

THE ISOTOPE RATIO C^{12}/C^{13} IN A COMET*

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ABSTRACT

High-resolution spectra of Comet Ikeya (1963a) show the $C^{12}C^{13}(1, 0)$ band at λ 4745 with measurable strength. Its intensity has been measured and compared with the intensity of two unresolved-triplet, rotational lines of $C^{12}C^{12}(1, 0)$. The structure of the isotope band has been computed to obtain the number of lines forming the observed head. From the theory of the excitation of comet lines by resonance fluorescence, we derive the isotope ratio C^{12}/C^{13} as 70 ± 15 . Solar-absorption features, although included, modify the excitation pattern of the C_2 lines only slightly, unlike the CN band which has strongly deficient solar radiation.

A feature at λ 4752 appears near $C^{13}C^{13}(1, 0)$. Its strength is too great to be compatible with $C^{12}/C^{13} \approx 70$, requiring an unacceptably low value. A discussion as to whether $C^{12}C^{13}$ can be de-excited by pure rotation, unlike the homonuclear C^{12} molecules, leads to no definite conclusion since the dipole moment of $C^{12}C^{13}$ is unknown. We believe that λ 4752 is largely affected by a blend with NH_2 . Another slight blend, at λ 4745, may require a slightly higher isotope ratio C^{12}/C^{13} .

The C^{12}/C^{13} ratio is near that on the earth. Some implications for the early history of the solar system are drawn. If the solar C^{12}/C^{13} ratio proves indeed to be very high the cometary C^{13} could have been produced by neutron irradiation.

I. INTRODUCTION

The recent appearance of several bright comets has permitted study of their spectra with relatively high resolution. One of us (Greenstein) observed Comet Ikeya (1963a) at Palomar, and obtained several heavily exposed spectra in the blue. Unfortunately, it was not possible to observe the comet except on two nights. Nevertheless, the spectra provide an opportunity of studying the resolution of the C_3 band (Fig. 1, *a*) of the CN (0, 0) band (Fig. 1, *b*) and especially of the Swan bands of C_2 (illustrated in Fig. 2, *a* and *b*). An attempt to photograph the Phillips bands of C_2 in the near infrared failed; they cannot be as enormously strong, compared to the solar reflection continuum, as are the Swan bands. This paper is concerned with the abundance ratio, a , of the C^{12}/C^{13} isotopes as deduced from the (1, 0) band of C^{12}/C^{13} . On the earth, with only small variations, $a \approx 90$. In meteorites the same high ratio is found, subject only to minor variability of chemical origin. In carbon-rich stars, Wyller (1960) found two values of a , either $\gtrsim 50$ or $3 > a > 10$. However, he now believes (Wyller 1964) that an entire range of a exists, down from the terrestrial value, and in some exceptional cases falling as low as 2. The smaller value of a is expected if the carbon-nitrogen cycle has processed the isotopes to their equilibrium concentration. In equilibrium $a \approx 4$, but obviously any admixture of newly synthesized C^{12} which has not suffered hydrogen burning will permit any ratio of $a > 4$. If comets are relics of the early history of the solar system, the C^{12}/C^{13} ratio is extremely important (Fowler, Greenstein, and Hoyle 1962). The solar value of $a > 40$ found by Greenstein, Richardson, and Schwarzschild (1950) was clearly a conservative lower limit which Wyller believes to be more nearly $a > 100$; Righini (1963) gives a as high as 10^4 .

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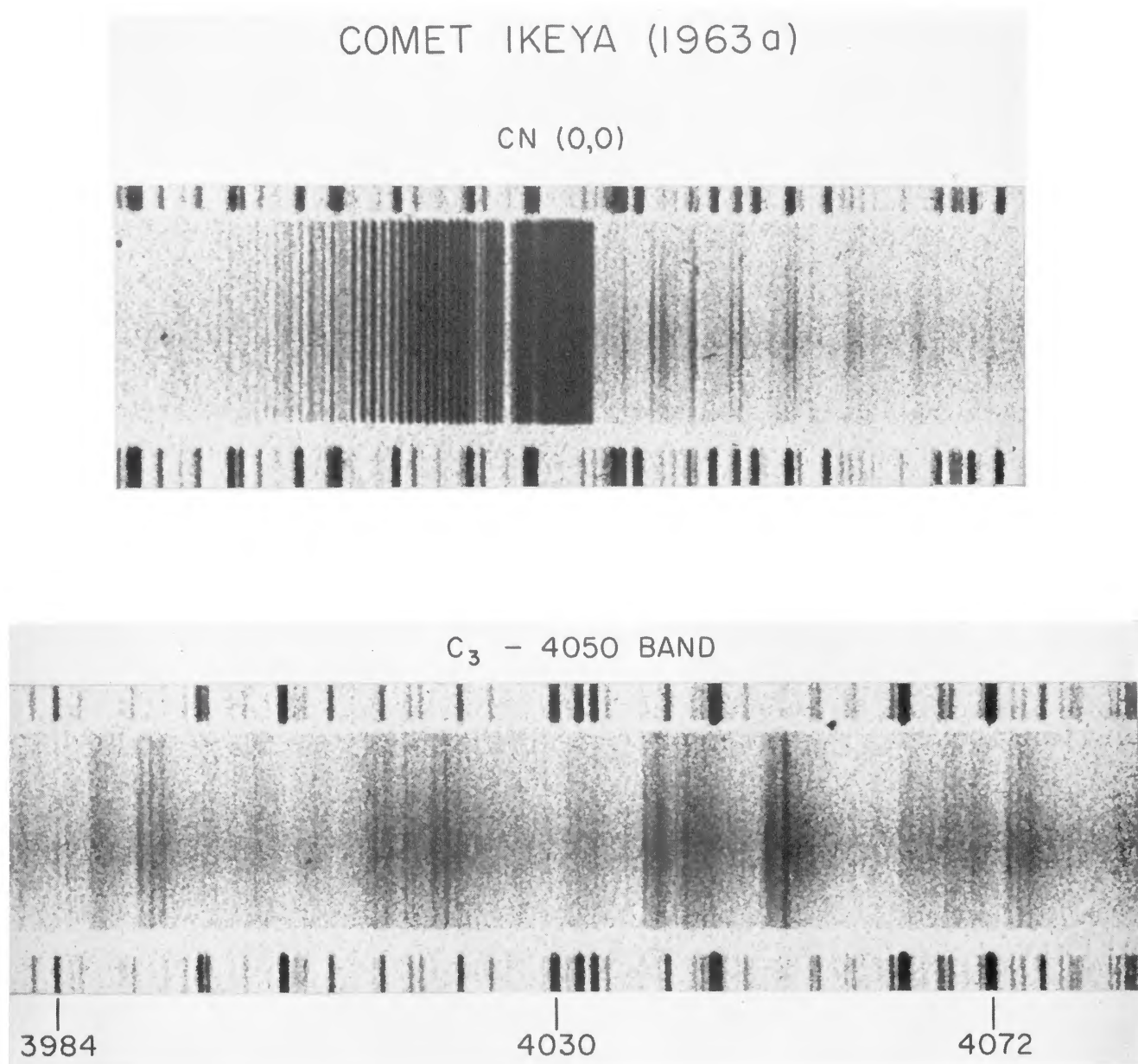


