

HIGH-RESOLUTION SPECTRA OF C₂ SWAN BANDS FROM COMET WEST 1976 VI

DAVID L. LAMBERT

McDonald Observatory and Department of Astronomy, University of Texas

AND

A. C. DANKS

European Southern Observatory

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ABSTRACT

A 0.3 Å resolution spectrum of the $\Delta v = +1$ sequence in the C₂ Swan system from comet West 1976 VI at a heliocentric distance $r_H = 0.78$ AU is found to correspond to a vibrational and rotational temperature of $T_{\text{exc}} = 3500 \pm 400$ K for the upper $d^3\Pi_g$ state. If intercombination transitions are neglected, the predicted temperature for C₂ excited by fluorescence in sunlight is considerably hotter than the observed temperature. The triplet C₂ states may be cooled by intercombination transitions linking the triplet and singlet states. The electronic transition moment $|R_e|_{ax}^2$ of the $a^3\Pi_u - X^1\Sigma_g^+$ transition is estimated by a method previously applied successfully to the Cameron system ($a^3\Pi - X^1\Sigma^+$) of CO. The predicted $|R_e|_{ax}^2$ is shown to be consistent with the estimate based on the relative intensity of the Mulliken (singlet) and Swan systems. It is pointed out that other intercombination transitions may also play a role.

On high-resolution spectra of selected lines in the Swan 0-0 band, several ¹²C¹³C lines are identified. Although the quality of the available data is inadequate, a feasibility study shows that, in order to determine the ¹²C/¹³C ratio, the 0-0 band is probably superior to the 1-0 ¹²C¹³C 4745 Å band head.

Subject headings: abundances — comets — molecular processes

1. INTRODUCTION

The C₂ Swan bands in the emission spectrum of a comet are excited through resonance fluorescence with the sunlight (Stawikowski and Swings 1960). The relative intensities of the different bands and the rotational lines within a band betray the populations within the electronic states of the C₂ molecule. Theoretical studies of population must recognize two characteristics of the molecule. First, C₂ is a homonuclear molecule, and therefore, vibrational and rotational electric dipole transitions within an electronic state are forbidden, as emphasized by Arpigny (1966a). In the absence of these transitions, high vibrational and rotational levels of the triplet states should be populated in the sunlight. Indeed, Stockhausen and Osterbrock (1965) predicted from calculations with a simple model molecule that the vibrational temperature for cometary C₂ should be close to the solar color temperature and independent of the comet's heliocentric distance. When these predictions were not confirmed by observations of the Swan band intensities from several comets (Mayer and O'Dell 1968; Gebel 1970; O'Dell 1971; A'Hearn 1975), Krishna Swamy and O'Dell (1977) identified the second of the above mentioned special characteristics: the Swan system, the $d^3\Pi_g - a^3\Pi_u$ transition, is not a self-contained and isolated system, because vibrational transfers within the lower ³Π state are effected via a cascade from the higher vibrational levels in $a^3\Pi_u$ to the $b^3\Sigma_g^-$ state, followed by a return to the lower vibrational levels in the $a^3\Pi_u$ state. This cascade involves emission of two photons in the infrared Ballik-Ramsay ($b^3\Sigma_g^- - a^3\Pi_u$) bands.

Introduction of this cascade into the resonance fluorescence calculations resulted in a decreased population of the excited vibrational levels (mainly $v \geq 4$) in the $a^3\Pi_u$ state and, also, a weak dependence of these populations on heliocentric distance. (Krishna Swamy and O'Dell also included the Fox-Herzberg [$e^3\Pi_g - a^3\Pi_u$] system in their calculations but noted that this system had a very small influence.) Krishna Swamy and O'Dell (1979) extended their calculations to include three singlet states with coupling between the triplet and singlet states occurring through the intercombination transition $a^3\Pi_u - X^1\Sigma_g^+$. In the absence of experimental or theoretical estimates for the probability of spontaneous emission $A(a-X)$, Krishna Swamy and O'Dell inferred $A \sim 10^{-3} \text{ s}^{-1}$ from measurements of the relative intensity of the Phillips ($A^1\Pi_u - X^1\Sigma_g^+$) and Swan band systems. Discovery of the Mulliken ($D^1\Sigma_u^+ - X^1\Sigma_g^+$) system in an ultraviolet spectrum of comet Bradfield 1979I enabled A'Hearn and Feldman (1980) to confirm the estimate of $A(a-X)$.

Additional calculations using a model molecule with four triplet states were reported by A'Hearn (1978), who used improved data for the C₂ transition probabilities and the solar flux. The predictions were compared with a low-resolution spectrum ($\lambda/\Delta\lambda \sim 450$) of comet Kohoutek 1973 XII. The relative intensities of the Swan $\Delta v = +2, +1, 0$, and -1 sequences and of the bands within each sequence were reproduced fairly well. A'Hearn included the rotational structure in the spectrum synthesis calculations but not in the statistical equilibrium calculations providing the level populations

for each electronic state. When observed and synthetic spectra were compared, the latter were characterized by a vibrational (T_{vib}) and rotational (T_{rot}) temperature for levels in the upper state. A'Hearn's (1978, 1981) calculations predicted that T_{vib} for a comet at 1 AU from the sun decreases from 5420 K for $v' = 1$ to 4510 K for $v' = 5$ with approximately uniform changes of ± 500 K for distance changes of ∓ 0.5 AU; here, T_{vib} is defined by the ratio of the equilibrium population $n(v')/n(0)$. The rotational temperature was taken as a free parameter. A'Hearn reported that a rotational temperature of 3000 K gave a good fit to the profiles of the overlapping bands comprising a single sequence.

Our study of comet West 1976 VI was intended to probe the C_2 band structure by using sufficient spectral resolution to resolve the rotational structure of the bands. The observed profile of the $\Delta v = +1$ sequence is compared in § III with predicted profiles computed for a range of excitation temperatures. This is the first time such a detailed comparison has been reported. Our second objective (see § IV) was to explore some improved methods for extracting the isotopic ratio $^{12}\text{C}/^{13}\text{C}$ from cometary C_2 observations. High spectral resolution is shown to be essential when seeking an accurate determination of this important isotopic ratio.

II. OBSERVATIONS

Comet West was observed at the McDonald Observatory with the 2.7 m reflector and the Tull coude spectrometer. Two series of observations of the C_2 bands are described here.

In the first series, we used a self-scanned Digicon (Tull, Choisser, and Snow 1975) as the detector to obtain spectra from 4650 Å to 4755 Å at a resolution of about 0.3 Å. These spectra cover a large part of the blue-degraded Swan $\Delta v = +1$ sequence with its 1-0 head at 4737 Å as well as the $^{12}\text{C}^{13}\text{C}$ 1-0 head at 4745 Å and several NH_2 features. The cometary spectrum is superposed on a weak spectrum of reflected sunlight from cometary dust grains. The intensity in the continuum longward of the 4737 Å head is a few percent of the intensity at the band head. The strongest solar absorption lines are easily identified in this continuum. The dust-contributed solar spectrum was readily subtracted. We observed the daytime sky with the same spectrometer set up. After applying the appropriate Doppler shift, we normalized the sky spectrum to the observed spectrum longward of the 4737 Å head but excluded regions where NH_2 was present in emission. A subtraction of this normalized spectrum then provided the emission spectrum of the comet. Figure 1 is an example of such a spectrum. This spectrum was obtained on the morning of 1976 March 21 when the comet was at a heliocentric distance $r_H = 0.78$ AU. Similar spectra were obtained on 1976 March 19 when $r_H = 0.74$ AU. The irregular zero level between the NH_2 features and the lack of evidence for the solar absorption lines are good indicators of a successful subtraction. Since Comet West was one of the dustiest of modern comets (A'Hearn, Thurber, and

Millis 1977), it provided a stiff test of the subtraction procedure. The entrance slit subtended $0''.5$ by $5''$ on the sky and was centered by eye on the brightest part of the comet. The exposure time was 40 minutes. The observed spectrum has been divided by the spectrum of the flat-field lamp in order to remove the small diode-to-diode variations and the small variation in instrumental sensitivity across the 100 Å bandpass.

A series of higher resolution spectra was obtained with the Tull (1972) spectrometer in a scanning mode with a GaAs photomultiplier as the photon-counting detector. We used an echelle grating with a cross-dispersing grating to isolate 2-3 Å intervals in the C_2 0-0 band. These spectra, which were taken to evaluate a new approach to determining the $^{12}\text{C}/^{13}\text{C}$ ratio, are discussed in § IV.

III. SYNTHETIC AND OBSERVED SPECTRA

a) The Synthetic Spectrum

Although the rotational structure of the Swan bands is clearly displayed in our spectra, the number of unblended lines is remarkably few. A synthesis of the spectrum facilitates the determination of the vibrational and rotational temperatures. Our approach was to find the excitation temperatures of the vibration-rotation levels in the upper $^3\Pi_g$ state by a trial-and-error fitting of the synthetic spectrum to the observed spectrum. Then, the observed temperatures are compared with those predicted from resonance fluorescence calculations with a model C_2 molecule (A'Hearn 1978, 1981; Krishna Swamy and O'Dell 1982).

