On the Use of Interference Spectrographs for the Study of Fine Structures in Molecular Spectra.

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Introduction. The high resolving powers conveniently obtainable, especially for the visible part of the spectrum, by the use of modern interference instruments may well be utilized for the study of a fine-structure in each rotational line of molecular band spectra, when the latter is suspected, by some reason or other, to be composed of several very closely situated components, or accompanied by satellites in close proximity to the main line. An individual band-line has usually a very small absolute intensity when compared with an atomic line; indeed, the total intensity associated with the emission of a single atomic line may be considered divided up into hundreds or more rotational lines of a whole band system belonging to a single molecular electronic transition. However, apart from the consequent increase in the time of exposure, which implies the necessity of taking much greater precautions against mechanical vibration and changes in the spectrograph due to temperature variation, the technique of photographing a fine-structure pattern of a band-line is the same in principle as with an atomic line.

As is well-known, a Michelson échelon grating or a Lummer-Gehrcke interference plate can magnify only a very small region of the spectrum without being overlapped by patterns of neighbouring "orders". Thus each such instrument has the so-called "range", characteristic of its construction and dependent on the wave-length. Two lines separated in wave-length farther than the range must therefore be resolved by means of an auxiliary or "coarse" dispersing system before or after sending the ray through the high-powered instrument to examine the individual structures. It is convenient, and only practicable for band study, to arrange matters so as to make the two dispersions at right angles to each other on the recording photographic plate, and we get a "crossed" spectrum, or a two-dimensional pattern of interference dots. In the case of a band spectrum each rotational line, at least at some distance from a head, must clearly be resolved from adjacent ones by the aid of this coarse dispersion.

When the region under examination is congested through overlapping of branches, or when treating a branch with very narrowly spaced rotational lines, the "coarse" dispersion may not be so coarse as one would be impressed by the word, since it is often necessary to use for this purpose a long focus plane grating or prism spectrograph, preferably of a small relative aperture to keep the patterns sharply defined; all these requirements pointing to still further prolongation of exposure time.

In the following are given brief descriptions of two studies in which such combined or "crossed" spectrographs were constructed and used.

Electronic Fine Structure in Helium Bands. The diatomic helium molecule, while formed with a very short life, has four electrons, two of which confine themselves in the molecular K-shell, not participating in the emission of visible light. With the remaining two valence electrons the system can have a set of singlet energy levels and a separate set of triplet levels, just like the He atom or the H_2 molecule with their two outer electrons. An inter-combination transition between a singlet and a triplet levels is extremely unlikely to occur in these light atomic or molecular systems, and any observed helium band should be classified either as a singlet-singlet transition with purely single rotational lines, or as a triplet-triplet transition with at least three very closely situated components corresponding to the theoretical spin fine-structures in the levels concerned, quite apart from any multiplication of branches caused by molecular rotation.

All these are very clear in theory and by analogy to other spectra, but, owing to the extreme smallness of spacings characteristic of the lightest atomic systems with their small nuclear charges, no direct experimental evidence had existed as to the multiple nature of lines belonging to those bands classified as "triplets", until R. S. Mulliken and G. S. Monk published a paper⁽¹⁾ dealing with this problem, and found, for the first time, on photographs taken in high orders of a large concave grating spectrograph, a beginning resolution in lines of various bands having the $1s\sigma^2\ 2p\sigma\ 2p\pi\ {}^3\Pi$ state either as the upper or the lower electronic level. They also found, in agreement with theoretical expectations, that no other level than the above $2p\pi\ {}^3\Pi$ (notations for the inner three electrons will be omitted hereafter) had a fine-structure of measurable magnitude.

At the suggestion of G. H. Dieke, now of Johns Hopkins University, the writer had, independently of Mulliken and Monk, examined the expected fine-structures in the band λ 6400 Å, $3s\sigma\ {}^3\Sigma \rightarrow 2p\pi\ {}^3\Pi$, $0 \rightarrow 0$, with a 40 plate glass échelon. At λ 6400 Å the échelon had a range $\Delta\lambda_{\max}$ of about 0.64 Å and a resolving power $\Delta\lambda/\lambda$ of about 3×10^5. The experimental arrangement for this work is roughly shown in Fig. 1.

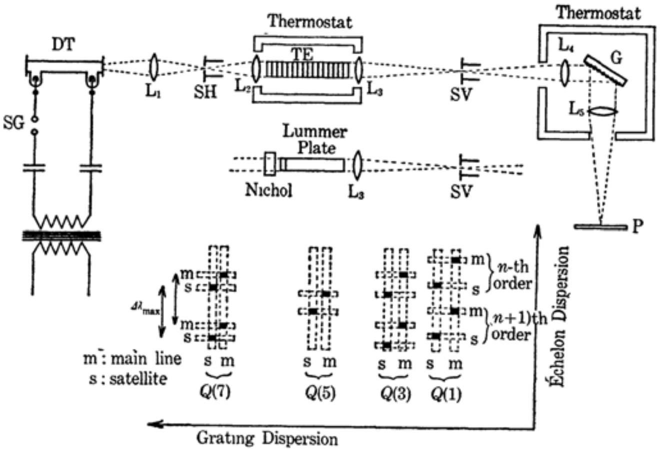

Fig. 1.