FIG. 1.—(a, bottom) The C₃ band in the region $\lambda\lambda$ 3980–4085. Comparison lines of Fe I. The shading toward longer wavelengths is partly caused by imperfect guiding on the nucleus of the comet and pre-exposure accentuating weak longward rotational features. The slit is 28" long, covering 15400 km of the head. Dispersion 18 Å/mm, original; heliocentric distance 0.72 u., before perihelion. (b, top) The CN(0, 0) band and part of the C₃ band in Comet Ikeya. Wavelengths $\lambda\lambda$ 3833–3925. Note the severe distortions of the smooth envelope of the intensity pattern of rotational lines of CN.

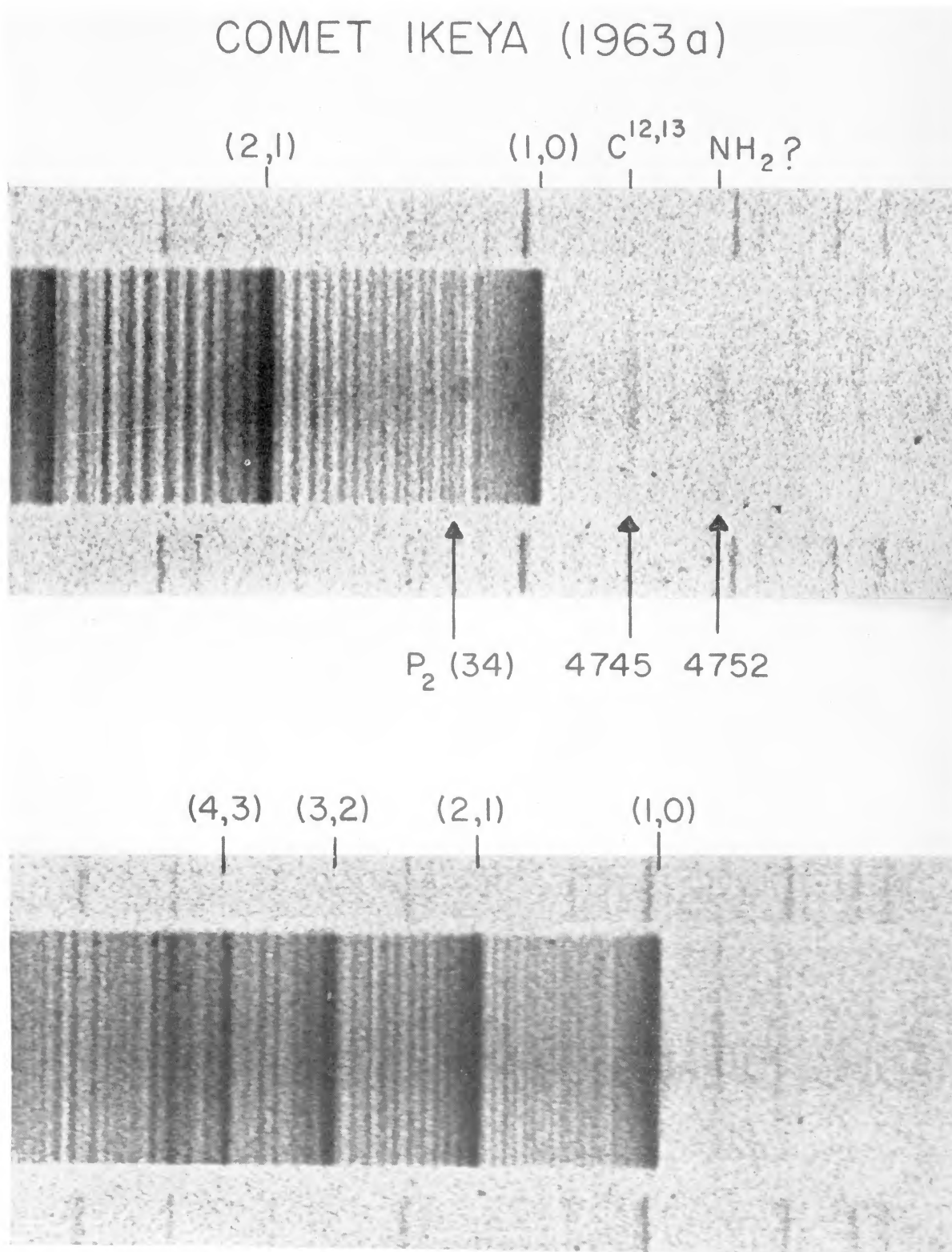


FIG. 2.—(a, bottom) Swan bands of C₂ in second order, 27 Å/mm, (focus poor). Note the weakly present λλ 4745, 4752 bands at the position of the C¹²C¹³, C¹³C¹³ (1, 0) heads. The λ 4745 band, which is somewhat more diffuse, is offset upward from the λ 4752 band, largely NH₂. (b, top) The C₂ (1, 0) bands in the third order, 18 Å/mm, with the isotope band at λ 4745 offset upward with respect to the λ 4752 band. Both features are diffuse, and λ 4745 is certainly broader than individual rotational lines of the C¹²C¹² band, i.e., λ 4745 is either a band head or multiple.

The carbon (1, 0) isotope bands, $C^{12}C^{13} \lambda 4745$ and $C^{13}C^{13} \lambda 4753$, were reported by Bobrovnikoff (1930) and Swings (1943). The low dispersion used in older investigations did not permit any abundance determination, but the conclusions derived from inspection of many old spectra were important. The C^{12}/C^{13} ratio was not as small as in some C^{13} -rich carbon stars, but was similar to the terrestrial value. Swings found that Comet 1940c, in spite of strongly exposed $C^{12}C^{12}$ bands, failed to show isotope bands. This last conclusion, if true, is very important, and requires further quantitative observations of various comets. It is now generally assumed that all comets belong to the solar family. If true variations of a are found in comets with definitely elliptical orbits, it should be possible to explore further the early history of the solar system by the methods of nuclear astrophysics.

Our spectra refer to only one comet, Ikeya. We develop the theory of the radiative fluorescence excitation of the Swan bands, taking into account the solar Fraunhofer lines.