In our calculations, the upper electronic state was represented by the five lowest vibrational levels and the first 80 rotational levels in each of the vibrational levels. The flux in an emission line from the optically thin cometary cloud is

$$F \propto n(v'J')A(v'J', v''J'')\sigma(v'J', v''J''),$$

where $n(v'J')$ is the level population, $A(v'J', v''J'')$ is the Einstein A -value, and $\sigma(v'J', v''J'')$ is the frequency of the transition $v'J' \rightarrow v''J''$.

The level populations were characterized by an excitation temperature. In most of the calculations, we used a single excitation temperature for all levels and made no distinction between the rotational and the vibrational temperatures. Excitation energies were calculated from the molecular constants given by Phillips and Davis (1968). Frequencies for all transitions were computed from these constants and included the perturbations identified by Phillips (1968). We checked the predictions against the laboratory line lists.

The A -values were computed from the standard expression

$$A_{v'J', v''J''} \propto S_{v'v''} \frac{S_{J'J''}}{2J' + 1} \sigma_{v'J', v''J''}^3,$$

where $S_{J'J''}$ is the Hönl-London factor, and $S_{v'v''}$ is the band strength which combines the electronic transition moment and the Franck-Condon factor. The Hönl-

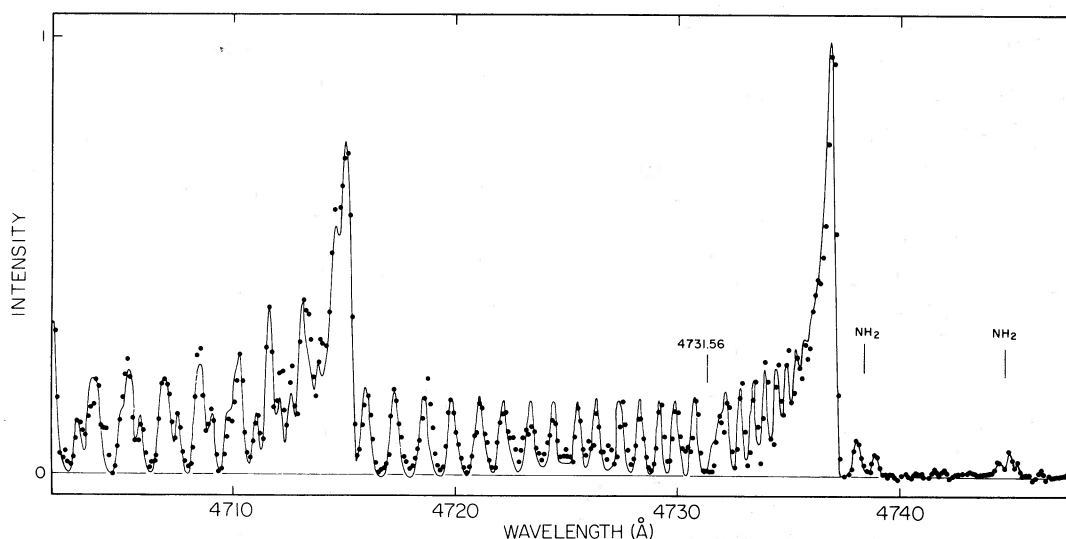


FIG. 1a

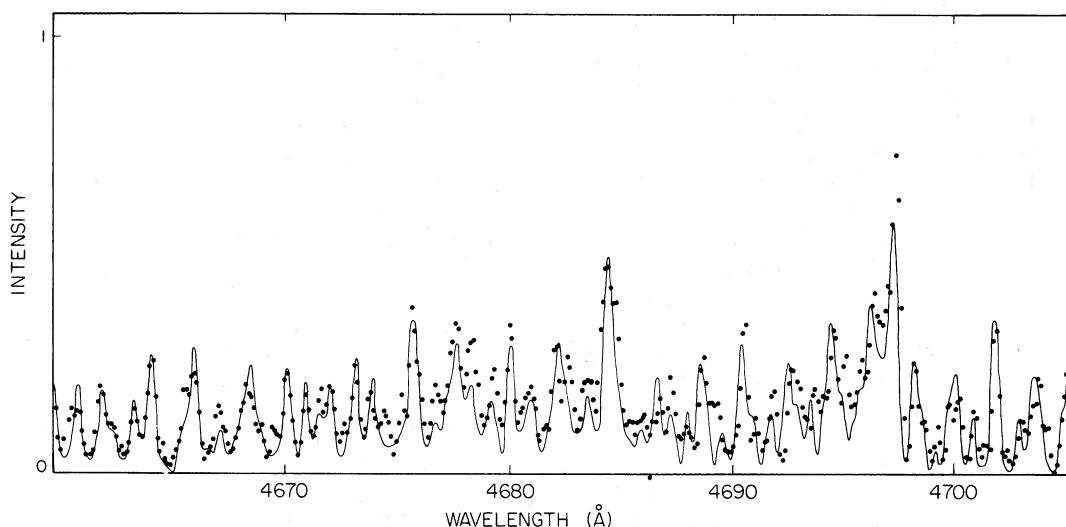


FIG. 1b

FIG. 1.—The C_2 Swan $\Delta v = +1$ sequence in comet West on 1976 March 21. The contribution of sunlight scattered by dust grains in the comet has been removed (see text). The solid line is a synthetic spectrum corresponding to an excitation temperature of 3500 K.

London factors were computed using a computer program described by Whiting (1972). We adopted the band strengths given by Danylewych and Nicholls (1974), which are confirmed by accurate measurements of the radiative lifetime of the $d^3\Pi_g$ state (Curtis, Engman, and Erman 1976).

The synthetic spectrum was convolved with a Gaussian profile having a width (FWHM) of 0.3 Å. Inspection of emission lines from the FeNe hollow cathode lamp observed just after the cometary observation shows that this Gaussian is an adequate representation of the instrumental profile except at the extreme ends of the bandpass. The high-resolution observations of C_2 lines show that the intrinsic line width is much less than the

0.3 Å slit width. Synthetic spectra normalized to unity at the 1–0 band head are shown in Figure 2 for excitation temperatures $T_{\text{exc}} = 3000, 4000$, and 5000 K. A synthetic spectrum for $T_{\text{exc}} = 3500$ K is shown with the observed spectrum in Figure 1.

The synthetic spectrum is a good fit to the observed spectrum almost everywhere. The most striking discrepancy appears at the 3–2 band head. We would not expect a perfect match for several reasons. For example, the NH_2 features, which cross this region, have not been included in the synthesis. We have not allowed at all for the effects of the solar absorption lines in the exciting spectrum. These lines should affect the population of a few rotational levels. Finally, our adoption of

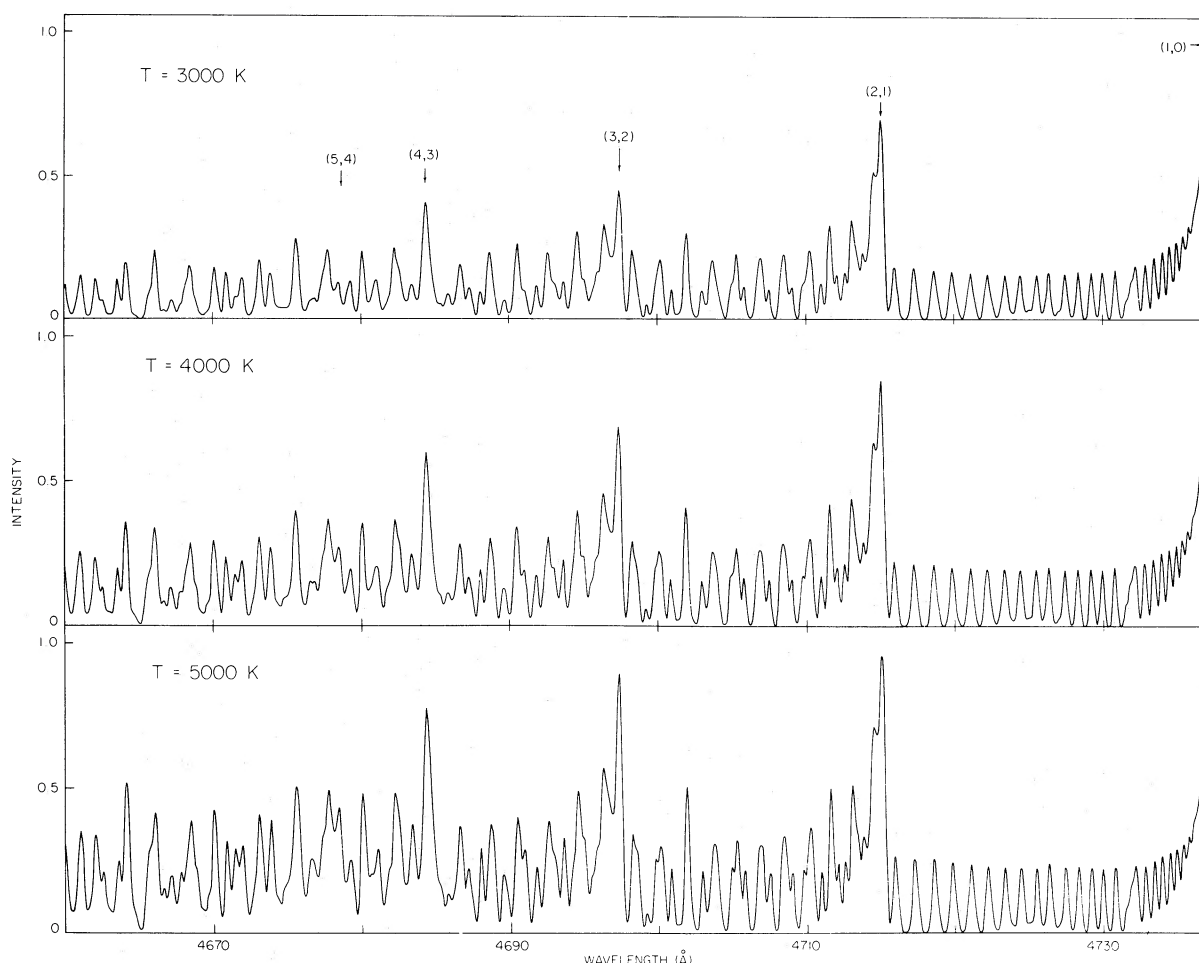


FIG. 2.—Synthetic spectrum of the C_2 Swan $\Delta v = +1$ sequence for the excitation temperatures $T_{\text{exc}} = 3000, 4000,$ and 5000 K

a single excitation temperature is surely too simplistic. The resonance fluorescence calculations predict that the vibrational temperature should decrease along the vibrational ladder.