The source DT of helium bands is an end-on, sealed pyrex discharge tube of 1 m. length and 2 cm. internal bore, containing pure helium gas at about 4 cm. Hg pressure. A heavy condensed discharge is maintained through the discharge tube and a zinc or aluminium spark gap SG in series. The light from the source is condensed by a lens L_1 on the horizontal échelon slit SH, made parallel by a collimator lens L_2 and passes the échelon TE. The diffracted rays are projected by an achromatic lens L_2 of 1 m. focal length on to the second vertical slit SV of a coarse-analysing spectrograph L_4GL_5 and form here horizontal interference fringes.

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(1) *Phys. Rev.*, **34** (1929), 1530.

The latter spectrograph contains a plane grating having 55,100 lines in its 9.3 × 7.6 cm.^{2} ruled area, and a camera lens of 3 m. focal length, giving a dispersion in the first order of about 3.2 Å per mm. on a photographic plate P. Thanks to the stigmatic nature of a plane grating spectrograph the directions of the two dispersions could be made perpendicular to each other as mentioned in the introduction, and the patterns produced on the plate are shown diagrammatically in the same figure, which may be compared with the final photograph obtained for the λ 6400 Å band reproduced in Fig. 3. The band happens to have a P-, a Q- and an R-branch and, fortunately, the λ 6402.246 Å line of neon, which was present in helium as an impurity, appears among the Q-lines nearly in a "double order" pattern, supplying a good standard for the determination of $\Delta\lambda_{\max}$.

The photograph shows a clear resolution of the one component of the triple structure in several rotational lines at the beginnings of the Q- and the P-branch as a weak satellite under each thick main line. R-lines are too weak at the beginning of the branch to give measurable patterns; each one of them, however, should have the same structure as the corresponding P-line labelled with the same rotational quantum number. The main lines themselves are still unresolved doublets, and on the original plate they do show obvious sign of resolution, as their dots are all rhomb-shaped, whereas if they were single the dots would be rectangular, defined by the parpendicular jaws of the two slits, just as the dots for the neon line are. But, as the source was not specially cooled with liquid air to suppress the Doppler effect, which may be quite appreciable with the light helium molecule, no quantitative measurement could be made of the separations in main lines. Result of measurements⁽²⁾ for the resolved components is tabulated below in Table 1. According to H. A. Kramers the upper $3s\sigma\,{}^3\Sigma$ state should also have a triple structure, but its spacings are far too smaller than those in the lower $2p\pi\,{}^3\Pi$ state, as confirmed by Mulliken and Monk. Therefore the value given in the table under each line-notation can be taken as one of the two spacings in the respective rotational level in the lower $2p\pi\,{}^3\Pi$ state. It decreases gradually as the rotational quantum number increases, exactly in accordance with theoretical calculations of the spin fine-structure for the rotating helium molecule. It may here be remarked that owing to special circumstances prevailing in the helium molecule, every other rotational level is lacking in each electronic state. Besides, lower levels for Q-lines and those for P- or R-lines are of different description or symmetry (c and d respectively). Hence, for this particular band, there is an odd sequence only of

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(2) *Nature*, **125** (1930), 529; *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **14** (1930), 105.

the rotational quantum number for the *Q*-branch, and an even sequence only for the *P*- or the *R*-branch.

Table 1. Band λ 6400 Å

Line	$Q(1)$	$Q(3)$	$Q(5)$	$Q(7)$	$Q(9)$	$Q(11)$	$Q(13)$	$Q(15)$
$\Delta\nu_c$ (cm.$^{-1}$)	0.354	0.281	0.290	0.278	0.266	0.271	0.24	0.21
Line	$P(2)$							
$\Delta\nu_d$ (cm.$^{-1}$)	0.268							

Isotopic Constitution of Gold from Gold Hydride Bands. Early in 1935 gold remained one of a very few elements the isotopic constitution of which had not been determined quantitatively by the mass-spectrograph, owing to the difficulty of producing a suitable positive ion source. Its accepted chemical atomic weight is 197.21, and in analogy to the closely similar elements silver and copper, it seemed highly probable that it would be a mixture of practically only the two isotopes of odd mass-numbers 197 and 199, with an abundance ratio $Au^{199}:Au^{197}$ of 1 to 8.3, or even 1 to 7.0, according as we take for the atomic mass unit $(1/16)O$ or $(1/16)O^{16}$ respectively.