II. OBSERVATIONS

Two plates of Comet Ikeya (1963a) before perihelion, Pd 7193, March 5, 1963, 3^h32^mU.T., and Pd 7200, March 6, 1963, 3^h48^mU.T., were taken with the Palomar coudé spectrograph at 18 Å/mm in the third order, using a baked IIa-0 emulsion. The heliocentric distance was 0.72 A.U. The projected slit width was equivalent to 0.35 Å. The guiding on the nucleus was only moderately good, as can be seen by the width of the reflection spectrum in the figures. The continuous spectrum was relatively weak in this comet. Only the inner 28" of the head is covered by the slit, because of the large scale, 1.3"/mm at the coudé focus. Pre-exposure by the reflection spectrum, in part, causes the weaker unresolved rotational structure of the C_3 bands to appear as a shading toward longer wavelengths. However, the C_3 bands may have intrinsic concentration toward the nucleus. Pre-exposure may have a slight effect on the CN(0, 0) band, which shows only small concentration toward the nucleus; high rotational lines are apparently concentrated to it in Figure 1, *b*. The Swan bands also have little intrinsic concentration toward the nucleus. The pre-exposure effect undoubtedly enhances both $\lambda\lambda 4745$ and 4753. However, on examining Figure 2, *a* (second order) and *b* (third order), we see a real difference between the distributions along the slit of $\lambda\lambda 4745$ and 4753, even though the definition in the second order (edge of plate) is not as good as in the third order. In both orders, $\lambda 4745$ lies *above* $\lambda 4753$, and is less concentrated toward the faint solar continuum. We later suggest that $\lambda 4753$ is not $C^{13}C^{13}(1, 0)$, but rather an NH_2 feature, but that $\lambda 4745$ is, in fact, $C^{12}C^{13}(1, 0)$. This vertical offset is real and suggests that $\lambda\lambda 4745$ and 4753 have different molecular sources. In Mrkos, similar vertical offsets were seen between different molecular lines, and even between different features of the same molecule. We return to this problem at the end of our discussion.

In Figure 3 we show a microphotometer tracing of the normal, third-order spectrum of the Swan band region, with various features marked. Both linear and transmission tracings were used to span the enormous intensity ratio between the normal and isotope bands.

The radial velocity of the comet with respect to the Sun was calculated from the elements of the orbits as $v_r = -17.3$ km/sec. Its radial velocity with respect to the Earth was measured by Mrs. Dorothy Locanthi as $v_\Delta = +61.8$ km/sec. She also measured wavelengths of the C^{12}/C^{13} band head and the rotational lines of $C^{12}C^{12}$. These velocities are needed for identification. A line of wavelength $\lambda(\text{lab})$ is observed at $1.0002060 \lambda(\text{lab})$ and is excited by solar radiation of wavelength $1.0000578 \lambda(\text{lab})$.

Our finite resolution is equivalent to a wavelength region containing about eight lines of each branch near the head, although it is ample to resolve lines away from the head. What we can measure dictates what we analyze. We therefore first compute the detailed structure of the bands before we describe the measures.

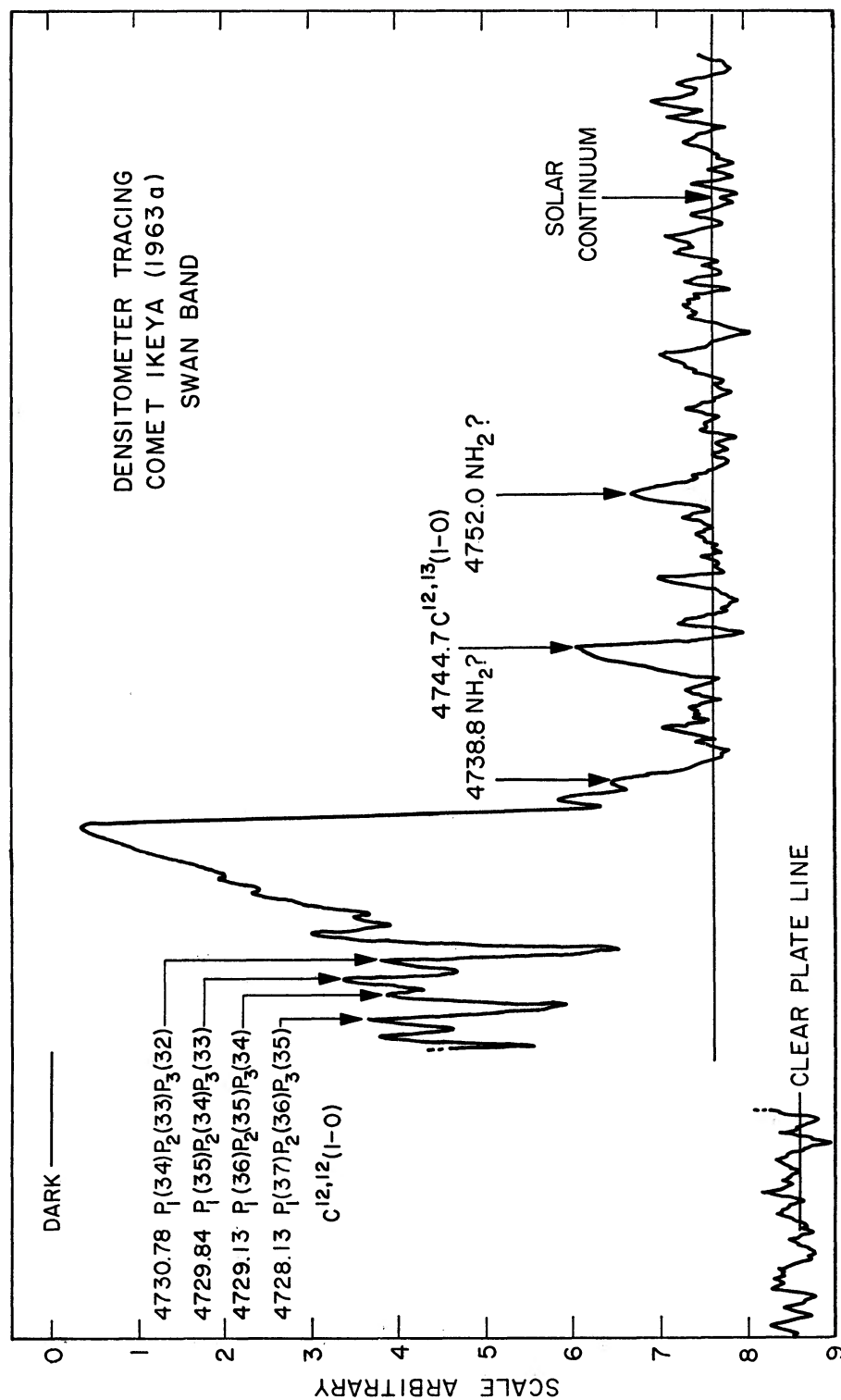


Fig. 3.—Densitometer tracing (arbitrary scale) of C₂ (1, 0) bands; rotational triplets measured are identified in the C¹²C¹³ band. The NH₃ features are marked.