Our comparisons of synthetic and observed spectra show that the excitation temperature $T_{\text{exc}} = 3500 \pm 400$ K provides a good representation of the comet West spectra at a heliocentric distance $r_H \sim 0.75$ AU. This temperature refers to the levels $v' = 1$ through 5. On the basis of the rotational structure of the 1–0 band, we estimate that the rotational temperature is equal to the vibrational temperature or $|T_{\text{vib}} - T_{\text{rot}}| \lesssim 500$ K. The vibrational temperature as judged by the fit to the band heads is defined to be about 400 K. The excitation temperature, $T_{\text{exc}} = 3500$ K, is considerably cooler than the predictions currently available.

Before discussing possible origins of this discrepancy between the observed and predicted excitation temperatures, we comment on previously reported differences between the temperatures T_{vib} and T_{rot} . A'Hearn (1978) noted that observations of the relative flux in the Swan band sequences $\Delta v = -2, -1, 0,$ and $+2$ for four comets

could be reproduced satisfactorily by his resonance fluorescence calculations (i.e., $T_{\text{vib}} \sim 5200$ K for $r_H \approx 1$ AU), but the profiles of the individual sequences required a rotational temperature $T_{\text{rot}} \sim 3000$ K for comet Kohoutek at $r_H = 1.0$ AU. This is not an isolated report of an apparently significantly hotter T_{vib} . Danylewych *et al.* (1978) reported $T_{\text{vib}} \sim 5000$ K with $T_{\text{rot}} \sim 3200$ – 3800 K from profiles of the $\Delta v = 0$ and $+1$ sequences in the two comets Kohoutek 1973 XII and Kobayashi-Berger-Milon 1975 IX. These temperatures were extracted from low-resolution (30 Å) spectrophotometric scans in which the band head structure is barely discernible within a single sequence. Since the observations provided just the three sequences $\Delta v = +1, 0,$ and -1 , the relative flux in these sequences is not critically dependent on the vibrational temperature. For example, the $\Delta v = 0$ and -1 sequences sample the same levels in the $d^3\Pi_g$ state; i.e., the bands are 0–0, 1–1, 2–2, ... in the $\Delta v = 0$ sequence and 0–1, 1–2, 2–3, ... in the $v = -1$ sequence. Within a single sequence, a distinction between T_{vib} and T_{rot} would seem to be uncertain at best from scans at 30 Å resolution. The

sequence-to-sequence flux ratios are sensitive to both the vibrational temperature and to the assumed electronic transition moment for the Swan system.

Within a single sequence, the band intensities are more a reflection of T_{vib} than the change of the electronic transition moment along the sequence. The electronic transition moment $R_e^2(r)$ appropriate to a given band is $R_e^2(\bar{r}_{v',v''})$ on the r -centroid approximation. (Here, r is the internuclear separation.) The small influence of R_e^2 on band intensities is readily seen by examining the r -centroids for the $\Delta v = +1$ sequence, where $\bar{r}$ runs from 1.368 Å for the 1-0 band to 1.401 Å for the 4-3 band. The r -centroid shows rather larger changes with a change of sequence; e.g., $\bar{r} = 1.368$ Å for the 1-0 band, 1.293 Å for the 0-0 band, and 1.224 Å for the 0-1 band. In short, T_{vib} estimates obtained from comparison of two sequences are sensitive to the adopted $R_e^2(r)$. Fortunately, the $R_e^2(r)$ variation with r is now quite well known from experiment and ab initio calculations.

A'Hearn's spectra of Kohoutek 1973 XII are at sufficient resolution to resolve partially the band heads within a sequence (see A'Hearn 1975). His synthetic spectrum was constrained by the vibrational level populations predicted by the resonance fluorescence calculations (i.e., $T_{\text{vib}} = 5200$ K for $r_H = 1.0$ AU). If the calculations overestimate T_{vib} , as appears probable from our analysis of a high-resolution spectrum, there will be a tendency to underestimate T_{rot} because the higher rotational lines from one band and the lower rotational lines from the next higher band in the sequence are intermingled. Hence, we suspect that A'Hearn's T_{vib} and T_{rot} are not independent quantities.

Two other excitation temperature determinations will be discussed briefly. We observed comet Kobayashi-Berger-Milon 1975 IX with the Tull spectrometer at a resolution of 0.65 Å. The 1-0 band provides $T_{\text{rot}} = 4500$ (+500, -1000) K for $r_H \sim 0.8$ AU, which is just consistent with Danylewych *et al.*'s estimate and our result for comet West at a similar heliocentric distance. Arpigny (1966b), who analyzed high-resolution spectra of the Swan 0-0 and 1-0 bands from three comets at distances $r_H = 0.55$ –0.97 AU, reported that $T_{\text{rot}} (= 4900$

± 500 K) was independent of heliocentric distance. Since the band profile changes are not outstanding for the range $T_{\text{rot}} = 3000$ –5000 K (see Fig. 2), accurate spectrophotometry is clearly essential in order to define T_{rot} to better than 1000 K. In obtaining a T_{rot} estimate, Arpigny used short wavelength intervals on his photographic spectra covering C_2 lines spanning a narrow excitation potential; we suspect that he may have underestimated the uncertainties afflicting the T_{rot} estimates. He also derived $T_{\text{vib}} \sim 6000$ K. It is probable that his higher value is attributable to the adopted band oscillator strengths—we have not checked the values used by Arpigny against the reliable values of Danylewych and Nicholls (1974).

There is a need now for additional high-resolution spectra in order to test more thoroughly the possible variation of excitation temperature within the vibronic structure of the $d^3\Pi_g$ state. Our investigation of Comet West suggests that $T_{\text{vib}} = T_{\text{rot}}$ is a good initial approximation.

b) The Vibrational Temperatures

i) Observed and Predicted Vibrational Temperatures

In their resonance fluorescence calculations, Krishna Swamy and O'Dell (1977, 1979) and A'Hearn (1978) represented the C_2 molecule by selected electronic states with vibrational but not rotational structure. Our comparison of the observed temperature $T_{\text{exc}} = 3500$ K for the $d^3\Pi_g$ state with predicted temperatures makes use of the predicted populations supplied by A'Hearn (1981) and Krishna Swamy and O'Dell (1982); see Table 1.

A'Hearn's calculations in which the C_2 singlet states are ignored predict for the distance $r_H = 0.75$ AU, which is close to the distance for comet West at the time of observations, a temperature $T_{\text{vib}} = 5150$ K ($v' = 2$), 4940 K ($v' = 3$), 4740 K ($v' = 4$), and 4515 K ($v' = 5$). Our derived $T_{\text{exc}} = 3500 \pm 400$ K is markedly lower than these predictions. The difference in the populations of the vibrational levels is striking; our spectrum requires $n(4)/n(1) \approx 0.13$, but the calculations predict $n(4)/n(1) = 0.22$, a 70% decrease.

TABLE 1
PREDICTED VIBRATIONAL TEMPERATURES

UPPER LEVEL (v')	T_{vib} (K) ^a							
	$r_H = 0.5$ AU				$r_H = 1.0$ AU			
	$ R_e ^2 = 10^{-4}$	10^{-5}	10^{-6}	A'H ^c	10^{-4}	10^{-5}	10^{-6}	A'H
2	3705	4950	5150	5340	2685	4240	4760	5015
3	3560	4775	4970	5160	2550	4040	4515	4765
4	3430	4580	4760	5015	2465	3845	4270	4550
5	3320	4390	4555	4795	2400	3680	4080	4315

^a T_{vib} computed from the population ratio $n(v')/n(1)$.

^b $|R_e|^2$ is the electronic transition moment (in atomic units) for the intercombination transition $a^3\Pi_u - X^1\Sigma_g^+$ (see text). T_{vib} for $|R_e|^2 = 10^{-4}$, 10^{-5} , and 10^{-6} from Krishna Swamy and O'Dell 1982.

^c The T_{vib} under A'H are from A'Hearn 1981, whose model molecule did not include the singlet states, i.e., $|R_e|^2 \equiv 0$.

