second gives the h.f.s. In this case, the width of the h.f.s. is given by

$$\Delta\sigma = (\Delta E)_{M_I=+I} - (\Delta E)_{M_I=-I}. \tag{8}$$

Hence in a Zeeman pattern, the sharpest lines should be found near the center of the p and of each s branch, for which cases $|M|$ is a minimum. An example of this is to be seen in Fig. 2, which shows the no-field line 4368.327A and its Zeeman pattern. A diagram of the h.f.s. for the lower parent level of this line, $a^5I^\circ_4$ without and with a magnetic field, according to Eqs. (1) and (7), is given in Fig. 3, where the h.f.s. spacing has been exaggerated in comparison with the separations of the Zeeman components.

CALCULATION OF g SUMS

In Table VII are given the g sums for Pr II levels arising from the configuration $f^3(^4I^\circ)\cdot s$. It will be noted that the agreement between the measured and theoretical sums is usually within a few tenths of a percent, though perturbations much greater than this cause deviations of the individual terms. In Table VIII, which gives the g sums for even levels, the agreement is not quite so satisfactory.

We desire to acknowledge the able assistance of workers on the M.I.T.-W.P.A. Wavelength Project, and of Mr. W. J. Hitchcock. A grant from the Rumford Committee of the American Academy of Arts and Sciences in support of the work is gratefully acknowledged.

NOVEMBER 15, 1941 PHYSICAL REVIEW VOLUME 60

On the $^2\Pi_u \rightarrow {}^2\Pi_g$ Bands of CO_2^+. Part I

S. MROZOWSKI
Ryerson Physical Laboratory, University of Chicago, Chicago, Illinois

(Received September 18, 1941)

The band spectrum appearing in emission in the region λ2900–4300 and believed to belong to the CO_2^+ or possibly CO_2 molecule has been studied and the excitation conditions found to be in substantial agreement with the former results of Duffendack and collaborators and of Smyth. The bands have been obtained with great intensity and photographs of most of them have been made in the second order of the 30-foot grating (actually obtained resolving power of 350,000). The rotational structure and the excitation conditions show that most of the bands belong to an extensive $^2\Pi \rightarrow {}^2\Pi$ system of bands of the molecule CO_2^+. The molecule is linear in both states; the lower $^2\Pi$ appears to be the ground state $^2\Pi_g$ and the upper $^2\Pi$ is the first excited state $^2\Pi_u$ of this molecule predicted by Mulliken. The complete rotational and vibrational analysis of this band system is still in progress; in this paper the analysis of 5 double bands of the $v''_1 = v''_2 = v''_3 = 0$ progression of the symmetrical vibration (v'_1 varying, $v'_2 = v'_3 = 0$) is presented. The results of the analysis are: $\nu_0^{(0,0)} = 28{,}532.60(^2\Pi_{3/2} \rightarrow {}^2\Pi_{3/2})$ and $\nu_0^{(0,0)} = 28{,}468.48(^2\Pi_{\frac{1}{2}} \rightarrow {}^2\Pi_{\frac{1}{2}})$. The vibrational intervals (i.e., the distances between the origins of successive bands in the progression) are: $\Delta G'_1 = 1126.71$; $\Delta G'_2 = 1122.66$; $\Delta G'_3 = 1120.22$; $\Delta G'_4 = 1120.04$ (all $^2\Pi_{3/2u}$) and $\Delta G'_1 = 1125.97$; $\Delta G'_2 = 1120.79$; $\Delta G'_3 = 1116.09$; $\Delta G'_4 = 1111.76$ (all $^2\Pi_{\frac{1}{2}u}$). Further for $^2\Pi_{3/2g} B''_0 = 0.3796$; for $^2\Pi_{\frac{1}{2}g} B''_0 = 0.3812$; for $^2\Pi_{3/2u} B'_0 = 0.3485$; $B'_1 = 0.3475$; $B'_2 = 0.3465$; $B'_3 = 0.3457$; $B'_4 = 0.3453$; for $^2\Pi_{\frac{1}{2}u} B'_0 = 0.3501$; $B'_1 = 0.3492$; $B'_2 = 0.3483$; $B'_3 = 0.3475$; $B'_4 = 0.3466$. The Λ-doubling is observable only in the $^2\Pi_{\frac{1}{2}} \rightarrow {}^2\Pi_{\frac{1}{2}}$ sub-bands in this progression; in $^2\Pi_u$ it is bigger than in $^2\Pi_g$ ($p''_0 = 0.004$ for $v''_1 = 0$) and increases fast with the vibrational energy.

INTRODUCTION

WHEN a gas through which a discharge is passing contains carbon dioxide (or CO), in addition to the bands belonging to CO and CO^+ a great number of bands appear in the spectrum in the region λ2800–4500: the most prominent of these is the double band at λ2883–2896, which appears whenever the smallest traces of CO_2 (or CO) are present. All these bands have been observed by many investigators (some of them as far back as 1802), but there was considerable uncertainty about their emitter, until Duffendack and collaborators[1–3] and later Smyth[4] showed rather definitely that they do belong to a triatomic molecule CO_2^+ or possibly CO_2. Their experiments were carried out with spectrographs of low dispersion; they tried to arrange the bands in progressions, and as we shall see from the results reported in this and in the following parts of this work, in several cases with considerable success. But several members of different progressions and consequently the level scheme suggested by Smyth[4] have not been confirmed.

The first photographs with high dispersion were made of the double band λ2883–2896 by Duncan,[5] but the resolution was insufficient to permit any conclusions concerning the type of the transition involved. A more extensive study of the spectrum with high dispersion was undertaken in this laboratory by Schmid. In the first part of his work Schmid[6] photographed the bands in the region λ3200–3900 in the third order of a 21-foot grating and showed that the stronger bands all possess two branches only, and fall into two classes: "non-staggering" and "staggering" bands. He measured the lines in 5 non-staggering (λ3247, 3370, 3503, 3545, 3674) and 5 staggering bands (λ3254, 3377, 3511, 3534, 3839) and determined that none of them shows an observable Zeeman effect (presumably in fields as high as 28,000 gauss). For the first three bands in each class, forming successive members of the two progressions *a* and *c* of Smyth, Schmid was able to find common combination differences. But a change of numbering by a half or one unit gave nearly as satisfactory combination differences so that it could not be decided which combination differences and which numbering (whole or half integral) is correct. Besides this, it was not certain whether the common combination differences belong to the upper or to the lower electronic state, and so the final numbering adopted by Schmid, and his B values, were to some extent arbitrary. But the simple structure of the bands showed conclusively that their triatomic emitter is linear in both upper and lower states. Schmid explained the staggering by a doubling of levels similar to Λ-doubling together with an absence of alternate levels due to the symmetry of the molecule. Mulliken[7] discussed the results of Schmid and pointed out various possible interpretations.