On the other hand, Aston's famous "packing fraction" curve crosses the zero axis near at the mass number 197, and $+11 \times 10^{-4}$ seemed to be too large for the packing effect per proton for the gold atom,(3) a figure which we must assume if we consider this element to be constituted entirely of Au^{197}.

Now, in the domain of diatomic band spectra, we know of the gold hydride, AuH, spectrum, extensively investigated in emission as well as in absorption. It has a system extending from the near ultra-violet down into the visible region, with individual bands of the simplest structure having purely single and comparatively wide-spaced rotational lines. A preliminary calculation, based on the conventional and approximate theory of rotational and vibrational isotope shifts in diatomic bands, showed that if Au^{199} existed in the ratio of about 1 in 7 to Au^{197}, every rotational line near at λ 4000 Å should be accompanied by a satellite at a separation $\Delta\nu$ of about 0.14 cm.$^{-1}$, or $\Delta\lambda$ of about 0.024 Å, on its shorter wave-length side, standing in an intensity relation comparable with that of abundance.

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(3) The packing fraction of gold is now obtained by Dempster (a short abstract of a report presented to the Chicago Meeting of the American Physical Society, November, 1937) as $+2.0\pm0.4$ $(\times10^{-4})$, by step-wise comparisons of gold with oxygen via copper[65]. From this the mass-spectrographic atomic weight of Au^{197} appears to be 197.039 ± 0.008.

This appeared a suitable problem for a reflecting échelon spectrograph the writer had for some time assembled out of parts, and an experiment was carried out in the following scheme (Fig. 2).

The light source S is a D.C. arc between gold poles burning in a hydrogen atmosphere of about 20 cm. Hg pressure, contained in a water-cooled metallic chamber. After passing a horizontal slit SH, and deflected by a small 45° prism RP, light enters a Littrow-mounted air-tight reflecting échelon chamber through a lens L_2 of 1.5 m. focus, projected back again by L_2, passes underneath RP, and fringes are formed on a vertical slit of a coarse-analysing prism spectrograph L_3PPL_4, which gives a linear dispersion of about 4 Å per mm. for λ 4000 Å. The reflecting échelon here used is made of 25 plane-parallel plates of fused silica, equal in thickness to about one-eighth of a wave-length, in optical contact, and platinized on its step surfaces. It has the range of about 0.1 Å and a theoretical resolving power of about 10^6 for the region aforementioned.

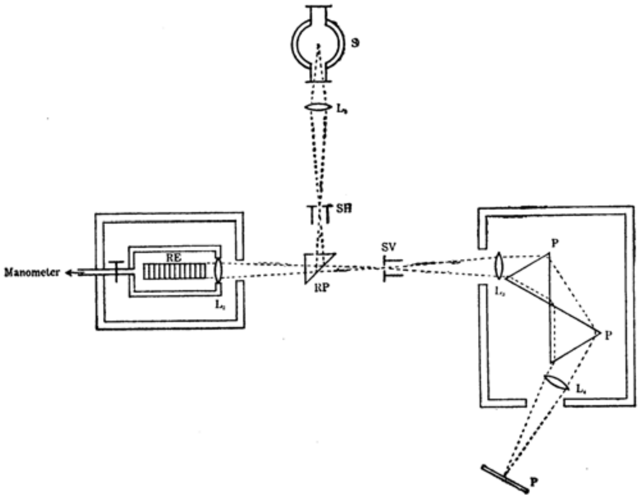

Fig. 2.

A reflecting échelon, first conceived also by Michelson, and constructed with a great precision of modern technique, is in principle no other than a kind of transmission échelon made of air, the steps of which are bounded by very rigid reflecting surfaces; and in passing twice through it, light suffers diffraction to give the enormous resolving power, which nearly matches that of a glass échelon of four times the plate number, with an added advantage of being perfectly free from weakening by absorption. Therefore it is essential to use it in a temperature-controlled air-tight box to keep the refractive index of the surrounding air constant during an exposure. By a slight change of air pressure diffraction angles change, and we can have the same effect of changing over from the "single order" position into the "double order" one for a particular wave-length, just as by tilting an ordinary glass transmission échelon against the direction of incidence to alter path differences.