When a model C_2 molecule including both triplet and singlet states is employed, the triplet state populations depend on the value adopted for the electronic transition moment $|R_e|^2$ of the intercombination transition $a^3\Pi_u-X^1\Sigma_g^+$, which Krishna Swamy and O'Dell (1979) assume is the only effective link between the singlet and triplet states. We show in Table 1 the predicted T_{vib} for $|R_e|^2$ (in atomic units) = 10^{-4} , 10^{-5} , and 10^{-6} . Extrapolation of T_{vib} to $|R_e|^2 \approx 0$ indicates that T_{vib} is 100–200 K cooler than A'Hearn's (1981) value. This difference must reflect differences in the adopted f -values for the triplet transitions, principally the Swan and Ballik-Ramsay systems. By interpolation in Table 1, we see that $|R_e|^2 \sim 5 \times 10^{-5}$ would give $T_{vib} \sim 3500$ K at $r_H \sim 0.75$ AU. We discuss below a theoretical estimate for $|R_e|^2$ and evidence based on the relative cometary fluxes of singlet systems and the Swan system. This discussion suggests that $|R_e|^2 \ll 5 \times 10^{-5}$, and so the observed T_{vib} of 3500 K is left unexplained by the currently available calculations (A'Hearn 1978; Krishna Swamy and O'Dell 1979).

The calculations providing the predicted T_{vib} employ a model molecule and a set of assumptions. The primary assumption is that the cometary C_2 molecules achieve statistical equilibrium with the sunlight with sufficient rapidity that neither production of C_2 from parent molecules nor destruction by photodissociation or chemical reactions—processes which could populate or depopulate preferentially certain levels in C_2 —is effective in determining the equilibrium populations. This assumption is examined below. A subsidiary assumption that the cometary cloud is optically thin in the Swan system lines affects both the T_{vib} determination via the synthetic spectrum and the statistical equilibrium calculations. Measured C_2 column densities confirm this assumption.

To date, the model calculations have ignored the rotational structure, but this omission should not greatly affect the predicted equilibrium populations and T_{vib} 's. However, we point out in § IV that the F_1, F_2, F_3 levels of the $^3\Pi$ states may have different populations thanks to the influence of the $a^3\Pi_u-X^1\Sigma_g^+$ transition. The use of smoothed solar fluxes instead of a spectrum with individual Fraunhofer lines is unlikely to be a source of serious error for the predicted T_{vib} 's. Of course, selected lines within a band will be affected through coincidences with strong Fraunhofer lines, but the predicted integrated intensity of a band should not be significantly affected by the neglect of the detailed rotational structure in the statistical equilibrium calculations.

The calculations further assume that collisions between C_2 and gas atoms or molecules are unimportant. Collisions will first produce a redistribution of population along the rotational ladder of a vibrational level in the $a^3\Pi_u$ state; the collisional cross section for a $v'J' \rightarrow v''J''$ transition should greatly exceed that for a $v'J' \rightarrow v''J'$ transition. Then, collisions will cool a rotational ladder to the gas kinetic temperature ($T < 1000$ K) as the vibrational levels are maintained at the higher T_{vib} . There is no evidence for a cooler rotational ladder

in comet West. Moreover, on substitution of reasonable values for the collision cross section, gas density, etc., the predicted rate for a collisional rotational excitation/de-excitation is much smaller than the rate for the same transition occurring via radiative excitation to the $^3\Pi_g$ state with a return to the $^3\Pi_u$ state. Hence, collisions may be safely neglected.

A key factor behind the predicted equilibrium populations is the model C_2 molecule. Without access to the detailed calculations, it is possible to give only a partial assessment of the effects on T_{vib} of errors in the adopted f -values for the electronic transitions and the addition of further electronic states. Independent calculations by A'Hearn (1978, 1981) and Krishna Swamy and O'Dell (1979, 1982) give T_{vib} 's differing by less than 200 K when the model C_2 molecules are limited to the triplet states. These authors employed different sets of f -value data. The data adopted by A'Hearn are compatible with the best available experimental and theoretical results; e.g., Curtis, Engman, and Erman (1976), Chabalowski, Buenker, and Peyerimhoff (1981), and Cooper (1981). If the model molecule is restricted to the triplet states, it is most improbable that the predicted T_{vib} can be depressed by about 1500 K to reach agreement with the observed $T_{exc} = 3500$ K.

In the next two sections, we scrutinize (1) the estimates of the transition moment $|R_e|^2$ for the $a^3\Pi_u-X^1\Sigma_g^+$ transition and (2) the assumption that the C_2 molecules attain a steady-state statistical equilibrium.

ii) The $a-X$ and Other Intercombination Transitions

Since the $a-X$ intercombination transition may play a key role in understanding cometary C_2 molecules, we examined carefully the published estimates of A_{ax} . Krishna Swamy and O'Dell (1979) noted that the relative fluxes in the C_2 Swan system sequences $\Delta v = 0, \pm 1$ require a transition moment $|R_e|^2 \lesssim 10^{-5}$. This limit must be moderately sensitive to the adopted variation with internuclear separation of the electronic transition moment for the Swan system. Comparisons of the flux in singlet and triplet (Swan) systems led to $|R_e|^2 \sim 1 \times 10^{-5}$ to 2×10^{-5} (see A'Hearn and Feldman 1980).

A'Hearn and Feldman (1980) compared their measured flux ratio of the Mulliken and Swan system $\Delta v = 0$ sequences with predictions provided by Krishna Swamy and O'Dell (1979). However, the predictions employ the Mulliken system f -value reported by Cooper and Nicholls (1975), but two measurements of the radiative lifetime of the upper state (Smith 1969; Curtis, Engman, and Erman 1976) provide an f -value larger by a factor of about 2.5. Inspection of Krishna Swamy and O'Dell's predictions shows that this larger f -value, which requires a smaller singlet population to match a given observed flux in the Mulliken system, corresponds to a reduction by more than a factor of 100 in the strength of the $a-X$ intercombination transition or $|R_e|^2 \sim 10^{-7}$. On the other hand, Krishna Swamy's estimate of this strength must be revised upward because the best estimate of the f -value for the Phillips system

has been reduced by a factor of 3 thanks to a measurement of the radiative lifetime (Erman *et al.* 1982) and an analysis of solar C₂ Phillips lines (Brault *et al.* 1982). With this revision, the observed flux ratio of the Phillips to Swan systems in comets demands a strength of the a -X transition which is inconsistent with the Mulliken-based result: $|R_e|^2 \sim 10^{-3}$. The probable explanation is that the observed flux of the weak Phillips 3-0 band was overestimated by a modest factor. In estimating the revisions to $|R_e|^2$, we assume that the improved f -value estimates for the singlet Phillips and Mulliken systems would not lead to substantially different equilibrium singlet state populations. An important point may not have received due stress in earlier discussions of the intercombination transition: the singlet-to-triplet flux ratio is rather a slowly varying function of the strength of the a -X system. For example, if the electronic transition moment $|R_e|^2$ varies from 10^{-5} to 10^{-7} , the ratio of the Mulliken to Swan $\Delta v = 0$ sequences at $r_H = 1.0$ AU varies from just 3.8 to 2.2 (A'Hearn and Feldman 1980). Clearly, a precise measurement of the flux ratio is needed to ensure a reliable estimate of $|R_e|^2$.

All of the previous discussions of the a -X transition have overlooked the possibility of predicting the strength of this transition. We follow here a recipe described by James (1971), who successfully predicted the strength of the Cameron ($a^3\Pi$ - $X^1\Sigma^+$) system in CO, a transition closely analogous to the a -X transition in C₂.

The a -X intercombination transition occurs as an allowed (i.e., electric dipole) transition owing to a mixing of the $a^3\Pi_u$ and $A^1\Pi_u$ states (and, perhaps, other singlet states) through the spin-orbit interaction. In an obvious notation, James showed that the electronic transition moment could be written

$$|R_e(r)|_{aX}^2 = \left| \sum_{v'''} \frac{\langle a^3\Pi_u, v' | H'(r) | A^1\Pi_u, v''' \rangle \langle A^1\Pi_u, v''' | R_{AX}(r) | X^1\Sigma_g^+, v \rangle}{E(a^3\Pi_u, v') - E(A^1\Pi_u, v''')} \right|^2, \quad (1)$$

where $R_{AX}(r)$ is the electronic transition moment for the Phillips ($A^1\Pi_u$ - $X^1\Sigma_g^+$) system, and $H'(r)$ is the operator for the spin-orbit $H'(r) = \sum_i a_i l_i s_i$. James showed that $|H'(r)| \equiv |A(v)|$, where A is the spin-orbit coupling constant for the $a^3\Pi$ state of CO. The lowest $^1\Pi$ and $^3\Pi$ in CO and C₂ are attributable to the electron configurations $\sigma\pi$ and $\sigma\pi^3$, respectively. Since these are complementary configurations to the half-filled shell $\sigma\pi^2$, we suppose that $|H'(r)| = |A(r)|$ also for C₂. The spin-orbit coupling constant A ($= -15.3$ cm⁻¹) for $a^3\Pi_u$ varies very little with vibrational level so that we assume $A(r)$ is independent of the internuclear separation r . If we adopt a similar assumption for the electronic transition moment of the Phillips system, equation (1) reduces to

$$|R_e|_{aX, v'v}^2 = A^2 |R_e|_{AX}^2 \times \left| \sum_{v'''} \frac{\langle a^3\Pi_u, v' | A^1\Pi_u, v''' \rangle \langle A^1\Pi_u, v''' | X^1\Sigma_g^+, v \rangle}{E(a^3\Pi_u, v') - E(A^1\Pi_u, v''')} \right|^2. \quad (2)$$