In the second part of his work Schmid[8] investigated the double band λ2883–2896, showed the presence of a Zeeman effect and suggested an interpretation as a $^2\Pi(a) \rightarrow {}^2\Pi(b)$ transition. But the resolution was unsatisfactory and the interpretation therefore doubtful. A little later Schmid[9] reported observations of the Zeeman effect in a group of bands near λ3600 which he believed to consist of four heads in two pairs forming a double band; the structure and the Zeeman effect of this band seemed to suggest a $^2\Sigma - {}^2\Pi$ transition. And finally Schmid[10] investigated a few bands using still higher resolving power (fourth and fifth orders of the 21-foot grating) and found a very slight staggering in the non-staggering bands λ3674 and λ3503. On the same pictures he found that the lines in the band λ3674 are very close doublets, and he discovered a similar doubling in high members of the non-staggering band λ3503 and of the staggering band λ3839. His conclusion was that probably all the bands show staggering and doublet structure of the lines if photographed with sufficiently great resolution.

In the same year 1933 Roy and Duffendack[11] studied the excitation potentials of the bands in question in a low voltage arc and showed that the double band λ2883–2896 has an excitation potential of 18.7 volts, slightly higher than that of all other bands (16.5 volt). Since the ionization potential of CO_2 was known to be ~14.2 volts, these experiments gave evidence that the molecule of CO_2^+ is the emitter of the double band λ2883–2896 and possibly also of the other bands.

In one of a series of papers on the electronic structure of molecules Mulliken[12] discussed the

---

[1] G. W. Fox, O. S. Duffendack and E. F. Baker, Proc. Nat. Acad. **13**, 320 (1927).

[2] O. S. Duffendack and G. W. Fox, Astrophys. J. **65**, 234 (1927).

[3] O. S. Duffendack and H. L. Smith, Phys. Rev. **34**, 68 (1929).

[4] H. D. Smyth, Phys. Rev. **38**, 2000 (1931) and **39**, 380 (1932).

[5] J. F. Duncan, Phys. Rev. **34**, 1148 (1929).

[6] R. F. Schmid, Phys. Rev. **41**, 732 (1932).

[7] R. S. Mulliken, Phys. Rev. **42**, 364 (1932).

[8] R. Schmid, Zeits. f. Physik **83**, 711 (1933).

[9] R. Schmid, Zeits. f. Physik **84**, 732 (1933).

[10] R. Schmid, Zeits. f. Physik **85**, 384 (1933).

[11] A. S. Roy and O. S. Duffendack, Proc. Nat. Acad. **19**, 497 (1933).

[12] R. S. Mulliken, J. Chem. Phys. **3**, 720 (1935).

electronic configuration of the normal state of the molecule of CO_2 and the lowest states of CO_2^+ derived from it by removal of one electron from different outer shells. He showed that above the normal state ${}^2\Pi_g$ of CO_2^+ there has to be a ${}^2\Pi_u$ state and, probably a little higher, a ${}^2\Sigma^+{}_u$ state. On the basis of the excitation potential and the structure of the double band λ2883–2896 he identified the ${}^2\Sigma^+{}_u$ state with the upper state of this band, and the continuous absorption appearing in the spectrum of CO_2 above 18 volts as the absorption leading to the excitation of this level. This interpretation found a very good confirmation in the recent work of Price and Simpson[13] on the absorption spectrum of CO_2, and so this point seemed to be fairly well established. But there was no continuous absorption observed in CO_2, which could be correlated with the photoelectric excitation of the ${}^2\Pi_u$, and therefore Mulliken[12] could only suggest a tentative correlation: the double band λ3660 as a $(0,0){}^2\Pi_u \to {}^2\Pi_g$ transition, and the remaining bands as transitions from still higher excited states to ${}^2\Sigma^+{}_u$ and possibly also to ${}^2\Pi_u$. But Mulliken was never satisfied with this correlation, the reasons being the following: (1) no other expected ${}^2\Pi_u \to {}^2\Pi_g$ bands besides the double band λ3600 were observed; (2) the excitation potential found by Roy and Duffendack[11] seems not to favor an interpretation involving higher levels than ${}^2\Sigma^+{}_u$; (3) the doublet structure of all lines in the staggering and non-staggering bands found by Schmid[10] cannot be reconciled with any attempted interpretation of the bands in question.

Since Dr. F. Bueso-Sanllehí already started a work on the ${}^2\Sigma^+{}_u \to {}^2\Pi_g$ double band, Professor Mulliken suggested to the author a year ago that he investigate the rest of the spectrum with the purpose of clearing up the mentioned difficulties. Some of the preliminary stages of this experimental work have been carried out in collaboration with Dr. F. Bueso-Sanllehí, who successfully concluded the analysis of the ${}^2\Sigma^+{}_u \to {}^2\Pi_g$ double band and reported it recently in this journal.[14] Subsequently the whole spectrum described by Duffendack and collaborators[1–3] and Smyth[4] has been obtained with very high intensity and all the stronger and many of the weaker bands have been photographed in the second order of the new 30-foot grating. The pictures showed that a great number of the bands belong to an extensive ${}^2\Pi \to {}^2\Pi$ system of bands; most of these correspond to transitions involving changes in the quantum number v_1 of the symmetrical vibration of the molecule CO_2^+, the quantum numbers of the antisymmetrical v_3 and bending vibrations v_2 remaining zero. The rotational analysis of this part of the system was first undertaken, and the results for the progression $v''_1=0$ are reported in this paper (the progression $v''_1=0$, $v'_1=0$, 1, 2, 3 and 4 is identical with progressions a_2-a_6 and c_3-c_7 of Smyth). The agreement of the combination differences with those from the rotational analysis of the ${}^2\Sigma^+{}_u \to {}^2\Pi_g$ double band,[14] and the direction of the staggering in the ${}^2\Pi_{\frac{1}{2}u} \to {}^2\Pi_{\frac{1}{2}g}$ sub-bands, give evidence that the lower ${}^2\Pi$ is the ground state ${}^2\Pi_g$ of the molecule CO_2^+ and the upper ${}^2\Pi$ is the ${}^2\Pi_u$ predicted by Mulliken[12] and mentioned above. The half-integral numbering of rotational lines which gave the best fit for the combination differences of the bands a_2-a_4 and c_3-c_5 in Schmid's[6] work but was considered by him as less probable than an integral numbering, has been shown to be correct; no staggering could be detected in the ${}^2\Pi_{3/2u} \to {}^2\Pi_{3/2g}$ sub-bands for $v''_1=0$ (for instance λ3503[10]). Also the doublet structure of the lines reported by Schmid[10] has not been confirmed, although the resolving power obtained is very much higher than that of the grating used by Schmid.

