SOME NEW ASTON BANDS IN HYDROGEN

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Broad nonintegral mass bands at the 0.66- and 0.75-u mass positions appear in the hydrogen mass spectrum at high pressure (10^{-4} Torr). A primary peak is also observed at the 1.5-u mass position. These Aston bands and mass peak may be interpreted as resulting from the creation and collision-induced reactions of the H_3^{++} ion, which would be formed in a surface reaction between H_3^+ and adsorbed hydrogen.

Back in 1963, in the course of a study of a hydrogen Aston band whose m/q ratio is 0.5 mass units per electron ("at the 0.5-u position"), McGowan noticed a small deformation of the band which suggested the presence of a further minor band at about the 0.75-u position. Such bands arise in mass spectra when ion-beam collisions with residual gas produce charge-exchange or dissociation reactions. The ion optics of Aston bands[1] suggested that for a 0.75-u band to arise in hydrogen collisions an ion of mass-to-charge ratio 1.5 had to intervene. The only candidate appeared to be the unlikely species H_3^{++}.

Since then we have made many more studies of the Aston banding in hydrogen, using different mass spectrometer tubes and source types. New bands have been observed, some of them requiring the H_3^{++} ion for their interpretation. Other corroborating experiments now permit us to formulate as a working hypothesis that the combination of three protons and one electron can be stable for at least 2 μsec.

For our experiments a high-yield inflection mass spectrometer[2] was used at a molecular hydrogen pressure of about $(0.5-3) \times 10^{-4}$ Torr, evenly distributed throughout the source and drift regions of the instrument. Ions were formed in the source by electron bombardment and then accelerated to about 1 keV for mass analysis in the usual way. While traversing the first "drift region" between the source and the analyzing magnet, ions could collide with neutral hydrogen molecules and by dissociation produce the Aston bands observed. Collisions could also take place between the analyzing magnet and the detector (second drift region) giving product ions which could be energy analyzed by a grid placed just before the detector. The latter was a wide-surface Be-Cu 12-stage electron multiplier with a stable gain of about 10^5. The use of a high-yield spectrometer at relatively high tube pressure with a very sensitive detector is a combination which does not appear to have been exploited elsewhere and no doubt partially explains why some of the bands were observed for the first time.

In Fig. 1 the mass spectrum of hydrogen as observed in our apparatus is shown for the mass 0.3- to 2-u region. The observed structure is shown in Table I.

The 0.5-u band is well known, while the 0.33-u band was observed by Smyth.[3] The new 1.33-u band observed here for the first time was predicted by Smyth. The intense primary peaks H^+ and H_2^+ have been extensively studied.
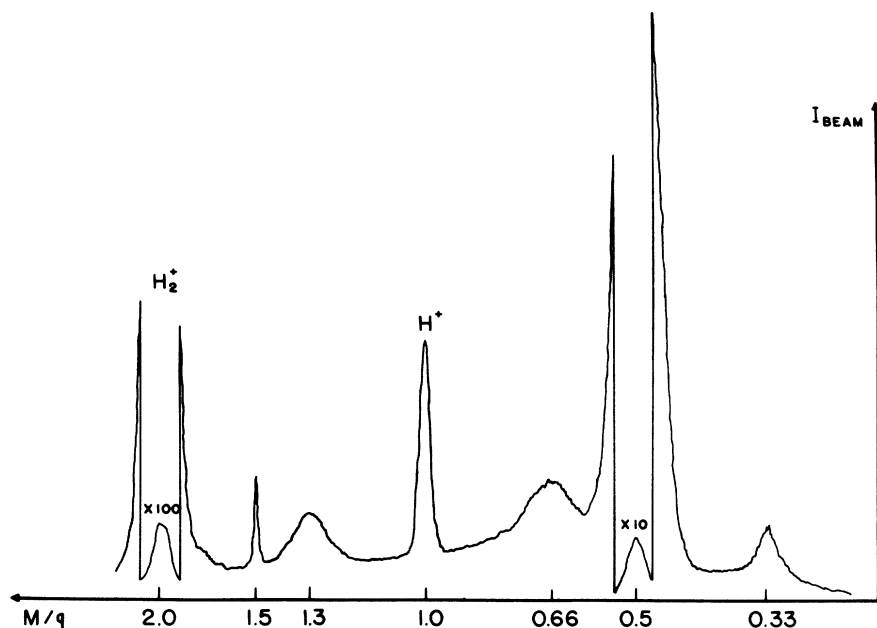
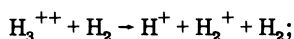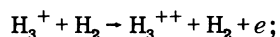The other two bands and primary peak are