Thanks to the near-equality of the equilibrium internuclear separations and vibrational constants, the overlap integral $\langle a^3\Pi_u, v' | A^1\Pi_u, v''' \rangle$ is large only for $v' = v'''$. Then, equation (2) with a modest loss of accuracy reduces to

$$|R_e|_{aX, v'v}^2 \approx \frac{A^2 |R_e|_{AX}^2 q_{v'v'}^{aA} q_{v''v}^{AX}}{[E(a^3\Pi_u, v') - E(A^1\Pi_u, v')]^2}. \quad (3)$$

The Franck-Condon factors $q_{v'v'}$ were computed from RKR potentials. We adopt $|R_e|_{AX}^2 = 0.075$ a.u. from Erman *et al.* (1982) and a direct conversion of the radiative lifetime without the statistical weight ratio $g'''/g = 2$; i.e.,

$$|R_e|_{AX, v}^2 = \frac{4.935 \times 10^5}{\tau_{v'''} q_{v''v}^3 q_{v''v}^3}.$$

This procedure yields $|R_e|_{aX}^2 = 1.2 \times 10^{-7}$ for the 0-0 band, an estimate in fine agreement with the revision of the value based on the Mulliken to Swan system flux ratio in comet Bradfield. Einstein A -values were computed from the relation

$$A_{v'v} = \frac{64\pi^4}{3h} v^3 |R_e|_{aX, v'v}^2 = 2.03 \times 10^{-6} \sigma^3 |R_e|_{aX, v'v}^2, \quad (4)$$

where σ is in cm⁻¹ and $|R_e|^2$ in atomic units.

Radiative lifetimes of the lowest vibrational levels in both the $a^3\Pi_u$ and $X^1\Sigma_g^+$ states are listed in Table 2. In their statistical equilibrium calculations, Krishna Swamy and O'Dell assumed apparently that the probabilities $A_{v'v}$ within the a -X transition scaled as $v_{v'v}^3 q_{v'v}^{aX}$. Through inspection of equation (2) and an application of the closure relation, we see that this is valid if $|E(a^3\Pi_u, v') - E(A^1\Pi_u, v''')|$ is independent of v' and v''' . This approximation is similar to our equation (3). Table 2 compares our estimates with estimates based

TABLE 2
PREDICTED RADIATIVE LIFETIMES

State	$\tau[s]^a$	$\tau[s]^b$
$a^3\Pi_u$		
$v' = 5$	30	58
4	60	80
4	75	110
2	160	210
1	460	560
0	18000	18000
$X^1\Sigma_g^+$		
$v = 4$	75	100
3	130	190
2	330	460
1	2300	2830
0	∞	∞

^a Radiative lifetime $\tau_{v'} = 1/\sum_j A_{v'v_j}$ with $A_{v'v_j}$ from eq. (3).

^b Based upon use of the Franck-Condon factors $q_{v'v}$ (see text) and normalized to give $\tau_{v'=0} = 18,000$ s.

on direct use of the Franck-Condon factors for the a - X transition. The differences between the two estimates do not exceed a factor of 2.

Our computed lifetimes are not strictly the radiative lifetime of an individual level (see James 1971 for a discussion of this point). James points out that the $a^3\Pi_0$ and $a^3\Pi_2$ levels for low rotational quantum numbers will have a radiative lifetime considerably in excess of the lifetime of the $a^3\Pi_1$ levels for which the computed lifetime is a fair approximation. All lifetimes decrease up the rotational ladder in such a way that $\tau(^3\Pi_0) \sim \tau(^3\Pi_2) < \tau(^3\Pi_1)$ for high rotational quantum numbers. We discuss later the possibility of detecting such differences in high-resolution spectra.

The model C_2 molecule employed to date may omit some significant connections between triplet and singlet states. Cooper (1982) points out that the $X^1\Sigma_g^+$ state may be partially mixed with the low-lying $b^3\Sigma_g^-$, the upper state of the Ballik-Ramsay system. This mixing will also facilitate the $a^3\Pi_u$ - $X^1\Sigma_g^+$ intercombination transition. Although a thorough calculation has not yet been completed, the electronic transition is probably comparable to that just computed, and the combined effect of the mixing of the singlet $A^1\Pi_u$ with $a^3\Pi_u$ and the triplet $b^3\Sigma_g^-$ with $X^1\Sigma_g^+$ can probably not account for the $|R_e|^2 \sim 10^{-4}$ a.u. needed to cool the vibrational ladder to the observed temperature. Intercombination transitions between more highly excited states may be important. Possible examples include $d^3\Pi_g$ - $A^1\Pi_u$, $c^3\Sigma_u^+$ - $X^1\Sigma_g^+$, and $A^1\Pi_u$ - $b^3\Sigma_g^-$.

Our semiquantitative argument is structured for the $c^3\Sigma_u^+$ state, which was discovered by Ballik and Ramsay (1963) through its perturbations on the upper state of the Phillips ($A^1\Pi_u$ - $X^1\Sigma_g^+$) system. Transitions involving $c^3\Sigma_u^+$ have not yet been identified. The c state lies below the upper state of the Swan system: $T_e(d^3\Pi_g) - T_e(c^3\Sigma_u^+) \sim 8227 \text{ cm}^{-1}$ (Chauville, Maillard, and Mantz 1977). The transition $d^3\Pi_g$ - $c^3\Sigma_u^+$ is allowed but transitions to the lower triplet levels $b^3\Sigma_g^-$ and $a^3\Pi_u$ are forbidden. The c - X transition, which would act in parallel with the a - X transition already considered by Krishna Swamy and O'Dell (1979), is reduced in importance because the $d^3\Pi_g$ state has a low equilibrium population relative to the $a^3\Pi_u$ state, but on the other hand, the transition probability for spontaneous emission may be considerably larger for the c - X transition because this probability scales with frequency as $A \propto \sigma^3 S$ (S is the transition moment and σ is the frequency), and $\sigma(c-X)/\sigma(a-X) \sim 17$ for the 0-0 transitions in these systems; i.e., $A_{cX}/A_{aX} \sim 5000$ is possible. However, the ratio A_{cX}/A_{aX} is much smaller for transitions from excited vibrational levels in the a state, e.g., $A_{cX}/A_{aX} \sim 10$ for the 4-2 band in the a - X system. In addition, $\Delta\Lambda = 0$ transitions may have a larger transition moment than $\Delta\Lambda = \pm 1$ transitions.

We attempt a preliminary assessment of the importance of the c - X transitions. Krishna Swamy and O'Dell (1977), who mislabeled the additional triplet state as $^3\Sigma_u^-$, report that they ran some fluorescence calculations with this triplet state included in the model

molecule. Since they did not give a detailed discussion of the model results, we presume that they found the $^3\Sigma_u^+$ state to be an unimportant influence on the steady-state equilibrium within the triplets. We concur. We compare the intercombination transitions c - X and a - X . In equilibrium, the population in the $c^3\Sigma_u^+$ state is

$$n_c = n_d A_{dc} / (R_{cd} + A_{cX}),$$

where R is the excitation rate from absorption of sunlight. The relative contributions of the two intercombination transitions as a leak from the triplet to the singlet states are then

$$L = \frac{n_c A_{cX}}{n_a A_{aX}} = \frac{n_d A_{cX}}{n_a A_{aX}} \frac{A_{dc}}{R_{cd} + A_{cX}}. \quad (5)$$

Before presenting our assessment of the numerical estimates of the rates, we note two limiting cases for L . If $A_{cX} < R_{cd}$,

$$L = \frac{n_d A_{cX}}{n_a A_{aX}} \frac{A_{dc}}{R_{cd}}, \quad (6)$$

where the term A_{dc}/R_{cd} is independent of the f -value for the d - c transition. Alternatively, if $A_{cX} > R_{cd}$,

$$L = \frac{n_d A_{dc}}{n_a A_{aX}}, \quad (7)$$

so that L is not set by the transition probability for the intercombination transition c - X . Note that we assume here the population ratio n_d/n_a to be little affected by the $c^3\Sigma_u^+$ state and adopt $n_d/n_a \sim 8 \times 10^{-8}$ at $r_H = 0.75 \text{ AU}$ (A'Hearn 1981).

The transition probability A_{dc} has not been measured or calculated. Indeed, the d - c transition has not been reported by laboratory spectroscopists. An upper limit to A_{dc} can be provided from the observations of the Swan system which show that the directly measured oscillator strength is consistent to within about 20% with the measured radiative lifetime of the $d^3\Pi_g$ state. Since $\tau(d^3\Pi_g) = 1/(A_{dc} + A_{da})$, we have $A_{dc} \lesssim 0.2 A_{da} = 3 \times 10^6 \text{ s}^{-1}$. The corresponding excitation rate is $R_{cd} \lesssim 1 \text{ s}^{-1}$. As indicated earlier, the c - X transition could be considerably more probable than the a - X transition, or $A_{cX}/A_{aX} \sim 5000$ for low vibrational levels in $a^3\Pi_u$.

With the above estimates, we find from equation (6) $L \sim 1200$ for low vibrational levels decreasing to $L \sim 2$ for $v \sim 4$ in $a^3\Pi_u$. In the alternative limit, equation (7) gives $L \lesssim 5000$ decreasing to $L \lesssim 10$ for $v \sim 4$ in $a^3\Pi_u$. These estimates suggest that, while the c - X (and other) transition may influence the triplet-to-singlet conversion, the rate seems too slow to cool the $d^3\Pi_g$ vibrational ladder to about 3500 K.