The analysis of all other bands belonging to the array (v'_1, v''_1) covering the range v'_1 from 0 to 7 and v''_1 from 0 to 3 is still in progress and the results will be reported as soon as the analysis is completed. Anticipating the publication of these results it may be mentioned that an interesting perturbation has been found in the state ${}^2\Pi_{3/2g}v''_1=1$, consisting in a vibrational perturbation, an anomalously big B'' value, and a Λ-doubling increasing approximately proportionally to the third power of the rotational number. Professor Mulliken suggests that the perturbation may be caused by interaction with levels having two quanta of bending vibration.

---

[13] W. C. Price and (Miss) D. M. Simpson, Proc. Roy. Soc. **169**, 501 (1939).

[14] F. Bueso-Sanllehí, Phys. Rev. **60**, 556 (1941).

A vibrational perturbation has been found to occur also in $^2\Pi_{3/2u}$ between $v'_1=4$ and 5, and a similar one for $^2\Pi_{\frac{1}{2}u}$ between $v'_1=6$ and 7. The slight staggering found by Schmid[10] in the band λ3674 has been confirmed (its existence is expected, since this band has been shown to be a $^2\Pi_{\frac{1}{2}u}\rightarrow{}^2\Pi_{\frac{1}{2}g}$ sub-band $v'_1=0\rightarrow v''_1=1$), but not the doubling of the lines (see above). Until now no complete explanation of the double band λ3660 has been found, but it is certain that the real structure is quite different from what Schmid's lower resolution photographs seemed to indicate.

Besides all these $^2\Pi_u\rightarrow{}^2\Pi_g$ bands belonging to $v'_3=v''_3=0$ and $v'_2=v''_2=0$, there are weaker bands, one group of which having the same structure as the bands described above probably belongs to different $v'_1\rightarrow v''_1$ transitions with $v'_3=v''_3=1$ and $v'_2=v''_2=0$. Another group of bands, which have a much more complicated structure (headless grouping of lines, several short branches) and seems to be associated with the $^2\Pi_u\rightarrow{}^2\Pi_g$ system, possibly belong to $v'_1\rightarrow v''_1$ transitions with $v'_3=v''_3=0$ and $v'_2=v''_2=1$. A rotational analysis of all those bands is planned. If, as appears probable, not all observed bands will fit into the $^2\Pi_u\rightarrow{}^2\Pi_g$ system, the remaining bands (most of them are weak), according to their energy of excitation (smaller than 18 volts[11]), have probably as emitter the molecule CO_2, since there are no more low-lying levels in the CO_2^+ molecule.

Experimental

The excitation conditions were carefully studied in order to find a source which would give the band spectrum in question with high intensity and, in view of its complexity, as free as possible from other spectra (the bands of CO and CO^+ interfere especially in the long wave-length region). Hollow cathodes of different size and a discharge in a quartz tube with two outer ring electrodes excited by a 4-meter oscillator were tried, the spectrum being photographed on a medium size quartz spectrograph. Discharge in pure CO_2, in CO_2+O_2, in pure CO, and in $CO+O_2$ were studied and in every case all bands have been found, in the last two cases with a little lower intensity than in the first two. The CO was obtained by decomposition of $Ni(CO)_4$, O_2 by decomposition of $KClO_3$ in presence of MnO_2, and the CO_2 was twice resublimed commercial carbon dioxide. The results show that in the discharge an equilibrium between CO_2, CO and O_2 is obtained, the concentration of O_2 having no practical importance. Addition of helium, although it enhances the whole spectrum, was found not suitable because it favors the emission of the CO and CO^+ bands by slowing down the process of recombination of the CO and O into CO_2. The equilibrium is reached in the discharge in a very short time, since no observable enhancement of the spectrum in flowing gas was found. Only moderately high speed of flow has been tried; it seems therefore possible that in the case of the experiments of Schmid[6] extremely fast pumping could have a beneficial influence. It has been found that by far the most important factors are the current density and the pressure.

The bands can be divided according to their behavior into three groups, of which the two last are less clearly distinct: (1) the double band $^2\Sigma^+_u\rightarrow{}^2\Pi_g$; (2) the bands $^2\Pi_u\rightarrow{}^2\Pi_g$ in the region 2900–3300A; (3) all bands in longer wave-length region (>3300A). The intensity of all bands in pure CO_2, or with addition of helium, increases at first with current density, but after reaching a maximum drops quite fast. For the $^2\Sigma^+_u\rightarrow{}^2\Pi_g$ band the maximum lies at higher current densities than for the rest of the bands; at such high currents the lower pressures favor the emission of this double band, at higher pressures the bands of CO and CO^+ are more and more prominent. Increase of pressure in the case of low currents has an enhancing effect on the long wave-length bands (3). They seem to be emitted from molecular states which are not excited directly by electron impact but are brought down from higher states by collisions. The results show that the highest excitation potential belongs to the double band $^2\Sigma^+_u\rightarrow{}^2\Pi_g$, as was shown before by Roy and Duffendack.[11] Besides the $^2\Sigma^+_u$ state directly excited by electron impact are mostly higher vibrational levels of $^2\Pi_u$ $v'_1=2-5$ (corresponding to $^2\Pi_u\rightarrow{}^2\Pi_g$ bands in the region (2)); into the lower levels $v'_1=0,1$ (bands in the region (3)) the molecules are brought down by subsequent collisions. The relative transition probabilities for electron excitation are to some extent similar to probabilities of absorption; since the *B* constant of the state $^2\Pi_g$ is about equal to that of the ground state of the CO_2 molecule, the excitation of the $^2\Pi_u$ state from the ground state of CO_2 in view of the large change in the *B* constant has to be connected with a corresponding change in vibrational energy. The complexity of the spectrum arising from the presence of several limits is probably the reason why the continuous absorption and the Rydberg series corresponding to a photo-ionization of CO_2 into the state $^2\Pi_u$ have not yet been detected in the far ultraviolet spectrum of CO_2.

