5600 Å, corresponding to the $3p\ ^2A_2'' \rightarrow 2s\ ^2A_1'$ electronic transition.

the D_3 molecules were produced in excited states. The emitted light was observed in a region about 1 cm behind the alkali-metal cell. The background light from excited alkali-metal atoms and dimers is very low for this arrangement. The light was analyzed with a monochromator having a resolution of 5 Å. The intensity was measured with a photon-counting system.

In this way the characteristic bands of D_3 around 5600, 5800, 6025, and 7100 Å were observed. They all correspond to transitions between electronic states with the main quantum numbers $n = 3$ and $n = 2$. The $n = 2$ levels predissociate and therefore contribute about 3 Å (Ref. 10) to the width of the lines, which are instrumentally broadened further. An example of the spectra is shown in Fig. 2. As the densities of the D_3^+ ions and the alkali-metal atoms are low, it is likely that only one-step processes take place. The D_3 formation is therefore attributed to the process



(where M is an alkali-metal atom and the asterisk indicates electronic excitation).

With the count rate of our optical system (100/s), the corresponding geometrical factors, the particle densities, and the beam velocity, the order of magnitude of the cross section for the formation of D_3 molecules in the states with $n = 3$ is estimated to be 10^{-19} cm². The charge transfer to D_3^+ is found to be fairly independent of the alkali-metal ion core: The rotational distributions within the D_3 bands and their intensities change little when different alkali metals (Na, K, Rb, and Cs) are used for charge transfer. The observed spectra, like the one shown in Fig. 2, are similar to those obtained from hollow-cathode discharges, e.g., with respect to the relative intensity distribution of the rotational lines.¹⁰ However, unlike the latter, they are free from D_2 lines.

The beam of radiating D_3 molecules behind the charge-exchange cell has a very small divergence. This was checked by imaging different sections of the beam. It therefore can be used to determine total lifetimes of the $n = 3$ levels of D_3 , which have not yet been measured. To this aim the light of a small section of the D_3 beam was monitored, while the charge-exchange cell was shifted by a few centimeters toward the ion source. The recorded intensity decreased purely exponentially for all states investigated, indicating that cascading from higher states should be negligible (see also below). Since the small divergence of the D_3 beam mentioned above means little momentum transfer during the charge-exchange process, the velocity of the molecules should differ little from that of the ions. Therefore the velocity of the radiating D_3 molecules can be assumed to be the same as that of the D_3^+ ions (0.4 mm/ns). With use of this value the lifetimes given in Table I were derived. They are compared with theoretical values given in the last column of Table I. These values were calculated by means of the electric dipole transition moments derived from *ab initio* calculations by King and Morokuma¹² for transitions between electronic states of H_3 . The fairly good agreement between theoretical and experimental results indicates that the decay of the states concerned is mainly radiative. This would be consistent with conclusions in Ref. 10 for these states. The shorter lifetime of the $3p\ ^2A_2''$ state of D_3 might be due to the mixing of this state with the $3d$ states¹³ which have shorter lifetimes.

So far no transitions of triatomic hydrogen molecules from the $n = 5$ and $n = 4$ states to the $n = 2$ state have been observed, though in the charge-exchange process states with $n > 3$ should also be populated.⁷ The corresponding bands are expected in the wavelength range between 4000 and 5000 Å. In the hollow-cathode discharge this spectral region is heavily distorted by D_2 emission lines. The fact that transitions from the higher-lying states are not observed in the beam experiment is an indication that population of the $n = 3$ states is more efficient by the direct charge-exchange process than by cascading from higher levels.

Experiments to excite higher Rydberg states in the D_3 molecular beam by laser radiation are presently under way. The excitation of the higher states can now be detected by the very sensitive method of electric field ionization, frequently applied in the investigation of Rydberg atoms, or by measurement of the decrease of the intensity of the transitions starting from the $n = 3$ states.¹¹

TABLE I. Lifetimes of different Rydberg states of D_3 with $n = 3$ measured from the exponential decay of the light intensity after the charge-exchange region (fourth column). In the first column the wavelengths of the rotational lines observed are listed, in the second the rotational transitions are given, and in the third the corresponding electronic transitions are given. The fifth column contains theoretical values.