III. THE STRUCTURE AND INTENSITY OF THE C_2 BANDS

To determine a we compare intensities of well-resolved emission lines of the Swan band $C^{12}C^{12}$, $A^3\Pi_u - X^3\Pi_g(1, 0)$, with the weak emission of the band head $C^{12}C^{13}(1, 0)$. The first resolved lines of $C^{12}C^{12}$ are, in fact, composed of the unresolved triplets of the P -branch. The intensity of a single P -component can be calculated using well-known formulae of the excitation mechanism of cometary emission lines. From an upper vibration-rotation level characterized by (v', J) , the intensity of emitted radiation is

$$I(v', J) \rightarrow [(v'', J+1)] = \frac{i_P}{i_P + i_R} \frac{A_{v'-v''}}{\Sigma A_{v'-v''}} h\nu c(v', J \rightarrow v'', J+1) N(v', J). \quad (1)$$

Here i_P and i_R are intensity factors related to the transition probabilities between rotational levels, $J \rightarrow J+1$ and $J \rightarrow J-1$, $A_{v'-v''}$ is the Einstein transition probability, and $N(v', J)$ is the number of molecules arriving in the upper state v', J per second. The energy is $h\nu$, where ν is in wavenumbers throughout. This upper state, J , of a given vibrational state, v' , is populated by absorption of the two lines, $P(J+1)$ and $R(J-1)$. If the populations in the lower states are given by Boltzmann's law, the number of molecules excited by solar radiation to the upper state, (v', J) , is

$$N(v', J) = c_1 N_{0,0} \sum_{x''=0}^3 \exp[-G_0''(x'')/0.7T] |R_{v'x''}|^2 \rho_\nu(x'') \quad (2)$$

$$\times \{i_P \exp[-F''(J+1)/0.7T] I_P(\odot) + i_R \exp[-F''(J-1)/0.7T] I_R(\odot)\}.$$

Here $N_{0,0}$ is the number of molecules in the lowest vibrational-rotational state; $|R_{v'x''}|^2$ the vibrational transition probability (King 1948); G_0'' , F'' , in wavenumbers are the molecular vibrational constants for the lower states; ρ_ν is the density of the solar radiation (Allen 1963), and $I(\odot)$ the percentage of solar continuous radiation remaining after depletion by Fraunhofer lines, at the wavelengths of the P - and R -transitions, after correction for the radial velocity of the comet. The contribution of the state $v'' = 3$ to the summation in equation (2) is less than 3 per cent. We use the *Utrecht Solar Atlas* to evaluate the correction for solar absorption lines. The i factors are given by Budó (1937).

We chose two independent, well-resolved triplets of rotational lines of the $(1, 0)$ $C^{12}C^{12}$ band, $\lambda 4730.78$ and $\lambda 4729.84$ from the cometary spectrum. These lines were identified with the carbon laboratory spectrum by Hunaerts (1950) as the unresolved triplets $P_1(34) P_2(33) P_3(32)$ and $P_1(35) P_2(34) P_3(33)$. We tabulate various factors for the lines used, as well as for analogous lines, $\Delta v = +1, 0, -1$, from Hunaerts (1950) and the residual intensity in the solar spectrum at the wavelengths exciting the transitions, together with the fine structure of the $C^{12}C^{12}$ lines, in Tables 1 and 2. The solar spectrum is roughly averaged over $0.4 \text{ \AA}$ centered on the excitation wavelength.

To simplify the calculations, the intensity of an unresolved triplet, $I(P_1 P_2 P_3)$, was assumed to equal $3I(P_2)$ and the average solar residual intensity, $I(\odot)$, was taken as $\frac{1}{3}[I(\odot)(\lambda_1) + I(\odot)(\lambda_2) + I(\odot)(\lambda_3)]$. The intensity factors i_{P_2} and i_{R_2} are intermediate between i_{P_1} , i_{R_1} and i_{P_3} , i_{R_3} (see Tables 1 and 2). Budó tabulated the formulae for the i factors; the molecular constants ω_0'' , B_v , and D_v permit computation of $G_0(v'')$ and $F''(J)$. As for the second term (involving A) in equation (1), we can write it in terms of $|R_{v'v''}|^2/|R_{v'x''}|^2$ multiplied by a function varying with frequency.

IV. THE STRUCTURE OF THE $C^{12}C^{13}(1, 0)$ BAND

The isotopic band $C^{12}C^{13}(1, 0)$, $\lambda 4744.7$, is composed of numerous rotational P triplets. The number of these rotational lines which form a head depends strongly on the spectral resolution. Given the structure of the $C^{12}C^{12}$ band, computation of the isotope shift gives us that of the $C^{12}C^{13}$ band. From Hunaerts' laboratory high-dispersion

spectra, the head of C¹²C¹²(1, 0) is composed of about twelve components within 0.15 Å. In the cometary spectrum at 18 Å/mm, the head is burnt out over about 1.1 Å. There are about $n^* = 42$ rotational P -components within such a region. We computed the isotope shift for the bands, $\Delta\nu = +1, 0, -1$, for this group of lines. The vibrational shift is given by $\Delta\nu$, the wavenumber difference between the normal and the isotope band,

$$\Delta\nu = \nu_v - \nu_v^i = [(1 - \rho)\omega_e'(v' + \tfrac{1}{2}) - (1 - \rho^2)\omega_e'x_e'(v' + \tfrac{1}{2})^2]$$
$$- [(1 - \rho)\omega_e''(v'' + \tfrac{1}{2}) - (1 - \rho^2)\omega_e''x_e''(v'' + \tfrac{1}{2})^2].$$

(3)