Corresponding experiments carried out with excitation by short waves with different pressures and variable power of the oscillations failed to reveal any difference in excitation potential of the two groups of bands (2) and (3). It was hoped that, similarly to what is found in atomic spectra,[15] the maximum intensity of a group of bands with lower excitation potential would appear at a correspondingly higher pressure. The experiments revealed only a higher excitation potential for the $^2\Sigma^+{}_u \rightarrow {}^2\Pi_g$ double band than for the remaining groups (2) and (3); the reason being that with increase of pressure the number of molecules dissociating into CO and O quickly increases (the effect occurs at such low pressures ($\ll 1$ mm Hg) that the excited CO_2 molecules dissociating during collisions seem to be in a metastable state). The spectrum of CO having the lowest excitation potential is so strongly excited at comparatively low pressures, that nothing definite can be said in this experiment about the difference of behavior of bands belonging to groups (2) and (3).

On the basis of the results of these preliminary experiments, a water-cooled hollow cathode with a rather large cross section was chosen (inside diameter of about 15 mm) for the final exposures on the big grating. The essential parts of the apparatus are described in the paper of Bueso-Sanllehí.[14] Most of the pictures were obtained with a current of 0.3–0.4 amp., under which conditions group (3) of bands has its maximum intensity and the spectra of CO and CO^+ do not interfere very seriously. Currents down to less than 0.1 amp. were tried, but the time of exposure increases so considerably (over 60 hours) that the relative weakening of the CO and CO^+ spectra is overbalanced by the loss in total intensity. The pressure of the flowing CO_2 gas was adjusted to give maximum intensity of the bands (3). Above a certain pressure the discharge in the cathode begins to be weaker, and since this limiting pressure is lower for lower currents, this is another reason why the bands (3) for low currents can be obtained only with relatively low intensity. The bands in the region 2950–4200A have been photographed in the second order, with a slit varying from 12 to 24 microns, on Eastman Process plates (all stronger bands) and Eastman 33 plates (the weaker bands). The exposure time varied from 6 to 48 hours. In the most favorable cases (as in the case of close doublets in the $(2,0)^2\Pi_{3/2} \rightarrow {}^2\Pi_{3/2}$ sub-band) a practical resolving power of 350,000 was obtained. As comparison spectrum the iron spectrum was used.

The wave-lengths were measured on a linear scale over a small region or regions (not exceeding 15 cm) on each plate by the automatic density comparator at M.I.T. (Cambridge, Massachusetts), through the kindness of Professor G. Harrison. Averages of mostly eight (sometimes six) M.I.T. readings from at least two different plates (backward and forward readings at two different heights, four readings for each plate) were taken. Independent measurements were made by the writer on a comparator in the case of three double bands (0,0), (1,0) and (2,0), and superior results were obtained in the case of closely spaced groups of lines (for instance doublets in (2,0)), the human eye being more sensitive for slight differences in density. But the time consumed in such measurements is considerable and therefore in the following such measurements were made only in exceptional cases of very complicated grouping of lines. Final wave-length values were obtained by addition of small corrections obtained from correction curves constructed with the help of the iron standards. Such correction curves should take care of the non-linearity of the dispersion of the grating and other possible sources of small errors. It was hoped at first that with a

---

[15] S. Mrozowski, Phys. Rev. **58**, 1086 (1940).

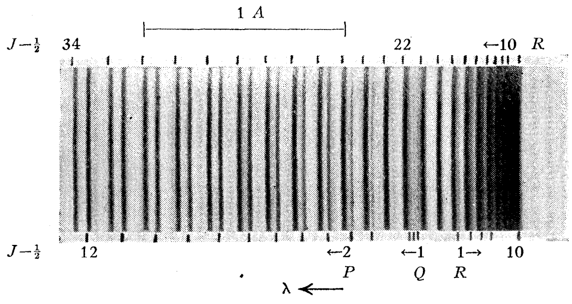

FIG. 1. (1,0) sub-band $^2\Pi_{3/2u} \rightarrow {}^2\Pi_{3/2g}$ of CO_2^+ at λ3370. Second order of the 30-foot grating. Exposure time 12 hours. Enlarged 12 times. Four lines are missing between the *R* and *P* branches; there is a very faint and diffuse line visible at $P(1\frac{1}{2})$, but probably it does not belong to the band.