Wavelength observed (Å)	Rotational transition	Electronic transition	τ_{obs} (ns)	τ_{theor} (ns)
5600	Q-branch	$3p \ ^2A_2'' \rightarrow 2s \ ^2A_1'$	29.0 ± 1	47.05
7110	Several	$\left\{ 3p \ ^2E' \rightarrow 2s \ ^2A_1' \right\}$	18.5 ± 1	21.2
7093	Several		18.5 ± 1	21.2
5771	Several	$\left\{ 3d \ ^2A_1', \ ^2E', \ ^2E'' \right\}$ $\rightarrow 2p \ ^2A_s''$	12.9 ± 1	$\left\{ 11.9 (3d \ ^2A_1') \right.$ $12.3 (3d \ ^2E'')$ $9.7 (3d \ ^2E')$
5746	Several		11.8 ± 1	
5717	Several		13.1 ± 1	

In the hollow-cathode discharge, it is also possible in principle to investigate the spectra of the mixed isotopic molecules D_2H and H_2D when appropriate gas mixtures of H_2 and D_2 are used. However, it is extremely difficult to assign them because the spectra of D_3 , H_3 , H_2 , D_2 , and HD are also present simultaneously. An ion-beam apparatus with mass selection as used in this experiment simplifies the problem. So, we used a pure D_2H^+ ion beam from the discharge in a 2:1 mixture of D_2 and H_2 and passed it through the cell containing potassium vapor. Spectra around 5600 Å, shown in Fig. 3(a), and 7100 Å could be recorded. They look similar to the corresponding D_3 spectra, but are shifted by 10 to 20 Å to the red. According to their origin, they have to be attributed to the neutral D_2H molecule. This is the first time that these spectra have been observed. A computer simulation assuming a rotational temperature of 200 K is shown in Fig. 3(b). According to these results, the spectrum around 5600 Å can be assigned to the $3p \ ^2B_1 \rightarrow 2s \ ^2A_1$ system of D_2H . An equilateral structure of the molecule has been assumed in both states, and the band origin and the equilibrium distances r_0' and r_0'' have been adjusted. The values obtained for the parameters are $\nu_{00} = 17834.4 \text{ cm}^{-1}$, $r_0' = 0.893 \text{ Å}$, and $r_0'' = 0.858 \text{ Å}$. Theoretical values of the inertial defect and of the centrifugal constants were included, but the perturbations¹³ between the $3p \ ^2B_1$ and $3d$ states were ignored. The structure near 5750 Å of Fig. 3(a) seems to belong to the $3d \rightarrow 2p \ ^2B_1$ system,¹³ but

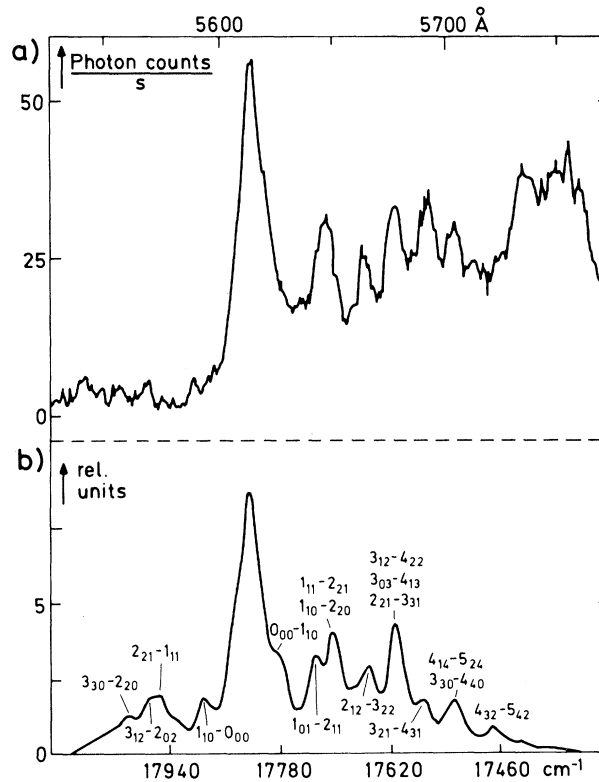


FIG. 3. (a) Emission spectrum around 5600 Å for a D_2H^+ ion beam neutralized in potassium vapor. It is interpreted as being emitted from excited D_2H molecules. (b) Computer simulated spectrum for the $3p \ ^2B_1 \rightarrow 2s \ ^2A_1$ band of D_2H . The numbers are asymmetric top quantum numbers $J_{K_-K_+}$ (Ref. 14).

the peak near 5690 Å is as yet unexplained.

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