assume reasonable data for the doublet structure of the third and fourth bands these have been bracketed in the table.

TABLE I.

n	λ	λ'	ν	ν'	$\delta\nu$	$\Delta\nu$	$\Delta\nu'$	$\Delta'\nu$	$\Delta'\nu'$
1	3.50μ	3.40μ	2860cm^{-1}	2940 cm^{-1}	80cm^{-1}	2860cm^{-1}	—	2940cm^{-1}	—
2	1.77	1.74	5650	5750	100	2790	70cm^{-1}	2810	130cm^{-1}
3	*[1.21]	[1.19]	[8270]	[8400]	[130]	2620	170	2650	160
4	*[0.930]	[0.917]	[10750]	[10900]	[150]	2480	140	2500	150
5	0.763	0.753	13100	13280	180	2350	130	2380	120
6	0.653	0.644	15300	15520	220	2200	150	2240	140
7	0.575	0.567	17390	17640	250	2090	110	2120	120

* 1.20 ± 0.01 and 0.93 ± 0.01 are the values observed thermally for these unresolved bands.

Since the $\delta\nu$ values are not the same for all of the bands the two broad components cannot be regarded as P and R branches of single bands.

Within the limits of certainty of the $\delta\nu$ values we may conclude that there is a linear relation between these values and n. From this we conclude that the coefficients of n differ in the two anharmonic formulas which relate ν and ν' independently to n. Furthermore, it can be seen that $\delta\nu$ will not extrapolate to zero when n equals zero, and from this fact we conclude that a constant term must appear in one or both of the equations. An inspection of the $\Delta\nu'$ and $\Delta'\nu'$ columns of the table indicates that the equation for the components of higher frequency requires no constant term. We are led therefore to the remarkable conclusion that a subtractive constant term must be included in the equation relating the lower frequency components to n. We have then $\nu_n' = a'n - bn^2$; $\nu_n = -c + an - bn^2$; $\delta\nu = c + (a' - a)n$. It is impossible to say whether there is any small change in the b coefficient.

The writer has already pointed out an instance in the case of ammonia in solution in which an additive constant must be included in the formula which relates a set of anharmonic overtones to their fundamental. (Jl. Franklin Inst. **208**, 507 (1929). A paper further supporting this interpretation has been submitted for publication). In that instance it was assumed that the constant term is a measure of the energy which goes to change the molecule to a form with slightly greater potential energy. In the present instance we are forced to conclude that a drop in the potential energy of the vibrator which yields the ν_n frequencies supplies the additional energy which the quantum lacks to produce the vibration. The behavior of the molecule in this respect is in a way similar to its behavior when producing an anti-Stokes line in a Raman spectrum. In the latter instance however the energy which the molecule gives up as it drops to a lower quantized level goes to increase the magnitude of the scattered quantum.

The data of the table cannot be used to decide whether we are dealing with a single kind of C-H vibrator which shifts at times to a lesser value of the restoring force, or with two distinct types of C-H vibrators. The writer however still inclines to his previous viewpoint that vibrations of one of the hydrogen atoms bonded to each carbon atom contribute to one component of the doublet series whereas vibrations of the second hydrogen atom contribute to the other component.

JOSEPH W. ELLIS

Physics Department,
University of California at Los Angeles,
February 4, 1930.

Secondary Emission from Metals by Impact of Metastable Atoms and Positive Ions

In studying the positive column of the noble gases, using plane sounding electrodes, some phenomena were observed, which could not be explained by the theory proposed by Langmuir[1] and applied by himself and Mott Smith[2] to the mercury arc. The simplest interpretation of the observed discrepancies, was to assume a secondary electron emission

[1] Langmuir, G. E. Rev. **26**, 731 (1923).
[2] Langmuir and Mott Smith, G. E. Rev., **27**, 449, etc. (1924).

from a negatively charged plane electrode, amounting to from 40 to 50% of the measured current. This value was obtained by comparing the measured current i_m and the current i_e, calculated from the observed thickness of the space-charge layer with the usual equations.[3] We have succeeded in proving directly that there is an electron emission from the electrode of that magnitude, and that it is principally due to impact of metastable atoms on the collecting electrode.

A plane circular collecting electrode (Ni) with a guard-ring was placed in the positive column of a neon discharge ($p=0.02$ mm) with hot cathode. At the center of the metal disk was a small hole, and behind this a Faraday box. The arrangement was such that the box was practically completely shielded from the radiation in the discharge. It was thought that a comparison of the ion current coming through the hole with the apparent ion current density on the central disk would give a measure of the secondary electron emission from the latter. Indeed, the chance for a secondary electron liberated in the Faraday box to get out is so small, that the current recorded at the box was supposed to be a pure positive ion current, provided the plate is sufficiently negative with respect to the gas (-125v) to keep out all electrons coming from the discharge. The experimental results were much more complicated than expected. Using different arrangements of potentials we proved that neutral particles, diffusing out of the main discharge through the gap between disk and guard-ring, caused a considerable electron emission from the metal parts behind the collector. This suggested that the secondary emission referred to above was due principally to the action of metastable atoms on the collector.[4]

More quantitative results were obtained in the same tube with another arrangement. Opposite to the plane collector with the guard ring, mentioned above, was a small hollow cylindrical one, whose axis was perpendicular to the plane collector. The near end, covered with Ni gauze, was exposed to the discharge, the sides and other end being shielded by glass. This cylinder was movable in the direction of its axis, i.e., perpendicular to the surface of the disk collector. Suppose the cylinder at a potential $V_c=-125$v with respect to the gas; it is then collecting a certain positive ion current i_c. The potential of the plate, V_p, originally -75v with respect to the gas, is now made more negative and the variation of i_c is studied as a function of V_p. As long as the plate is positive with respect to the cylinder, no secondary electrons from the plate can reach the latter, since in falling through the positive space charge layer on the disk they can only acquire an energy corresponding to V_p. When the potential of the plate reaches V_c, the ion current i_c shows a decrease due to incoming electrons originating in the space charge sheath on the plate. The mean free path of the electrons with a velocity corresponding to V_p depends on the degree of ionization and can be determined experimentally in each case by varying the distance between the cylinder and the plate, all other conditions remaining the same. Knowing the electron mean free path and the secondary electron current at a given distance, the secondary emission from the plate can be computed and is found to be from 40 to 50% of the total current i_p.

When the current voltage curve of the secondary electrons is differentiated, a velocity distribution curve is obtained which shows that most of the electrons have at least an energy corresponding to V_p; it follows that they must be liberated at the plate or at a very small distance from it. In addition to the energy, acquired in falling through the space charge sheath, they possess energies of a few volts which are probably initial energies of emission. Some velocity distribution curves show that there are also electrons produced in the sheath at some distance from the plate, but only in small numbers. The interpretation proposed earlier[5] that the electrons are principally due to photoelectric ionization in the sheath has to be given up. The experiments are continued with an improved apparatus to study the influence of different factors on the secondary emission.

W. UYTERHOEVEN
M. C. HARRINGTON
Palmer Physical Laboratory,
Princeton, N. J.,
February 10, 1930.

[3] Uyterhoeven, Phys. Rev. **31**, 931 (1928); Proc. Nat. Ac. Sc. **15**, 32 (1929).

[4] Oliphant, Proc. Roy. Soc. **A124**, 228, 1929.

[5] Morse and Uyterhoeven, Phys. Rev. **31**, 827 (1928); see also de Groot Naturwiss. **17**, 13 (1929).