dispersion of about 0.4A/mm an accuracy of about ±0.0005A could be obtained. But in the course of measurements it became clear that the experimental correction curve cannot be constructed with such a high degree of accuracy. The experimental correction curves deviate from the parabolic correction curves obtained from the grating formula so seriously (some of them differ in the maximum correction by as much as 100 percent; their shape is unsymmetrical) that no general interpolation formula can be found and the correction curves have to be obtained graphically. In view of the scarcity of iron standards such procedure involves much uncertainty. A careful study has shown that the deviations from the theoretical formula originate in the photographic plates themselves and in slight errors in the shape of the grating circle or plate-holder. The former are caused by waves on the surface of the glass and the emulsion, extending over considerable areas and detectable when three or more plates are available for comparison, and also by the distortions of the emulsion during the process of drying, which lead to smaller deviations of the readings from different plates (not exceeding ±0.001A) and varying over small areas of a few millimeters only. Although all these plate errors can be eliminated by taking averages of readings from many plates, selected as not having any waves, the irregularities in the grating circle remain uncorrected. Since these irregularities are very small and cannot be avoided (in the spectral region studied a deviation of 0.1 mm of the distance from the center of the circle in a region of 5 cm in the plate will cause a shift of the maximum of the wave-length correction curve in the maximum by about 0.04A, which corresponds to about 80 percent of the height of the maximum in the theoretical curve), the only way to increase the accuracy of the results would be to have at disposal more standard lines in the comparison spectrum. In view of the very high resolving power of the grating, greater sharpness of lines than that given by an arc in air is desirable. A hollow cathode discharge tube containing a substance rich in lines with interferometrically determined wave-lengths should be suitable for all investigations carried out with big gratings. Errors caused by the pole effect, pressure shift and so on would be not present for such a tube. It would be advisable to determine the wave-lengths of such standards with the interferometer in vacuum[16] and subsequently to drop the deeply rooted but very uncomfortable spectroscopic custom and use in the future vacuum wave-lengths only. This change would not affect in practice the low-dispersion investigations, but would be of great help in case of studies with high dispersion, since the calculation of reciprocals on calculating machines is faster and more reliable than the evaluation of wave numbers by interpolation from the tables of Kayser.

In the present work all wave-lengths were determined to four decimals, and correspondingly the wave numbers were evaluated to three decimals from the tables of Kayser, but in view of the magnitude of possible errors discussed above in all tables the last decimal has been omitted by rounding up to the nearest second decimal. The wave numbers for lines belonging to weaker bands, for instance for the bands (4,0) given below, are correspondingly less exact than for the stronger bands, since they are evaluated from more sensitive but coarser grained plates.

RESULTS

The $v''_1=0$ progression of bands

The five double bands belonging to the progression $v''_1=0$ are situated on the short

---

[16] A start in this direction has been made by W. E. Williams and A. Middleton, Proc. Roy. Soc. **172**, 159 (1939).

TABLE I. *Sub-bands* $^2\Pi_{3/2u}\rightarrow{}^2\Pi_{3/2g}$.

$J-\frac{1}{2}$	(0,0) $\nu_0=28532.60$ Unres. *Q* branch edge $\nu=28532.60$		(1,0) $\nu_0=29659.31$ Resolved *Q* branch $Q(1\frac{1}{2})=29659.28$, $Q(2\frac{1}{2})=29659.13$, $Q(3\frac{1}{2})=29658.92$		(2,0) $\nu_0=30781.97$ Unres. *Q* branch edge $\nu=30781.92$		(3,0) $\nu_0=31902.19$ *Q* branch edge overlapped by $R(20\frac{1}{2})$		(4,0) $\nu_0=33022.15$ No *Q* branch observed		$^2\Pi_{3/2g}(v_1''=0)$	
	R	*P*	*R*	*P*	*R*	*P*	*R*	*P*	*R*	*P*	Δ_2F_0'' Aver.	1st diff.
1	28534.23	missing	29661.00	missing	—Cu—	missing		missing				
2	34.76	28530.60	61.56	29657.33	30784.09*		31904.28				4.55	
3	35.27	29.68	62.06	56.46	84.56*	30779.01	04.75				6.07	1.52
4	35.68	28.73	62.46	55.50	84.97*	78.04		31898.26			7.60	1.53
5	36.06	27.67		54.43	85.31*	77.00		97.26*			9.11	1.51
6		26.59		53.32	85.57*	75.87		96.12			10.63	1.52
7		25.40		52.14	85.74*	74.69		94.88			12.15	1.52
8		24.20		50.90	h	73.43	06.05 h	93.58	33026.08 h		13.67	1.52
9	36.88 h	22.91	63.54 h	49.60	85.92 e	72.10	06.05 e	92.27	33026.08 e	33012.27	15.18	1.51
10	36.88 e	21.56	63.54 e	48.23	85.92 a	70.71	06.05 a	90.84	33026.08 a	10.88	16.70	1.52
11	36.88 a	20.16	63.54 a	46.79	d	69.26	06.05 d	89.33	d	09.35	18.22	1.52
12	d	18.67	63.43 d	45.30	85.74*	67.73		87.85		07.92	19.75	1.53
13		17.14	63.26	43.73	85.57*	66.17	05.58	86.23		06.25	21.26	1.51
14		15.54	63.02	42.11	85.31*	64.50	05.34	84.58	25.40	04.57	22.78	1.52
15	36.24	13.90	62.70	40.43	84.97*	62.78	04.97	82.86	25.00	02.87	24.31	1.53
16	35.89	12.16	62.32	38.67	84.56*	60.96	04.51	81.12	24.61	01.07	25.81	1.50
17	35.50	10.42	61.88	36.83	84.09*	59.13	04.04	79.22*	24.09	32999.18	27.33	1.52
18	35.04	08.55	61.38	34.96	—Cu—	57.21	03.48	77.20*	23.48	97.20	28.85	1.52
19	34.54	06.63	60.81	33.01	82.99	55.24	02.87	75.21*	22.86	95.22	30.37	1.52
20	33.96	04.68	60.20	31.01	82.30	53.19	02.16	73.12*	22.10	93.12	31.89	1.52
21	33.33	02.65	59.49	28.92	81.57	51.06	01.40	70.99*	21.42	90.98	33.40	1.51
22	32.61	00.58	58.75	26.79	80.76	48.89	00.58	68.80*	20.53	88.81	34.92	1.52
23	31.87	28498.41	57.93	24.59	79.90	46.63	31899.64	66.48	19.62*	86.51	36.43	1.51
24	31.04	96.18	57.05	22.32	78.99	44.34	98.71	64.19	18.71	84.11	37.94	1.51
25	30.17	93.92	56.11	20.00	77.98	41.96	97.67	61.73	17.63	81.77	38.46	1.52
26	29.22	91.60	55.11	17.59	76.95	39.52	96.59	59.27	16.50*	79.24	40.98	1.52
27	28.22	89.18	54.03	15.13	75.82	36.99	95.43	56.71	15.45	76.62	42.50	1.52
28	27.14	86.72	52.89	12.61	74.64	34.43	94.22	54.10*	14.20	74.08	44.01	1.51
29	26.02	84.20	51.70	10.03	73.37	31.79	92.93	51.44*	12.93	71.40	45.53	1.52
30	24.82	81.61	50.42	07.38	72.04	29.08	91.54	48.69*	11.48	68.69	47.04	1.51
31	23.58	78.95	49.10	04.67	70.67	26.28	90.13	45.89*	10.12	65.85	48.56	1.52
32	22.25	76.24	47.72	01.88	69.20	23.46	88.63*	43.00	08.73*	63.04	50.08	1.52
33	20.88	73.48	46.24	29599.03	67.67	20.59	87.08	40.03	07.08*	60.07	51.60	1.52
34	19.45	70.62	44.73	96.14*	66.09	17.59*	85.49	37.06	05.28	57.04	53.11	1.51
35	17.94	67.76	43.14	93.15	64.43	14.55	83.74		03.67*		54.62	1.51
36	16.37	64.82*	41.49	90.10	62.71	11.46	82.08*		02.00		56.14	1.52
37	14.75	61.79	39.77	87.00	60.92	08.28*	80.21*				57.65	1.51
38	13.05	58.70*	38.03	83.86	59.05	05.08*	78.22*				59.16	1.51
39	11.30	55.59	36.18	80.64*	57.12	01.79	76.36				60.67	1.51
40	09.51	52.42	34.32	77.40*	55.15	30698.43*					62.18	1.51
41	07.65	49.11	32.33	74.05*		94.98*					63.69	1.51
42	05.69	45.80	30.28	70.65		91.50					65.21	1.52
43	03.71	42.42	28.17	67.07		87.94					66.72	1.51
44	01.64	38.96*	26.00	63.56							68.25	1.53
45	28499.53	35.45	23.78								69.77	1.52
46	97.32	31.88	21.49								71.28	1.51
47	95.10	28.26*	19.11								72.79	1.51
48	92.81	24.54	16.65								74.30	1.51
49	90.45	20.83	14.20								75.81	1.51
50	87.96	17.02										
51	85.54											
52	82.93											