FIG. 1. Mass spectrum of hydrogen in the 0.3- to 2-u region obtained at a pressure of 10^{-4} Torr in the tube. The band at 0.75 u is not present.

tentatively assigned as follows:

0.66 u, Aston band from the reaction

$$H_3^{++} + H_2 \rightarrow H^+ + H_2^+ + H_2;$$

0.75 u, Aston band from the reaction

$$H_3^+ + H_2 \rightarrow H_3^{++} + H_2 + e;$$

1.5 u, "primary" peak, H_3^{++}.

All of these features may thus be interpreted in terms of the H_3^{++} ion, and no other explanation has so far suggested itself.

Supporting evidence is as follows: The 0.66-u band only appears when the pressure is high enough to produce the 0.5-u band (about 10^{-4} Torr in our apparatus, i.e., when collisions involving hydrogen beams occur). The appearance potential of the 0.66-u band is that of $H_2^+ \pm 0.1$ eV.

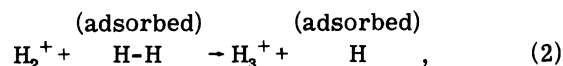Since the latter is postulated as the source of the H_3^{++} via H_3^+, the 0.66- and 0.75-u bands should appear at this ionizing potential. The 0.75 band is too weak to permit a precise measurement, but appears at the potential for $H_2^+ \pm 1$ eV. The doubly charged H_3^{++} band at 0.75 eV should be retarded by one half the potential used to accelerate the parent H_3^+ ion, and it is. Similar considerations apply to the 0.66-u band, but experimentally it is not completely retarded. This is presently attributed to a neutral component arising from charge exchange of the product H^+ in H_2 at the relatively high tube pressure. The 1.5-u peak appears at the ionizing potential of H_2^+ and is retarded by the beam accelerating potential as it should be. Variations of the bands with pressure were also observed. To verify the technique, the pressure dependence of the peaks at

Table I. Identification of observed structure of the mass spectrum of hydrogen shown in Fig. 1.

Mass position (u)	Nature	Particle	Reaction
0.33	Aston band	H^+	$H_3^+ + H_2 \rightarrow H^+ + 2H_2^+$
0.5	Aston band	H^+	$H_2^+ + H_2 \rightarrow H^+ + H + H_2$
0.66	Aston band		
0.75[a]	Aston band		
1.0	Primary peak	H^+	$H_2 + e \rightarrow H^+ + H + 2e$
1.33	Aston band	H_2^+	$H_3^+ + H_2 \rightarrow H_2^+ + H + H_2$
1.5	Primary peak		
2.0	Primary peak	H_2^+	$H_2 + e \rightarrow H_2^+$

[a]See Fig. 2.