Of course, the excitation rate R_{Xc} is too slow to contribute to the steady-state equilibrium. Hence, the c - X transition operates in one direction only; other transitions may convert singlet to triplet states. Note that the a - X transition can provide limited conversions from singlet to triplet and triplet to singlet as the $a^3\Pi_u$ and $X^1\Sigma_g^+$ vibrational ladders overlap. Radiative excitations $X \rightarrow a$ or $a \rightarrow X$ is prohibitively slow.

iii) *Is Statistical Equilibrium Attained?*

Statistical equilibrium appears valid, as the following sketch demonstrates. Suppose that two electronic states n' and n'' are linked by fluorescence. The rate of excitation $R_{n''n'}$ will be far slower than the rate of de-excitation $A_{n''n'}$ (the Einstein A -value). It is readily shown that

$$a = \frac{R_{n''n'}}{A_{n''n'}} = \frac{1}{4} \left(\frac{R_\odot}{A} \right)^2 \frac{1}{r_H^2 \exp(hv/kT_b) - 1} \quad (8)$$

where r_H (in AU) is the heliocentric distance, the ratio of the astronomical unit to the solar radius $A/R_\odot = 215$, and T_b is the brightness temperature of the Sun at the wavelength $\lambda_{n''n'}$. With $a \ll 1$, an initial population in n' and n'' resulting from the breakup of the parent molecules will be eroded and the steady-state equilibrium achieved on a time scale.

$$\tau_{eq} \sim NR_{n''n'}^{-1},$$

where N is the number of levels within n'' (and n'); see Arpigny (1964), who introduced and justified this heuristic argument with a detailed calculation for the CN $B-X$ violet system. For the C_2 Swan system, we have $R_{n''n'} \sim 0.3 \text{ s}^{-1}$ and $N \sim 100$ or $\tau_{eq} \sim 300 \text{ s}$. The number of vibrational levels is considerably less than 100. The lifetime of a cometary C_2 molecule, $\tau_{tot} \sim 10^5 \text{ s}$ (Delsemme and Moreau 1973; A'Hearn, Thurnber, and Millis 1977), far exceeds τ_{eq} . However, the triplet states responsible for the Swan and Ballik-Ramsay bands are linked to the singlets by weak intercombination transitions which could determine the effective time scale for the C_2 molecule to attain statistical equilibrium in sunlight, but we see from Table 2 that apart from $v' = 0$ in $a^3\Pi_u$, the radiative lifetimes of the $a^3\Pi_u$ and $X^1\Sigma_g^+$ levels satisfy the condition $\tau_{rad} \ll \tau_{tot}$. In short, the C_2 molecules reach a steady-state statistical equilibrium in which all traces of initial populations resulting from breakup of a parent molecule and the distortions produced by selective dissociation are erased.

The excitation rate $R_{ad} \sim 0.3 \text{ s}^{-1}$ for the Swan system shows that vibrational equilibrium should be maintained in spite of the intercombination transitions $a-X$ with the highly vibration-dependent rate of spontaneous de-excitation because $R_{ad} > \sum_v A_{v'v}^{aX}$. This claim, however, ignores a possible contribution to triplet-singlet conversions from transitions such as $c \rightarrow X$. If $L \sim 1000$, the effective time scale $\tau_{cX} \sim \tau_{aX}/L$ (see Table 2 for τ_{aX}) is reduced close to or even below τ_{eq} .

Rotational equilibrium is reached through the electronic transitions, and the estimate $\tau_{eq} \sim 300 \text{ s}$ with $N \sim 100$ covers the necessary time scale. Since $^{12}C_2$ is a homonuclear molecule, pure rotational transitions in the $X^1\Sigma_g^+$ (and other) states are restricted to electric quadrupole (and higher order) transitions providing radiative lifetimes (van Dishoeck and Black 1982) far in excess of τ_{eq} . Hence, the quadrupole transitions have a negligible influence on the statistical equilibrium. Electric dipole transitions are allowed for $^{12}C^{13}C$ owing to a failure of the Born-Oppenheimer approxi-

mation, but again the radiative lifetimes are longer than τ_{eq} (Danks, Lambert, and Arpigny 1974).

IV. THE $^{12}C/^{13}C$ RATIOa) *Introduction*

Precise estimates of the chemical composition of comets and their comparison with the composition of the solar system and the interstellar medium could yield insights into the origin of comets. The molecular emission bands are a potential source of isotopic abundance ratios. Here, we discuss methods for the extraction of the $^{12}C/^{13}C$ ratio from the C_2 Swan bands. Reviewing the analyses of the interstellar molecular lines, Wannier (1980) noted that the interstellar gas near the Sun is characterized by the ratio $^{12}C/^{13}C = 60 \pm 8$; i.e., the gas is enriched by a factor of 1.5 in ^{13}C relative to the solar system, where $^{12}C/^{13}C = 89$. A contemporaneous review (Penzias 1980) proposed a smaller overabundance factor of 1.3 ± 0.2 . More recently, Wilson, Langer, and Goldsmith (1981) analyzed weak millimeter lines of $^{12}C^{18}O$ and $^{13}C^{18}O$ from three dark clouds to obtain a mean ratio $^{12}C/^{13}C = 75 \pm 8$. Owing to chemical fractionation this ratio may be a lower limit. If the solar neighborhood is homogeneous, the $^{12}C/^{13}C$ ratio may after all be very similar to the solar system ratio. Enrichment of ^{13}C is expected as material processed by the CN cycle from stellar interiors is returned to the interstellar medium. If the cometary $^{12}C/^{13}C$ ratio could be measured to high precision and the interstellar medium can be shown to be ^{13}C enriched, an exciting question seems answerable, Are comets outlying members of the solar system or intruders from interstellar space?

b) *The 1-0 Band of the Swan System*

All previous attempts to detect $^{12}C^{13}C$ lines have sought the 1-0 band head of $^{12}C^{13}C$ at 4745 Å. Because of the vibrational isotopic wavelength shift, the $^{12}C^{13}C$ 1-0 head is displaced to the red of the blue-degraded $^{12}C_2$ head at 4737 Å. Figure 3 shows the bands as observed with the McDonald spectrometer and an acetylene flame. For the 0-1 and other bands in the $\Delta v = -1$ sequence, the $^{12}C^{13}C$ bands are displaced to the blue and, therefore, into the $^{12}C_2$ rotational structure. The isotopic wavelength shift is small for the 0-0 bands, and $^{12}C^{13}C$ lines are close to their $^{12}C_2$ equivalents, see below.

In the first attempt at a quantitative analysis of the 4745 Å 1-0 $^{12}C^{13}C$ band head, Stawikowski and Greenstein (1964) noted that this band head was blended with several NH_2 lines. Owen (1973) refined the separation of the NH_2 and $^{12}C^{13}C$ contributions in an analysis of photographic spectra of comet Tago-Sato-Kosaka 1969 IX. Photoelectric spectra of comet Kohoutek 1973 XII at resolutions of 0.14–0.5 Å enabled Danks, Lambert, and Arpigny (1974) to resolve partially the NH_2 lines from the $^{12}C^{13}C$ head. None of these attempts at a determination of the $^{12}C/^{13}C$ ratio have achieved the precision necessary to distinguish solar

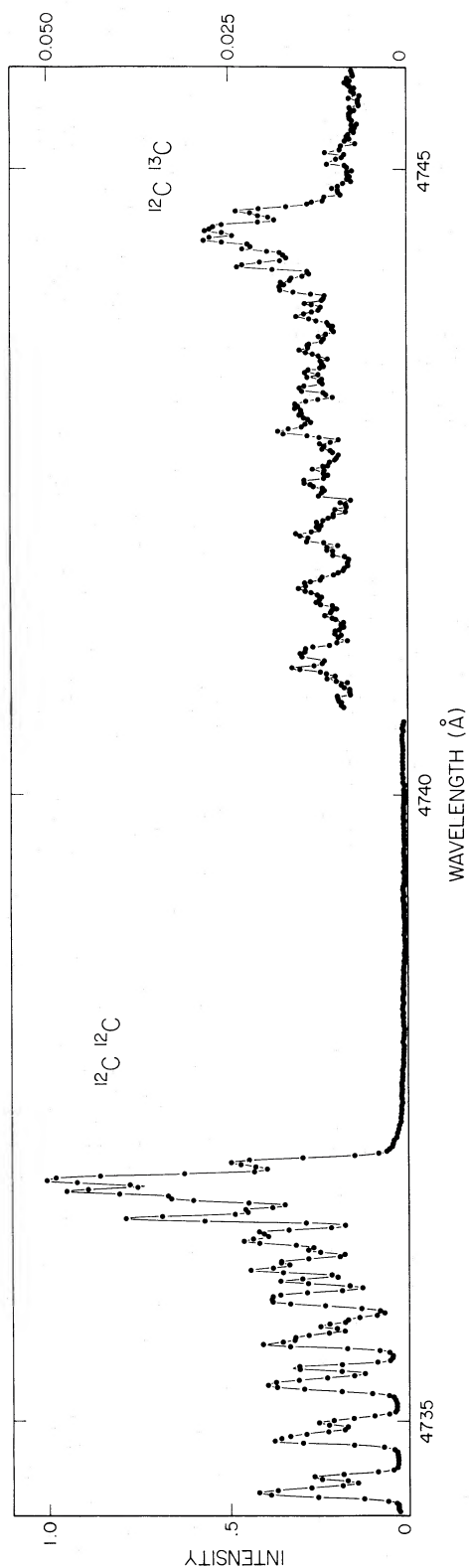


FIG. 3.—The spectrum of an acetylene flame showing the 1–0 band heads of $^{12}\text{C}_2$ and $^{12}\text{C}^{13}\text{C}$. Note the expanded intensity scale for the $^{12}\text{C}^{13}\text{C}$ spectrum.

system and interstellar $^{12}\text{C}/^{13}\text{C}$ ratios. The $^{12}\text{C}^{13}\text{C}$ head has been detected and the $^{12}\text{C}/^{13}\text{C}$ ratio measured to a precision of $\pm 30\%$ – 50% . The keys to a more precise result are (1) cometary spectra of improved resolution and signal-to-noise ratio, (2) a thorough treatment of the resonance fluorescence in $^{12}\text{C}_2$ and $^{12}\text{C}^{13}\text{C}$, and (3) an adequate discussion of the blending NH_2 lines. In this section, we discuss that latter problem.