wave-length side of sequences of bands and since all bands in the spectrum are degraded toward the red, they are almost completely free from overlappings. An exception is the sub-band $^2\Pi_{3/2}\rightarrow{}^2\Pi_{3/2}(3,0)$, which is overlapped by a grouping of lines belonging probably to the bending vibration $v'_2=v''_2=1$. Since the double band (4,0) is weak, very complete data have been obtained only for three $^2\Pi_{3/2}\rightarrow{}^2\Pi_{3/2}$ and four $^2\Pi_{\frac{1}{2}}\rightarrow{}^2\Pi_{\frac{1}{2}}$ sub-bands. In the $^2\Pi_{3/2}\rightarrow{}^2\Pi_{3/2}$ sub-bands ((0,0), (1,0) and (2,0)) weak *Q* branches (in one case resolved into separate lines) were observed, and in the case of two bands it was possible to establish definitely that four lines were missing near the origin, as expected. In Fig. 1 an enlargement of a photograph of the $^2\Pi_{3/2}\rightarrow{}^2\Pi_{3/2}$ sub-band of the (1,0) band is reproduced. For the (2,0) sub-band, where the *P* and *R* branches almost coincide, the high resolving power of the grating permitted resolving the lines into very narrow doublets, one *P*, one *R*, determining their wave numbers, and checking with high accuracy the absence of staggering. The complete resolution of all these three $^2\Pi_{3/2}\rightarrow{}^2\Pi_{3/2}$ sub-bands (except for a few lines at the head) permitted settling of the numbering of the lines in the *P* and *R* branches directly without use of the combination relations in each of these sub-bands independently. No *Q* branches have been observed in $^2\Pi_{\frac{1}{2}}\rightarrow{}^2\Pi_{\frac{1}{2}}$ sub-bands and therefore for all remaining sub-bands the numbering has been settled by finding

TABLE II. *Sub-bands* $^2\Pi_{\frac{1}{2}u} \rightarrow {}^2\Pi_{\frac{1}{2}g}$.