TABLE 1
TRANSITIONS POPULATING THE UNRESOLVED TRIPLET λ 4730.78
C¹²C¹²(1,0), $P_1(34)$, $P_2(33)$, $P_3(32)$

$v'-v''$	Rotational Structure	$\lambda(\text{lab})$	$\lambda(\text{exc})$	$I_{\odot}(\lambda_{\text{exc}})$	i Factors	
1-0	$P_1(34)$ $P_2(33)$	4730 78	31 05	0 80	33 95	32 94
	$P_3(32)$	30 89	31 16	0 93		31 96
	$R_1(32)$ $R_2(31)$	4684 36	84 63	0 78	32 95	31 94
	$R_3(30)$	84 55	84 82	0 94	.	30 95
1-1 ..	$P_1(34)$ $P_2(33)$	5118 06	18 35	0 97	33 95	32 94
	$P_3(32)$	18 24	18 53	1 00		31 96
	$R_1(32)$ $R_2(31)$	(5064 35)	64 64	0 35	32 95	31 94
	$R_3(30)$	(64 39)	64.68	0 35	..	30 95
1-2 .	$P_1(34)$ $P_2(33)$	5567 31	67 63	0 98	33 95	32 94
	$P_3(32)$	67 48	67 80	0 96		31 96
	$R_1(32)$ $R_2(31)$	5504 46	04 78	1 00	32 95	31 94
	$R_3(30)$	04 67	04 99	1 00		30 95

TABLE 2
TRANSITIONS POPULATING THE UNRESOLVED TRIPLET λ 4729.84
C¹²C¹²(1,0), $P_1(35)$, $P_2(34)$, $P_3(33)$

$v'-v''$	Rotational Structure	$\lambda(\text{lab})$	$\lambda(\text{exc})$	$I_{\odot}(\lambda_{\text{exc}})$	i Factors	
1-0.	$P_1(35)$ $P_2(34)$	4729 86	30 15	0 75	34 96	33 94
	$P_3(33)$	30 01	30 28	0 95		32 96
	$R_1(33)$ $R_2(32)$	4682 52	82 79	0 95	33 95	32 95
	$R_3(31)$	82 61	82 88	0 99	. . .	31 95
1-1.	$P_1(35)$ $P_2(34)$	5116 88	17.17	0 98	34 96	33 94
	$P_3(33)$	16 88	17 17	0 98		32 96
	$R_1(33)$ $R_2(32)$	(5061 59)	61 88	0 98	33 95	32 95
	$R_3(31)$	(61 62)	61 91	0 98		31 95
1-2	$P_1(35)$ $P_2(34)$	5565 37	65 69	0 50	34 96	33 94
	$P_3(33)$	65 61	65 93	0 95		32 96
	$R_1(33)$ $R_2(32)$	5500 75	01 07	1.00	33 95	32 95
	$R_3(31)$	00 97	01 29	0.98		31 95

The ratio of the reduced masses of the nuclei gives ρ

$$\mu_i \equiv \frac{m_{12}m_{13}}{m_{12} + m_{13}} = 6.242751, \quad \mu = \frac{m_{12}m_{12}}{m_{12} + m_{12}} = 6.001901,$$

$$\rho \equiv (\mu/\mu_i)^{1/2} = 0.9805199, \quad \rho^2 = 0.9614193.$$

The rotational shift is calculated from the masses and from F (see below).

$$\Delta\nu = (1 - \rho^2)(F' - F''). \quad (4)$$

The isotope molecular constants were derived from those for $C^{12}C^{13}$ by the transformations given by Herzberg (1939). The intensity rules are the same; Jenkins (1948) checked this type of computation for the (0, 0) band when he used very high spectroscopic resolution and enriched $C^{12}C^{13}$ samples to study the nuclear spin of C^{13} . Jenkins found that the line-intensity ratios agreed, within the errors of possible contamination, with his sample isotope ratio, a , i.e., that the intensities of $C^{12}C^{12}/C^{12}C^{13}/C^{13}C^{13}$ were nearly in the expected ratios, $a^2/2a/1$. The nuclear spin of C^{13} does not affect our conclusions.

The computed structure of the isotope (1, 0) band is shown in Table 3. Similar detailed tables of the (1, 1) and (1, 2) bands are required for the study of the details of the excitation of lines of the (1, 0) band. Such tables were computed but are not reproduced. All relevant lines were tabulated with the solar wavelengths for excitation of their upper level. The depletion factor, $I_\lambda(\odot)$, of the solar radiation was estimated from the *Utrecht Solar Atlas*. We list $P^i(J'')$ for the three P -components, for $J'' = 9$ to 23 and $R^i(J'')$ for $J'' = 7$ to 22, near the P -head at λ 4744 and in the R^i -branch, $\lambda\lambda$ 4730–4712. Correspondingly, in the (1, 1) and (1, 2) bands we use the P^i -heads at $\lambda\lambda$ 5130 and 5577 and the R^i -branches near $\lambda\lambda$ 5110 and 5550. In general, these regions are relatively free of strong solar absorption lines, only about ten lines having $I_\lambda(\odot)$ below 0.8. We can see in Table 3 that this is also true for the isotope (1, 0) band. In consequence the isotope band should have a smooth profile, completely unlike the highly distorted CN(0, 0) band.

The intensity factors, i , are a function only of J , the vibrational Einstein $A_{v'-v''}^i \propto |R_{v'-v''}|^2 (\nu^{i_{v'-v''}})^3$ differ, for the isotope bands, only because of the small difference of wavenumber, $\nu^i - \nu$. The electronic wave functions could differ slightly, through the difference in the mass factor ρ , which we neglect. If the isotope molecules have the same Boltzmann excitation temperature of their lower rotational states, $T = 3000^\circ \text{K}$, as the normal molecules, then the difference in strength of isotope and normal rotational lines may be interpreted as a difference in abundance, after proper correction for differences in the solar exciting radiation. We merely rewrite equation (2) with superscripts, i , for relevant quantities referring to the isotope with the molecular abundance, N_{00}^i , replacing N_{00} .

We assumed the observed intensity of the isotope band to be the sum over the intensities of the rotational components. In the wavelength range, $\Delta\lambda = 0.9 \text{ \AA}$, there are thirty-eight single P -components from λ 4744.69 to λ 4743.78, in the P -head. We calculate the intensity of the observed "head" of the $C^{12}C^{13}(1, 0)$ within $0.91 \text{ \AA}$ from the approximate expression

$$I[C^{12}C^{13}(1, 0)] = n^* I_{P_2(17)}^i, \quad (5)$$

with $n^* = 38$. We are justified in this approximation because of the smoothness of $I_\lambda(\odot)$ in this region, and because the band intensity factors, i_P and i_R , vary slowly and are nearly linear (as in Tables 2 and 3). We chose $P_2(17)$ as a typical line close to the mean of the thirty-eight lines appearing in the head, computing $I_{P_2(17)}^i$ with allowance for the average depression of the solar exciting radiation.

Since, from Table 3 and our other computations, we find that the effect of the solar-absorption lines is rather small and could have been neglected, the absence of an isotope band cannot be caused by low available solar intensity for the fluorescence process. In the CN(0, 0) band, the solar absorption produced by this same feature and by nearby, very strong, atomic lines causes the cometary band to be sensitive to wavelength shifts, and to differ from comet to comet, depending on radial velocity. This cannot occur for C₂ bands in general, since the solar C₂ bands are very weak and their region generally clear of atomic lines.