There are effectively four NH_2 lines blended with the $^{12}\text{C}^{13}\text{C}$ 1–0 head to comprise the 4745 Å feature in cometary spectra. Three NH_2 lines totaling four components were classified by Dressler and Ramsay (1959) as belonging to the (0, 14, 0) band; i.e., (0, 14, 0) $^2A_1$ –(0, 0, 0) $^2B_1$, where $^2A_1$ is the excited state and $^2B_1$ the ground state. The fourth line assigned a rotational classification (Vervloet and Merienne-Lafore 1978) may belong to the (1, 10, 0)–(0, 1, 0) band; the identification of the vibrational level in the $^2B_1$ state is certain, but the designation of the upper vibrational level in $^2A_1$ is not yet certain.

In Figure 4, we show the relative positions of the NH_2 and $^{12}\text{C}^{13}\text{C}$ lines. Two of the NH_2 lines lie to the red of the $^{12}\text{C}^{13}\text{C}$ head. On spectra of moderately high resolution, this pair is resolved from the remaining NH_2 (2 lines)– $^{12}\text{C}^{13}\text{C}$ blend. We have already demonstrated that this resolution is now possible for moderately bright comets (comet Kohoutek 1973 XII, Danks, Lambert, and Arpigny 1974; and comet Kobayashi-Berger-Milon, our unpublished data). Recent improvements to high-resolution spectrometers at several observatories should ensure that spectra at this resolution

are routinely acquired. Therefore, we consider first a procedure for removing the two NH_2 lines from the blend containing the $^{12}\text{C}^{13}\text{C}$ 1–0 head.

The (0, 14, 0)–(0, 0, 0) NH_2 lines near 4745 Å are identified on the partial term diagram (Fig. 5) showing the allowed transitions terminating on the $N = 2$ level in the upper state. In its simplest form, our procedure assumes that the two components of the 2_{12} – 3_{22} doublet at 4745.19 and 4744.89 Å are of equal intensity. In cometary spectra, the latter line is blended with one component of the 2_{11} – 3_{21} doublet, whose other member at 4744.46 Å is blended with the $^{12}\text{C}^{13}\text{C}$ 1–0 head. The intensity of the 4744.89 Å 2_{11} – 3_{21} line is obtained as the difference between the observed 4744.89 and the 4745.19 Å lines. Then, a second application of the assumption that the components of a doublet are of equal intensity provides an estimate of the intensity of the 4744.46 Å line. The small contribution of the other NH_2 line, the newly classified line at 4744.30 Å, could be estimated by observing a line at 4718.04 Å from the same upper state. This latter line appears not to be blended with either other NH_2 or $^{12}\text{C}_2$ lines; we have not checked for possible $^{12}\text{C}^{13}\text{C}$ blends.

The key assumption behind this simple and direct method for separating the NH_2 and $^{12}\text{C}^{13}\text{C}$ contributions to the 4745 Å emission feature is open to observational and theoretical examination. Two or more additional lines, all in the (0, 14, 0)–(0, 0, 0) band, originate from the same upper state as the NH_2 lines at 4745 Å. Although we have not conducted a thorough survey, sufficient lines can probably be resolved on high-resolution (say 0.3 Å) spectra from adjacent $^{12}\text{C}_2$, (weak) $^{12}\text{C}^{13}\text{C}$, and other NH_2 lines to permit the intensity of the 4745 Å NH_2 components to be estimated from the intensity of an NH_2 line sharing the same upper state and a measured or predicted branching ratio. Additional laboratory experiments or theoretical calculations are probably required before the branching ratios are known to adequate accuracy.

A resonance fluorescence calculation for NH_2 would indicate whether a population imbalance in the doublet states occurs as a result of a Fraunhofer line depressing the radiative excitation rate in one or more lines. Such a calculation could be a detailed one, but a cruder calculation might suffice; for example, it might be adequate to describe the population in the (0, 0, 0) $^2B_1$ level by an excitation temperature ($T \sim 200$ K?) and to compute excitation rates into the 2_{11} and 2_{12} levels with due allowance for the Fraunhofer lines. The excitation temperature could be set from the observed relative intensity of the adjacent NH_2 features from $N' = 1$ (4738 Å), $N' = 3$ (4752 Å), and $N' = 4$ (4761 Å).

The proposed scheme for separating the NH_2 lines from the $^{12}\text{C}^{13}\text{C}$ 1–0 band head is, even in its simplest formulation, an improvement on the procedure used by Danks, Lambert, and Arpigny (1974). They adopted laboratory measurements of the NH_2 line intensities without a correction for the different excitation conditions, overlooked the interrelationships between the NH_2 lines, and neglected to account fully for the effects

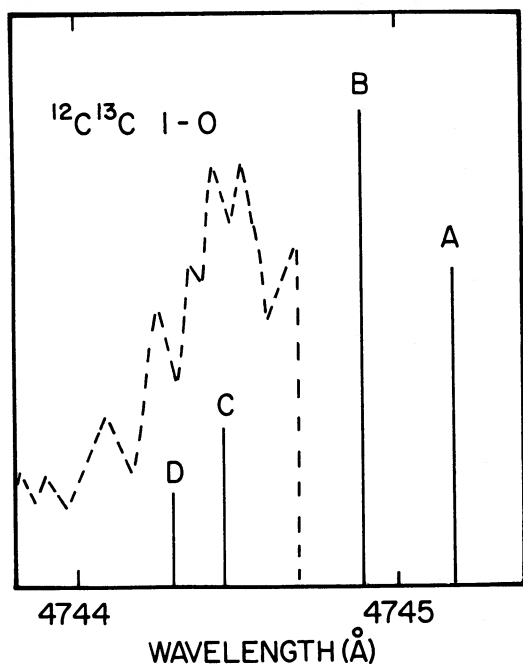


FIG. 4.—A schematic spectrum of the 4745 Å blend of the $^{12}\text{C}^{13}\text{C}$ 1–0 head with NH_2 lines. The NH_2 lines A, B, and C are identified on the term diagram in Fig. 5. The NH_2 line D is discussed in the text.

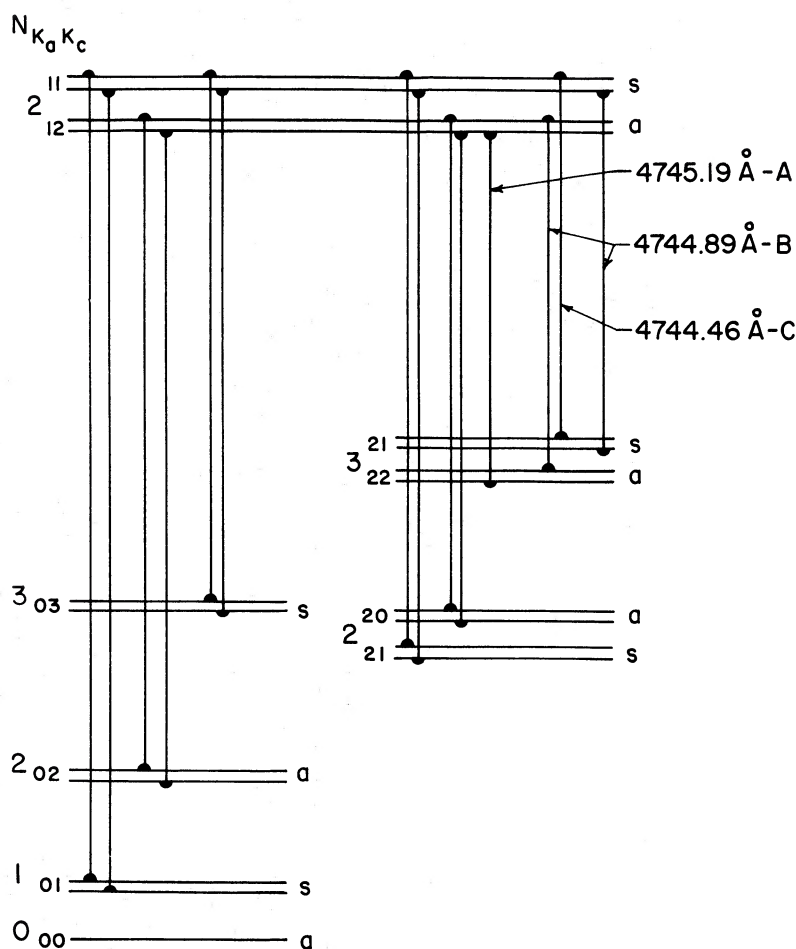


FIG. 5.—A partial term diagram for NH_2 showing the origin of the three lines—A, B, and C in Fig. 4—from the $(0, 14, 0)-(0, 0, 0)$ band that are blended with the $^{12}\text{C}^{13}\text{C}$ 1-0 head at 4745 Å.

of the Fraunhofer lines on the resonance fluorescence in NH_2 . However, our improved scheme would not lead to a drastically different or more accurate estimate of the $^{12}\text{C}/^{13}\text{C}$ ratio in Kohoutek 1973 XII because the weak 4745 Å feature was there dominated by NH_2 , and the uncertainty of the $^{12}\text{C}^{13}\text{C}$ contribution, after NH_2 subtraction, is set primarily by the low total signal.