1 and 2 u was found to be linear, and that of the band at 0.5 u to be quadratic, as is expected. The 0.33-u peak as interpreted would result from three collisions and should have a pressure dependence of order 3 — which it has. The 1.5-u peak presumably represents the H_3^{++} ion formed in the source from H_3^+. The sequence for its production would be

$$e + H_2 \rightarrow H_2^+ + 2e, \tag{1}$$

$$\begin{array}{cccc} & \text{(adsorbed)} & & \text{(adsorbed)} \\ H_2^+ + & H\text{-}H & \rightarrow H_3^+ + & H \end{array}, \tag{2}$$

$$H_3^+ + e \rightarrow H_3^{++} + 2e. \tag{3}$$

Therefore the 1.5-u peak should have a quadratic dependence on the source electron current. A series of measurements using two sources of different surface area and at pressures varying from 6×10^{-5} to 3×10^{-4} Torr confirms the quadratic variation over the electron current range from 4 to 9 μA. Above 9 μA a saturation effect causes the peak to level off; below 4 μA the increase of the peak is not even proportional to the electron current. We attribute this to insufficient degassing of the source surfaces at the resulting low source temperature. The intensity of the 1.5-u peak has a quadratic pressure dependence which, in the context of our working hypothesis, implies nonsaturation of the surface by H_2, an implication which finds some support in the large production of H_3^+. Further work is necessary to elucidate the interesting problems which the surface dissociation of H_2 implies in this case.

Confirming experiments were made by varying the surface of the source which was bombarded by the electron beam. Reducing it greatly reduced the production of H_3^+, corresponding to a result previously observed by Carette,[4] although the contribution of ionizing electrons which may have been insufficiently collimated and thus reflected from the surface is not perfectly established. As a result of these considerations we are led to consider that H_3^+ may be formed on the surface of the source as a result of an encounter between an H_2^+ ion and a loosely bound molecule of hydrogen adsorbed on the surface. The H_3^{++} ion is formed by the Aston-band reaction giving the band at 0.75 u, but more copiously by the surface reaction in which an H_2^+ ion combines with a hydrogen atom as before, and is released from the surface as a result of an ionizing electron collision rather than thermally as in the case of H_3^+. A reaction similar to that

producing the 0.66-u band should produce H_2^+ as a band at the 2.66-u position. It is also observed.

The band at 0.75 u only appears if the pressure in the spectrometer rises above 3×10^{-4} Torr and disappears when the pressure rises above 6×10^{-4} Torr. Instrument sensitivity is partly responsible for this restricted range, as the band, although always reproducible, is always very small (Fig. 2). It is to be expected that the reaction producing H_3^{++} (at 0.75 u) will have a much smaller probability than that producing H^+ (at 0.33 u) or H_2^+ (at 1.33 u). The time of flight of 1000-eV, $m/q = \frac{3}{2}$ ions in our instrument is about 2 μsec, which establishes a lower limit on its lifetime.

Finally, some of the experiments were repeated with deuterium. The primary peak at 3 u (corrected for DH^+) which corresponds to that at 1.5 u in hydrogen was observed under similar conditions. The Aston band at 1.33 u (2×0.66 u) was also observed. No isotopic effects, multiple-collision effects in the drift regions, or atom-exchange reactions lend themselves satisfactorily to an explanation of the new bands.

The simplicity of the H_3^{++} structure has suggested theoretical studies. Although previous ones, e.g., Conroy,[5] have indicated instability, recent methods[6] show that the combination may well be stable. Dr. G. Herzberg has communicated privately to us a calculation of the H_3^{++} ground state obtained by adding the energy of repulsion of the nuclei to the electronic energy given by Conroy and Bruner. The resultant potential function has a slight minimum which indicates that one or two vibrational levels could be accommodated, resulting in a lifetime of the order we have observed. Subsequently, Dr. Conroy has written to Dr. Herzberg that more refined calculations do not indicate the existence
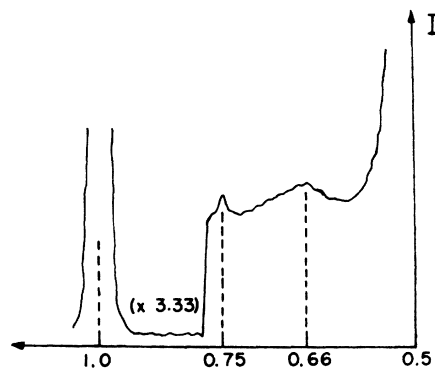

FIG. 2. Band at 0.75 u, with tube pressure at 4×10^{-4} Torr.

of a minimum. We have also had private com-
munication from Professor M. C. R. McDowell
whose theoretical treatment of the analogous
H^{--} indicates a possibility of stability.