TABLE 3

THE ROTATIONAL STRUCTURE OF THE ISOTOPE BAND (1,0), C¹²C¹³, THE CORRESPONDING $R(J-2)$ TRANSITIONS, THE EXCITATION WAVELENGTHS, AND SOLAR INTENSITIES

J''	ROTATIONAL STRUCTURE			EXCITATION WAVELENGTH			SOLAR INTENSITY		
	$P_1^i(J'')$	$P_2^i(J'')$	$P_3^i(J'')$	λ_1	λ_2	λ_3	$F_{\odot}(\lambda_1)$	$F_{\odot}(\lambda_2)$	$F_{\odot}(\lambda_3)$
9			4743 79			4744 06			100
10		4743 68	44 07		4743 95	44 34		100	55
11	4743 60	43 95	44 26	4743 87	44 22	44 53	100	85	90
12	43 87	44 16	44 42	44 14	44 43	44 69	95	60	95
13	44 08	44 32	44 57	44 35	44 59	44 84	55	95	95
14	44 26	44 42	44 69	44 53	44 69	44 96	90	95	95
15	44 42	44 57	44 69	44 69	44 84	44 96	95	95	95
16	44 48	44 57	44 69	44 75	44 84	44 96	95	95	95
17	44 57	44 57	44 57	44 84	44 84	44 84	95	95	95
18	44 57	44 57	44 57	44 84	44 84	44 84	95	95	95
19	44 48	44 42	44 42	44 75	44 69	44 69	95	95	95
20	44 42	44 32	44 26	44 69	44 59	44 53	95	95	90
21	44 26	44 16	44 08	44 53	44 43	44 35	90	60	55
22	44 08	43 95	43 78	44 35	44 22	44 05	55	85	100
23	43 87	43 68		44 14	43 95		95	100	

TABLE 3—Continued

J''	ROTATIONAL STRUCTURE			EXCITATION WAVELENGTH			SOLAR INTENSITY		
	$R_2^i(J'')$	$R_2^i(J'')$	$R_3^i(J'')$	λ_1	λ_2	λ_3	$F_{\odot}(\lambda_1)$	$F_{\odot}(\lambda_2)$	$F_{\odot}(\lambda_3)$
7			4730 67			4730 94			80
8		4730 43	29 54		4730 70	29 71		60	65
9	4730 10	29 29	28 31	4730 37	29 56	28 58	90	90	50
10	29 02	28 12	27 10	29 29	28 39	27 37	85	90	40
11	27 84	26 88	25 79	28 11	27 15	26 06	90	70	90
12	26 66	25 61	24 51	26 93	25 88	24 78	100	100	100
13	25 53	24 31	23 12	25 80	24 58	23 39	100	90	95
14	24 13	22 95	21 77	24 40	22 22	22 04	75	50	50
15	22 77	21 58	20 28	23 04	21 85	20 55	90	100	100
16	21 40	20 14	18 84	21 67	20 41	19 11	100	100	100
17	20 00	18 68	17 28	20 27	19 95	17 55	100	100	85
18	18 56	17 15	15 76	18 83	17 42	16 03	100	100	100
19	17 02	15 60	14 13	17 29	15 87	14 40	100	70	30
20	15 50	13 98	12 51	15 77	14 25	12 78	55	80	90
21	13 89	12 38	.	14 16	12 65		80	90	
22	12 30		..	12 57	.		90		

We compute the strength of an individual P -line of a $C^{12}C^{12}$ band by combining equations (1) and (2) and introducing some simplifications and auxiliary functions, from

$$I[P_2(J+1)] = C_1 N_{00} h\nu c Y_{v'} \frac{i_{P_2}}{i_{P_2} + i_{R_2}} \frac{A_{v'-v''}}{\sum_0^3 A_{v'-x''}}, \quad (6a)$$

$$Y_{v'} = \sum_{x''=0}^3 \exp[-G_0(x'')/0.7T] \rho_v(x'') |R_{v'-x''}|^2 X_{x''}, \quad (6b)$$

and

$$X_{x''} = i_{P_2} \exp[-F_2''(J+1)/0.7T] I_{P_2(\odot)} + i_{R_2(\odot)} \exp[-F_2''(J-1)/0.7T] I_{R_2(\odot)}, \quad (6c)$$

with F_2 computed from molecular constants and

$$F_2(J) = B_v \left[J(J+1) + \left(\frac{4}{3}\right) \frac{Y_2 - 2J(J+1)}{Y_1 + 4J(J+1)} \right] - D_v \left(J + \frac{1}{2}\right)^4, \quad (6d)$$

with $Y = A/B_v$ giving

$$Y_1 = (Y - 4)Y + \frac{4}{3}, \quad Y_2 = (Y - 1)Y - \frac{4}{9}, \quad (6e)$$

and

$$G_0(v'') = \omega_e v'' - \omega_e x_e v''^2. \quad (6f)$$

The Einstein A 's are obtained from $|R|^2$ from $A \propto |R|^2 \nu^3$. The same formulae (6a-f) are used with proper changes of constants and with superscript i for the isotope.

If, instead, to compare with observations, we wish to compute the strength of the entire head of a band, integrating over the rotational structure, we must obtain an average of $X_{x''}$ over all J 's. The answers are the same for normal and isotope bands, except for the $I_P(\odot)$ and $I_R(\odot)$ factors; we find it convenient to take an average of the solar-radiation depletion factors. We compute, therefore, the ratio of the predicted strengths of the $C^{12}C^{13}(1, 0)$ head to the $C^{12}C^{12}(1, 0)$ and $(2, 0)$ heads, from an equation like (6a) with $X_{x''}^i/X_{x''} \approx 1$, inserting the correction for the absorption lines into $\rho_v(x'')$ in equation (6b).