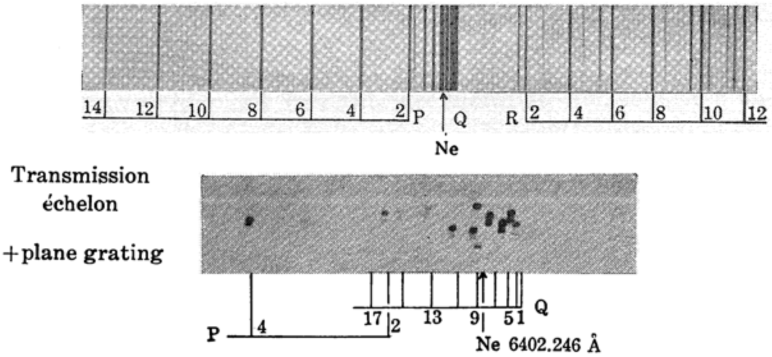

Fig. 3. He$_2$ band λ 6400 Å, $3s\sigma\,^3\Sigma \rightarrow 2p\pi\,^3\Pi$, 0 → 0. Plane grating.

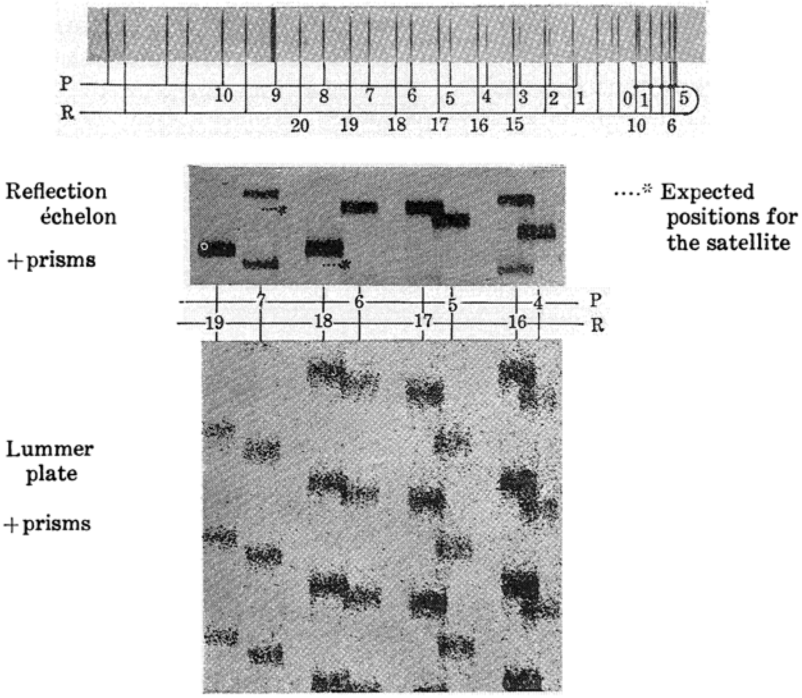

Fig. 4. AuH band λ 3973 Å, $^1\Sigma^* \rightarrow {}^1\Sigma$, 0 → 1. 15-Foot concave grating, 2nd order.

The final photograph obtained with this arrangement for the 0→1 vibrational band of the AuH $^1\Sigma^* \rightarrow {}^1\Sigma$ system at λ 3973 Å is shown in Fig. 4. Notwithstanding the circumstance that the source used was an ordinary arc only inefficiently cooled by running water, the main line in each pattern for every rotational member is sufficiently sharp to be regarded as purely single, and accompanied by no trace at all of a satellite, which should show up at a separation of about one-fifth of the range or the distance between the fringes of the main line in two consecutive orders, if it had an intensity about one-seventh of that of the latter.

This negative result⁽⁴⁾ is quite against the expectation stated at the beginning of this section, but was confirmed by experiments using two alternative arrangements, in which the reflecting échelon was replaced by the 40-plate glass échelon described in the previous section, or a high-resolving quartz Lummer-Gehrcke plate; the patterns by the latter are shown also in the same reproduction (cf. Fig. 1 for the arrangement).

Meanwhile during this work, A. J. Dempster of Chicago University had elaborated a spark source of gold ions for his mass-spectrograph and communicated the same negative result to Nature,⁽⁵⁾ stating in a more quantitative way that the ratio of $Au^{199}:Au^{197}$ is much smaller than 1 in 500. Thus the complete agreement of the results obtained by the two quite independent methods, although the band-spectroscopic one is less direct than, and therefore of a supplementary nature to, the mass-spectrographic, confirmed the non-existence of a natural isotope of gold with mass number 199, and the hitherto accepted chemical atomic weight of this element seems, by the reason stated earlier, to need a revision.⁽³⁾

In conclusion, the writer wishes to express his most sincere thanks to Prof. M. Katayama of Faculty of Science, Tokyo Imperial University, for unchanging encouragements the writer received throughout his spectroscopic researches after graduation from the Department of Chemistry.

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(4) *Nature*, **136** (1935), 476; *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **28** (1935), 129.

(5) *Nature*, **135** (1935), 993; also L. Sibaiya, working with hyper-fine structures of atomic gold lines using a Lummer-Gehrcke plate, arrived at the same conclusion, *Proc. Indian Acad. Sci.*, A, **2** (1935), 313.