	(0,0) $\nu_0=28468.48$		(1,0) $\nu_0=29594.41$		(2,0) $\nu_0=30715.20$		(3,0) $\nu_0=31831.29$		(4,0) $\nu_0=32943.05$		$^2\Pi_{1/2g}(v_1''=0)$	
$J-\frac{1}{2}$	*R*	*P*	*R*	*P*	*R*	*P*	*R*	*P*	*R*	*P*	Δ_2F_0'' Aver.	1st diff.
0		missing	29595.56*	missing	30716.19	missing		missing		missing		
1			96.19*		16.86*	30714.05		31830.10			3.05	
2		28466.47	96.66*	29592.40	17.37	13.18		29.21			4.60	1.55
3		65.56	97.20*	91.48	17.91*	12.26		28.33			6.13	1.53
4	28471.63	64.60	97.52*	90.49	18.25	11.26		27.30			7.67	1.54
5		63.55	97.92*	89.43	18.61*	10.24		26.30			9.17	1.50
6		62.43	98.12*	88.34		09.09	31834.92*	25.14			10.70	1.53
7		61.29	98.47*	87.13	19.06*	07.92	31834.92*	23.96	32946.90		12.20	1.50
8	72.78* h	60.03	98.47* h	85.94	19.06* h	06.64	35.20 h	22.62	32946.90 h	32934.30*	13.73	1.53
9	72.88 e	58.78*	98.60 e	84.66	19.30 e	05.35	35.20 e	21.35	32946.90 e	33.13*	15.25	1.52
10	72.88 a	57.43	98.60 a	83.27	19.30 a	03.93	35.20 a	19.90	32946.90 a	31.56*	16.78	1.53
11	72.88 d	56.06	98.60 d	81.87	19.30 d	02.52	35.20 d	18.49	32946.90 d	30.22*	18.29	1.51
12	72.78*	54.56	98.47*	80.36	19.06*	00.98	34.92*	16.91		28.52*	19.82	1.53
13	72.78*	53.09	98.47*	78.84	19.06*	30699.44	34.92*	15.34	46.46	27.05*	21.34	1.52
14	72.55	51.43	98.12*	77.22	18.61*	97.74	34.45	13.60	46.03	25.16	22.87	1.53
15	72.35	49.86	97.92*	75.56	18.40	96.10	34.22	11.95	45.77	23.58	24.39	1.52
16	72.02	48.12	97.52*	73.78	17.91*	94.26	33.68	10.01	45.18	21.58	25.92	1.53
17	71.69	46.42	97.20*	72.04	17.59	92.48	33.35	08.25	44.80	19.83	27.44	1.52
18	71.20	44.54	96.66*	70.11	17.00	90.51	32.63	06.21	44.04	17.68	28.98	1.54
19	70.78	42.71	96.19*	68.24	16.50	88.63	32.14	04.30	43.54	15.80	30.49	1.51
20	70.18	40.72	95.56*	66.20	15.77	86.49	31.31	02.09	42.65	13.50	32.02	1.53
21	69.67	38.78	95.00	64.22	15.17	84.50	30.71	00.06	42.01	11.51	33.54	1.52
22	68.95	36.65	94.18	62.02	14.28	82.23	29.71	31797.75	40.95	09.08	35.08	1.54
23	68.31	34.59	93.49	59.94	13.59	80.12	28.96	95.59	40.17	06.95	36.60	1.52
24	67.43	32.32	92.54	57.59	12.54	77.70	27.87	93.09	39.01	04.33	38.13	1.53
25	66.65	30.15	91.76	55.37	11.70	75.44	27.01	90.83	38.12	02.07	39.64	1.51
26	65.66	27.81	90.66	52.92	10.52	72.93	25.74	88.19	36.83	32899.36	41.17	1.53
27	64.82*	25.47	89.76	50.59	09.56	70.55	24.74	85.79	35.77	96.95	42.68	1.51
28	63.69	22.96	88.52	48.01	08.28*	67.88	23.37	83.02	34.30*	94.06	44.22	1.54
29	62.71	20.55	87.49	45.55	07.16	65.37	22.25	80.50	33.13*	91.56	45.73	1.51
30	61.44	17.94	86.14	42.82	05.73	62.55	20.66	77.59	31.56*	88.54*	47.26	1.53
31	60.34	15.40	85.00	40.26	04.54	59.94	19.41*	74.93	30.22*	85.86	48.78	1.52
32	58.96	12.64	83.51	37.40	02.94	56.99	17.74*	71.83	28.52*	82.63	50.31	1.53
33	57.77	10.02	82.24	34.70	01.62	54.24	16.37	69.11	27.05*	79.93	51.82	1.51
34	56.26	07.15	80.64*	31.71	30699.88	51.16	14.48	65.86		76.59	53.35	1.53
35	54.94	04.40	79.26	28.90	98.43*	48.31	13.03	62.99		73.69	54.87	1.52
36	53.31	01.35	77.48*	25.78	96.57	45.05*	11.07	59.60		70.08	56.40	1.53
37	51.84	28398.47	76.00	22.85	94.98	42.07	09.48	56.59		67.21	57.92	1.52
38	50.10	95.34	74.11*	19.60	92.99	38.70	07.31	53.09		63.49	59.45	1.53
39	48.52	92.37	72.47	16.54	91.35	35.62	05.58	49.97		60.43	60.96	1.51
40	46.64	89.13	70.44*	13.16	89.16	32.08	03.25	46.31		56.60	62.48	1.52
41	44.97		68.70	10.01	87.35	28.87	01.41	43.03		53.30	64.00	1.52
42	42.97		66.54	06.45	85.05	25.19	31798.95	39.20		49.36	65.52	1.52
43	41.16		64.68	03.18	83.12	21.86	97.00	35.82		46.12	67.01	1.51
44	38.96*		62.39	29499.54	80.70	18.06	94.41	31.87		41.81	68.53	1.52
45	37.10		60.40	96.18	78.67	14.62*	92.34	28.38		38.39	70.04	1.51
46	34.81		57.99	92.39	76.08	10.66	89.60	24.28		34.05	71.57	1.53
47	32.81			88.84*	73.90	07.10	87.40	20.76			73.07	1.50
48	30.41			84.90*	71.19	03.00	84.50	16.44			74.59	1.52
49	28.26*			81.28*	68.92	30599.34	82.22	12.76			76.11	1.52
50	25.77			77.27	66.03	95.10		08.29			77.65	1.54
51	23.47			73.46	63.64	91.27		04.50				
52				69.30*	60.65							
53				65.41	58.15							
54				61.10	54.96							

common combination differences $\Delta_2F''_0$. Since the wave-lengths are much more precise than in Schmid's[6] measurements, the $\Delta_2F'''_0$'s from different bands differ from the average values not more than ± 0.02 cm^{-1} and there can be found only one solution for the numbering. The wave numbers of the lines and the origins of the bands are presented in Tables I and II; the wave numbers marked by asterisks belong to lines which are blended. In the same tables are presented also $\Delta_2F''_0$ values, most of them being weighted averages of eight numbers (M.I.T. wave-length determination for five and direct measurements on measuring machine for three bands). The constants in the expression for the rotational energy terms of an inverted case **a** $^2\Pi$ state $T(J)=BJ(J+1)+DJ^2(J+1)^2\pm p(J+\frac{1}{2})+\cdots$ (p equal zero for $\Pi_{3/2}$) were obtained from the data of Table I and II by application of well-known graphical methods. For the vibrationless ground state of the molecule CO_2^+ we have:

$^2\Pi_{3/2g}$:

$$B''_0=0.3796\pm 0.0003;$$
$$D''=-(1.3\pm 0.3)10^{-7};$$

$^2\Pi_{\frac{1}{2}g}$:

$$B''_0=0.3812\pm 0.0003;$$
$$D''_0=-(1.3\pm 0.3)10^{-7};$$
$$p''_0=+0.004\pm 0.0015.$$

Since the $^2\Pi_g$ state is inverted $A=-159.5$[14] the difference of the effective B values according to a formula of Hill and Van Vleck[17] for diatomic molecules should be equal to $2B^2/A=-0.0018$,

---

[17] Cf. R. S. Mulliken, Rev. Mod. Phys. 2, 113 (1930).