V. MEASUREMENT AND RESULTS

The comet continuum, essentially that of the Sun, with an unknown (and uncorrected) effect of selective reflection or scattering, was used as the standard of our equivalent emission-line strengths in arbitrary units, w and w^i . We first measure the strength of the two, well-resolved $C^{12}C^{12}$ lines at $\lambda\lambda$ 4730.78 and 4729.84, which according to Tables 1 and 2 are $P_2(33)$ (blended with $P_1[34]$ and $P_3[32]$) and $P_2(34)$ (blended with $P_1[35]$ and $P_3[33]$). The ratio of emission line widths are

$$\frac{w_\lambda(4730.78)}{w_\lambda^i(4744.7 - 0.9\text{\AA})} = 2.3, \quad \frac{w_\lambda(4729.84)}{w_\lambda^i(4744.7 - 0.9\text{\AA})} = 2.9.$$

The computations were carried out from equation (6a) for the particular lines of $C^{12}C^{12}(1, 0)$ and for n^* lines of $C^{12}C^{13}(1, 0)$ near the head, where as we have said above

(eq. [5]) a typical isotope line in the head was taken as $P_2(17)$. If the ratio of isotope abundances is

$$\frac{C^{12}}{C^{13}} \equiv a, \quad N_{00^{12,12}}/N_{00^{12,13}}/N_{00^{13,13}} = a^2/2a/1. \quad (7)$$

From $\lambda 4730.78$ we obtain the relation

$$\frac{3}{n^*} \frac{202,424}{216,300} \frac{N_{00^{12,12}}}{N_{00^{12,13}}} = 2.3, \quad (8a)$$

or $N_{00^{12,12}}/N_{00^{12,13}} = 0.819 n^* \approx 31.1$, i.e., $a = 62$. From $\lambda 4729.84$ we obtain

$$\frac{3}{n^*} \frac{229,690}{216,300} \frac{N_{00^{12,12}}}{N_{00^{12,13}}} = 2.9, \quad (8b)$$

or $N_{00^{12,12}}/N_{00^{12,13}} = 0.910 n^* \approx 34.6$, i.e., $a = 69$. The error of the measured ratios is at least 20 per cent because of blending and the uncertainty on the tracing of the cometary continuum to which the emission-line intensities are referred.

We now turn to use of the integrated intensity of the band heads $C^{12}C^{12}(1, 0)$ and $C^{12}C^{12}(2, 0)$ as compared to $C^{12}C^{13}(1, 0)$. The $(1, 0)$ head is extremely strong, essentially at the limit of photographic photometry (as can be seen from the spectra reproduced). The measured strength of the $(1, 0)$ band is probably only a lower limit, since it is heavily overexposed. We find

$$\frac{w_{1,0}(\lambda 4737)}{w_{1,0}^i(\lambda 4745)} > 15,$$

which, from the calculations based on the simplified equation (6a), gives $N_{00^{12,12}}/N_{00^{12,13}} > 15$, or $a > 30$. It is possible that there is self-absorption in the individual rotational lines of the $C^{12}C^{12}$ band in the inner portions of the comet. Houziaux (1960) gives a maximum density of C_2 molecules in a comet head as $3 \times 10^3 \text{ cm}^{-3}$ at a radius of 500 km or $1.5 \times 10^{11} \text{ cm}^{-2}$. However, Arpigny (1963) kindly informs us that the apparent magnitude of Comet Ikeya gives a C_2 density of $2 \times 10^{13} \text{ cm}^{-2}$ at 500 km from the nucleus. Arpigny believes that Houziaux's densities are underestimated. From the f -value of the C_2 band system, 0.03, we deduce $f \approx 5 \times 10^{-3}$ for a strong rotational line of the $(1, 0)$ band. If we broaden the line over about 1 km/sec by internal motions, the mean absorption coefficient per molecule, within a single line, is only $\langle l_\nu \rangle \approx 6 \times 10^{-14} \text{ cm}^2$. For 2×10^{13} molecules per cm^2 column, we obtain $\langle \tau_\nu \rangle \approx 1.2$, i.e., some self-absorption near the head of a comet. If the volume density varies as $1/R^2$ the surface density decreases outward as $1/R$, where R is the distance from the nucleus. At a typical point in our spectrum, say $7''$ from the nucleus, or 3500 km, $\langle \tau_\nu \rangle \approx 0.2$, i.e., essentially negligible. Thus there may be a small saturation effect near the nucleus, but none sufficient to affect the isotope ratio deduced from the mean spectrum.

A more meaningful comparison is with the band head at $\lambda 4382$, $(2, 0)$ of $C^{12}C^{12}$, although this region is more strongly affected by solar absorption lines. The observed ratio was

$$\frac{w_{2,0}(\lambda 4382)}{w_{1,0}^i(\lambda 4745)} = 2.5$$

with an error of about 20 per cent. Changing the band width from 0.9 to 1.3 Å did not change this value appreciably. A correction factor should be included to allow for the difference in the brightness of the cometary continuum between these somewhat widely spaced wavelengths. Both the solar energy density and the reflectivity of the comet are

involved. The solar flux, corrected for lines, changes by 5 per cent; unless the reflectivity changes greatly in this short wavelength range, we are justified in omitting any correction. From our computations, the expected ratio of band-head strengths was

$$\frac{995.55}{15160.50} \frac{N_{00^{12,12}}}{N_{00^{12,13}}} = 2.5, \quad (9)$$

giving $N_{00^{12,12}}/N_{00^{12,13}} = 38.1$, or $a = 76$.

In summary, we have an accordant set of computations of $a = 62$, 69 , or 76 from individual lines and the $(2, 0)$ band. Since all three use the single measurement of the $C^{12}C^{13}(1, 0)$ band head, they are all subject to the error in that single measurement. If, as is possible, a small portion of $\lambda 4744$ arises from a weak NH_2 emission, then $a = 70 \pm 15$ seems a reasonable value, which may be slightly less than the true value. Therefore, the terrestrial and cometary values of the C^{12}/C^{13} ratio may be nearly the same.

VI. SOME CRITIQUES OF THE METHOD

A most obvious problem concerns the certainty with which we can ascribe the $\lambda 4745$ feature to the $C^{12}C^{13}(1, 0)$ band, if we cannot accept $\lambda 4752$ as $C^{13}C^{13}(1, 0)$. The $\lambda 4752$ wavelength coincides with the head of the computed $C^{13}C^{13}$ band. However, the intensity ratio $\lambda 4745/\lambda 4752$ is about 2 or 3. The number of molecules of $C^{12}C^{13}/C^{13}C^{13}$ is then about 2 or 3, since the frequency, excitation, and solar-energy density factors are near unity. Then from equation (7b) we find $a \approx 1.5$, in complete disagreement with our other determinations. The $\lambda 4752$ feature is far too strong, and the value of a it requires would predict that $\lambda 4745$ be one-third as strong as $\lambda 4737$, which is unacceptable. In addition, the $(2, 0)$, and $(3, 1)$ bands would be predicted to be observable in $C^{12}C^{13}$, at $\lambda 4395$ and $\lambda 4384$, respectively. No traces of band heads are seen at these wavelengths. On the other hand, with $a \approx 70$, the predicted $\lambda 4752$ $C^{13}C^{13}(1, 0)$ is $\frac{1}{140}$ of the $C^{12}C^{13}(1, 0)$, which is unobservably faint. The conclusion is either that $\lambda 4752$ is blended with a dominant band of another molecule, or that both $\lambda 4745$ and $\lambda 4752$ are so blended and that a is very large compared to the value we deduce; the first possibility was already suggested by Swings (1956). With the weakness of the $\lambda 4745$ $(1, 0)$ feature here observed, the possibility that $\lambda\lambda 4724$ and 4706 heads of $C^{12}C^{13}(2, 1)$ and $(3, 2)$ are observable seems very remote, although they have been suggested on old, low dispersion spectra.