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EVIDENCE FOR A "RADIATIVE AUGER EFFECT" IN X-RAY PHOTON EMISSION

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A broad x-ray emission structure with several maxima has been found on the low-en-
ergy side of the $K\alpha_1\alpha_2$ line in Mg, Al, Si, and S. It is interpreted as a radiative $K \rightarrow L^2$
transition resulting in the simultaneous emission of a photon and an L-shell electron.

Usually an x-ray inner-hole state decays either
through a radiative or a nonradiative transition.
However, other decay modes are possible.
Bloch[1] suggested that an atom may be able to
emit an x-ray photon and a valence-shell elec-
tron simultaneously instead of undergoing a "for-
bidden" quadrupole transition. Here we report
observation of yet another possible decay mode,
one in which a photon and an inner L-shell elec-
tron are emitted simultaneously instead of the di-
pole allowed $K\alpha$ line. Following Bloch we call
this the "radiative Auger effect," but we might al-
so call it the "atomic internal Compton effect"
from its analogy to nuclear γ emissions involving
the simultaneous ejection of an atomic electron.[2]

In the course of our search[3] for a many-body
structure situated on the low-energy tail of the
$K\alpha$ line in Al metal we extended our measure-
ments to energies below the expected range for
the many-body effects. Here we found a broad
structure with several "bumps," the intensity of
the highest peak being about 0.05% of the intensi-
ty of the $K\alpha$ line. A similar structure has also
been found in compounds, but here we limit our
discussion to measurements on the elements in-
vestigated so far, namely, Mg, Al, Si, and S.

The plane-crystal spectrometer equipment
used has been described previously[4] with the ex-
ception of a new vacuum chamber which allows
an improved angular resolution. The specimens
were excited by the radiation from a chromium-
anode x-ray tube. The fluorescent radiation
from Mg was recorded with a potassium acid
phthalate crystal ($2d = 26.64$ Å), that from Al with
an ammonium dihydrogen phosphate crystal ($2d$

$= 10.648$ Å), and that from Si and S with an ethyl-
ene diamine tartrate crystal ($2d = 8.808$ Å). In
the cases of Al, Si, and S the spectra were also
obtained with the potassium acid phthalate crys-
tal in order to make sure that there were no ex-
tra reflections involved due to the analyzing crys-
tal.[5] As an example of the new structure we
show in Fig. 1 records of the low-energy side of
the S $K\alpha$ line. The energies of the peaks labeled
E_1, E_2, A, B, C, and D were determined rela-
tive to the energy of the $K\alpha$ line from at least
three independent measurements. The energy
of the $K\alpha$ line was taken from the table of Bear-
den.[6]

The measured peak energies are given in Ta-
ble I, where we have also compared the energies
of the maxima A, B, C, and D with the known
KLL Auger electron energies of the elements.[7]
The energies of the peaks agree closely with the
known Auger energies corresponding to various
terms of the final state in the intermediate cou-
pling. Note also that the peaks at A, B, C, and
D have greater half-widths than the $K\alpha$ peak.
All this is consistent with the following interpre-
tation: Instead of the initial K hole being filled
with emission of either a full-energy $K\alpha$ photon
or a full-energy Auger electron, there is a si-
multaneous emission of a lower energy photon
$\hbar\omega$ and excitation of an L-shell electron. In Fig.
1(b) the peaks E_1 and E_2 correspond to transi-
tions in which the L-shell electron has been ex-
cited into bound states whereas each of A, B, C,
and D represents the approximate beginning of a
continuous band of x-ray energies. Within each
of these bands the energy $\hbar\omega$ of the photon satis-