which is in excellent agreement with the value -0.0016 found. In the second part of this work, where $\Delta G''$'s will be given, it will be shown that the obtained D''_0 value is exactly equal to the value expected on the basis of the elementary formula $D_e = -4B_e^3/\omega_e^2$. The decrease in the first differences of the $\Delta_2F''_0$'s for high J values caused by the term with coefficient D''_0 is easily visible in Table I. High precision in the measurements is essential for the evaluation of the constant p''_0 of the Λ-doubling, since the first differences of the $\Delta_2F''_0$'s in Table II are equal to $4B''_0 \pm 2p''_0$ and errors amounting to a few hundredths of a wave number would make the evaluation of p''_0 impossible (the second differences, which should be equal to $\pm 4p''_0$ amount to only ± 0.016 cm^{-1}!). The errors given for p''_0 represent the reliability of the result in the opinion of the author including all possible systematical errors. The results of Bueso-Sanllehí[14] show, however, that my $\Delta_2F''_0$ values are in excellent agreement with his analysis of the $^2\Sigma^+{}_u \rightarrow {}^2\Pi_g$ double band as regards the reported p''_0 value; since his analysis is quite sensitive to a small change in p''_0, probably the value 0.004 is very close to the true value of p''_0. According to a formula of Van Vleck[18] the value $p''_0 = 0.004$ could be explained by the presence of a $^2\Sigma^+{}_g$ state at about 60,000 cm^{-1} above the $^2\Pi_g$ state (we assume a relation of "pure precession" between the two states, with $l = 1$ for $^2\Pi_g$). The exact value of p''_0 is important for all data concerning the Λ-doubling, since the p's for all other vibrational states of $^2\Pi_{\frac{1}{2}u}$ and $^2\Pi_{\frac{1}{2}g}$ can be obtained from it using the differences $p''-p'$, which in turn can be easily evaluated from the study of the first differences in the P and R branches.

No tables of combination differences for the upper levels of the reported bands are given here, since after completion of the analysis of other bands much more exact Δ_2F' values will be available (as weighted averages from several bands each). Therefore the B' and $\Delta G'$ values reported below should be considered as provisional only. The constants are:

$^2\Pi_{2/3u}$:	$B'_0 = 0.3485$		
	$B'_1 = 0.3475$		$\Delta G'_1 = 1126.71$
	$B'_2 = 0.3465$		$\Delta G'_2 = 1122.66$
	$B'_3 = 0.3457$		$\Delta G'_3 = 1120.22$
	$B'_4 = 0.3453$		$\Delta G'_4 = 1120.04$
$^2\Pi_{\frac{1}{2}u}$:	$B'_0 = 0.3501$	$p'_0 - p''_0 = \pm 0.0033$	
	$B'_1 = 0.3492$	$p'_1 - p''_0 = \pm 0.0040$	$\Delta G'_1 = 1125.97$
	$B'_2 = 0.3483$	$p'_2 - p''_0 = \pm 0.0050$	$\Delta G'_2 = 1120.79$
	$B'_3 = 0.3475$	$p'_3 - p''_0 = \pm 0.0062$	$\Delta G'_3 = 1116.09$
	$B'_4 = 0.3466$	$p'_4 - p''_0 = \pm 0.0094$	$\Delta G'_4 = 1111.76$

The errors are for B' ± 0.0004, for $p' - p''_0$ ± 0.0003, for $\Delta G'$ ± 0.08. The Λ-doubling may be attributed largely to the influence[18] of the upper state $^2\Sigma^+{}_u$ of the double band $\lambda 2883$–2896, and all p's must then be positive, like p''_0. (It is practically certain that there can be no $^2\Sigma^+{}_u$ level below the $^2\Pi_u$. Besides for $p' - p''_0 < 0$ there would be a change in sign from p'_0 to p'_2. See also below about the symmetry of the levels.) The discussion of the p' values in relation to the distance of the perturbing $^2\Sigma^+{}_u$ state will be postponed; p'_0 appears to be considerably smaller than the value $+0.023$ calculated with the formula of Van Vleck assuming a relation of pure precession between the two states with $l = 1$ for $^2\Pi_u$. The difference in B'_0 values for the two substates $^2\Pi_{3/2u}$ and $^2\Pi_{\frac{1}{2}u}(0.0016)$ is somewhat smaller than the theoretical value 0.0025.

The direction of the staggering in all $^2\Pi_{\frac{1}{2}u} \rightarrow {}^2\Pi_{\frac{1}{2}g}$ sub-bands (the smaller distances appear in $P(J+1) - P(J)$ or $R(J+1) - R(J)$ for $J - \frac{1}{2}$ even) and the assumption $p' - p''_0 > 0$ are consistent with the requirement that only $-$ levels in $^2\Pi_u$ and $+$ levels in $^2\Pi_g$ are present.[19]

In conclusion the author wishes to express his sincere thanks to Professor R. S. Mulliken for his great kindness, continued interest and many important suggestions, and to Dr. F. Bueso-Sanllehí, Dr. A. Turkevich and Miss L. H. Woods for frequent and very valuable help given in the experimental part of this work.

---

[18] Cf. R. S. Mulliken and A. Christy, Phys. Rev. 38, 87 (1931).

[19] See, for instance, Fig. 108, p. 262 in Herzberg's book on *Molecular Spectra and Molecular Structure*, Vol. I (New York, 1939).

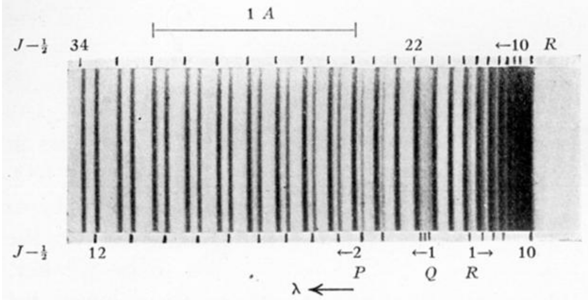

FIG. 1. (1,0) sub-band $^2\Pi_{3/2u} \rightarrow {}^2\Pi_{3/2g}$ of CO_2^+ at λ3370. Second order of the 30-foot grating. Exposure time 12 hours. Enlarged 12 times. Four lines are missing between the R and P branches; there is a very faint and diffuse line visible at $P(1\frac{1}{2})$, but probably it does not belong to the band.