Swings (1943) suggested that $C^{12}C^{13}(1, 0)$ could be weakened below the value predicted in this paper by a mechanism of pure rotational depopulation of the excited states. Both $C^{12}C^{12}$ and $C^{13}C^{13}$ are homonuclear and have zero dipole moment. In addition, there are twelve electrons in orbitals, completely paired. Therefore, pure rotational transitions are highly forbidden. Nevertheless, $C^{12}C^{13}$ is not homonuclear, even though the mass difference is small. Therefore $C^{12}C^{13}$ has a weak, but quite unknown, dipole moment that permits rotational de-excitation. However, the vibrational or rotational transitions from a typical level, to which we observe electronic transitions, occur in the far infrared. For equal values of the radial quantum integral, $|R|^2$, the transition probability which varies as ν^3 , becomes very small compared to an electronic transition probability. Further, the pure rotation of $C^{12}C^{13}$ would have only a small dipole movement, likely to be much smaller than 10^{-2} of that of a heteronuclear molecule with unpaired electrons. (For H_2 as compared to HD the ratio is near 10^{-2} , but the mass difference of H and D will have a much larger effect than that of C^{12} and C^{13} .) Were rotational depopulation to be effective in $C^{12}C^{13}$, then the true isotope ratio would be that derived from $\lambda 4752$ $C^{13}C^{13}$ band as compared to the $\lambda 4737$ $C^{12}C^{12}$ band. The value of the ratio of the intensities is poorly determined, but is of the order of 50 or greater, i.e., $a \geq 7$.

But we remain quite uncertain of the identification of $\lambda 4752$. Both cometary emis-

sions 4745 and 4752 were observed by Fehrenbach (1963) in the spectrum of Comet Ikeya taken at Haute-Provence Observatory. Woszczyk (1962) compared the laboratory data of Dressler and Ramsay (1959) with the spectrum of Comet Mrkos in this spectral region, one incompletely measured by Greenstein and Arpigny (1962). Arpigny is now studying Comet Ikeya on our new plates. There are three relevant NH_2 lines of the $\text{II}(0, 14, 0)$ in this spectral region, $\lambda\lambda$ 4738, 4745, 4752 all close to $(1, 0)$ heads of the C_2 isotopes, with theoretical relative intensities $3/1/2$. We find a very weak line, a shading just longward of the $(1, 0)$ $\text{C}^{12}\text{C}^{12}$ head at λ 4738 in Figure 2. Arpigny (private communication) believes that λ 4738 is the $[(0, 14, 0) 1_{10}-2_{20}]$ and that λ 4752 is $[(0, 14, 0) 3_{12}-4_{22}]$ of NH_2 . The relative intensities are compatible with Figure 2, although λ 4738 must be affected by the $\text{C}^{12}\text{C}^{12}$ head. What we have called $\text{C}^{12}\text{C}^{13}$, at λ 4745, however, is clearly stronger, and the NH_2 $[(0, 14, 0) 2_{11}-3_{21}]$ line at λ 4745 should contribute only a small part of the observed feature which we have measured as $\text{C}^{12}\text{C}^{13}$. We believe that the underestimate of α could be 20 per cent, which would raise it to nearly the terrestrial ratio. The laboratory wavelength of the other NH_2 feature, λ 4751.95 (laboratory intensity $1d$), places it squarely on the supposed $\text{C}^{13}\text{C}^{13}$ head. Other transitions of NH_2 in this neighborhood include Σ and $\Delta(0, 13, 0)$, a line of comet intensity 3 at λ 4922; there are three laboratory lines of 0 intensity at $\lambda\lambda$ 4744.28, 44.89, 45.18. Lines of laboratory intensity 1 observed in Comet Ikeya are $\lambda\lambda$ 4853.5, 4910.2, but some lines of intensity 2 are missing. The number of NH_2 lines and their near coincidence with C_2 isotope heads may explain older low resolution indications of large C^{13} abundance; the strength of λ 4745, however, seems too large to be explained except by the presence of C^{13} in nearly the terrestrial concentration. Of known bands of other diatomic molecules, there exists only a $(0, 0)$ transition of AlH , $^1\Pi-^1\Sigma'$, at λ 4752 involving an excited lower electronic state, $^1\Sigma'$, and therefore negligible.

VII. NUCLEAR SIGNIFICANCE OF THE ISOTOPE RATIO

On the basis of the Comet Ikeya spectrum, we believe that the $\text{C}^{12}/\text{C}^{13}$ ratio of 70 ± 15 is essentially the same as the terrestrial value. Thus cometary material could have come from the same region of the solar nebula as did the Earth and meteorites, or from interstellar matter (where we know only that $\text{C}^{12}/\text{C}^{13} > 5$). It could not have come directly from material at the center of a star in which the CN cycle had reached equilibrium, where $\text{C}^{12}/\text{C}^{13} \approx 4$, or from a star in which helium burning had occurred, i.e., where $\text{C}^{12}/\text{C}^{13}$ could be very large. One important result of Righini's very large $\text{C}^{12}/\text{C}^{13}$ ratio for the solar surface, if correct, is that the cometary material could not have originated in the same way as did the solar surface or the outer planets. Fowler *et al.* (1962) speculate about neutron irradiation of solids in the solar neighborhood during the formation of the planetesimals. $\text{C}^{12}(n, \gamma)\text{C}^{13}$ would produce C^{13} in reasonable concentrations, but only in regions not too far from the Sun. According to Fowler *et al.*, the neutron supply was probably insufficient in the outer portions of the solar nebula and the major planets to alter the composition in this region, especially since $\text{H}^1(n, \gamma)\text{D}^2$ captures exhaust neutrons if hydrogen is present in its cosmic abundance. Thus, if only C^{12} existed primevally, the C^{13} in the comets must have been formed in the solids. Then later, this material needed to be placed in eccentric orbits of large semimajor axis, presumably in the process of removal of the hydrogen and during transfer of angular momentum. If the solar $\text{C}^{12}/\text{C}^{13}$ ratio is less extreme and near 100 (Greenstein *et al.* 1950), then no such drastic event is required. If comets should ever arrive from other stellar or planetary systems, there is a possibility of a variable isotope ratio.

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