Variants of our proposed scheme appropriate to very high and low resolution spectra should be noted. At high resolution (i.e., the cometary emission lines are fully resolved), the two NH_2 lines within the $^{12}\text{C}^{13}\text{C}$ 1-0 band will be resolved so that the $^{12}\text{C}^{13}\text{C}$ intensity corresponding to lines within a specified interval of rotational quantum number will be obtainable directly. This possibility should be realizable for the next bright comet.¹ At lower resolution such that the 4745 Å feature is not even partially resolved, the NH_2 contribution

¹ Other obvious possibilities occur for high-resolution spectra. These include searches for the $^{12}\text{C}^{13}\text{C}$ band heads which are intermingled with the $^{12}\text{C}_2$ rotational structure; e.g., the 0-1 and 1-2 bands, which according to Krishna Swamy and O'Dell (1979) are comparable in intensity to the 1-0 and 2-1 bands. We discuss below the $^{12}\text{C}^{13}\text{C}$ lines in the 0-0 band.

corresponding to emission from levels with $N' = 2$ should be estimated by interpolation from the intensities of the $N' = 1, 3, 4, \dots$ features and a calculation of the resonance fluorescence for NH_2 . The small contribution from the 4744.30 Å NH_2 line may be estimated from high-resolution spectra of brighter comets.

c) The 0-0 Band of the Swan System

The 1-0 band is the obvious target for a $^{12}\text{C}/^{13}\text{C}$ determination because the $^{12}\text{C}^{13}\text{C}$ and $^{12}\text{C}_2$ lines are segregated. Unfortunately, NH_2 , not $^{12}\text{C}^{13}\text{C}$, so dominates the cometary emission line at 4745 Å that moderate-to-high resolution is necessary to resolve at least partially the $^{12}\text{C}^{13}\text{C}$ 1-0 band head from the NH_2 lines. At about the same resolution, individual $^{12}\text{C}^{13}\text{C}$ lines in the 0-0 band are resolvable from $^{12}\text{C}_2$ lines. Since the 0-0 band is approximately 4 times more intense than the 1-0 band and several $^{12}\text{C}^{13}\text{C}$ lines should be detectable in a short wavelength interval, the 0-0 band deserves serious consideration in future attempts to determine the $^{12}\text{C}/^{13}\text{C}$ ratio.

Isotopic wavelength shifts in the 0-0 band are sufficiently large that the $^{12}\text{C}^{13}\text{C}$ lines are displaced

clear of their parent $^{12}\text{C}_2$ line. Inspection of the $^{12}\text{C}_2$ and $^{12}\text{C}^{13}\text{C}$ line lists revealed several $^{12}\text{C}^{13}\text{C}$ triplets which should be observable at high resolution. Our search in comet West was limited to portions of the interval between the 1-1 and 0-0 P -branch band heads at 5129 Å and 5164 Å. We obtained spectra at resolutions of 0.10–0.15 Å over approximately 2 Å intervals centered at 5132.2, 5134.6, 5136.3, 5158.0, 5159.1, and 5160.6 Å. This selection includes all but two of the preselected intervals in which $^{12}\text{C}^{13}\text{C}$ triplets might be expected to be resolved at these resolutions. The unobserved regions include the $^{12}\text{C}^{13}\text{C}$ P -branch triplets at 5131.2 Å ($N'' = 47$) and 5142.3 Å ($N'' = 41$).

Our spectrum of the 5158 Å region is shown in Figure 6. The weak lines to the red of P -branch triplet were unexpected and obliterate a candidate $^{12}\text{C}^{13}\text{C}$ P -branch triplet. On reflection, the additional lines were

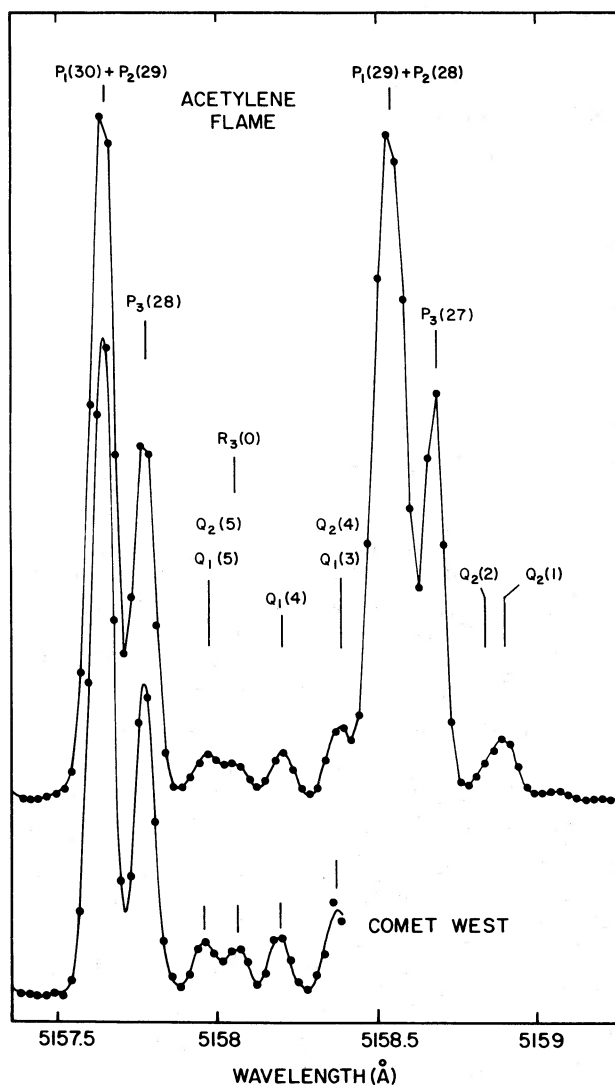


FIG. 6.—High-resolution spectra of comet West and an acetylene flame showing several initial members of the Q_1 - and Q_2 -branches; lines superposed on the P -branch triplets are not identified

identified as the initial members of the Q_1 - and Q_2 -branches; the accompanying Q_3 lines have small rotational line strengths and are not identifiable in our spectra. The standard reference for the Swan system (Phillips and Davis 1968) does not list any Q -branch lines. Our identifications are based upon the laboratory spectra and the wavelengths predicted from the molecular constants. The surprise appearance of these Q -branch lines followed by the realization that other previously unobserved very weak C_2 lines could be superposed on the $^{12}\text{C}^{13}\text{C}$ triplets led us to record the acetylene flame spectrum at the maximum possible resolution. Interfering weak lines include higher members of the Q -branches as well as several satellite lines.

Our highest quality spectra span the $^{12}\text{C}_2$ triplets $P_1(47)$, $P_2(46)$, and $P_3(45)$ and $R_1(18)$, $R_2(17)$, and $R_3(16)$ and include the $^{12}\text{C}^{13}\text{C}$ P -branch triplet (see Fig. 7). A higher resolution flame spectrum shows the $^{12}\text{C}^{13}\text{C}$ triplet resolved into three components and blended with a $^{12}\text{C}_2$ Q -branch triplet. The Λ -type doubling of the $^{12}\text{C}^{13}\text{C}$ lines is clearly resolved. At this resolution, the six components blend into three features, which are labeled a , b , and c in Figure 8. Component c is the line P_{3f} but also includes a small contribution from the satellite $^5R_{32}(10)$. Component b , consisting of three lines P_{1f} , P_{2f} , and P_{3e} , is unblended. The intensity of this feature relative to the $^{12}\text{C}_2$ P triplet yields an isotopic abundance ratio $^{12}\text{C}/^{13}\text{C} = 90$, the expected ratio for a terrestrial sample. Feature a , comprising P_{1e} and P_{2e} , is partially blended with $^{12}\text{C}_2$ $Q_3(27)$. Direct comparison of the intensity of a without a correction for the Q -branch line yields $^{12}\text{C}/^{13}\text{C} = 60$. A definitive correction for the Q line is difficult because we lack a precise wavelength, but as judged by the strength of the neighboring Q_1 and Q_2 lines, the Q_3 line contribution can account for the anomalously low $^{12}\text{C}/^{13}\text{C}$ ratio. Figure 8 also shows other satellite lines. The important message conveyed by this and the other high-resolution spectra is that all weak $^{12}\text{C}_2$ lines must be taken into account—in particular, at moderate resolution, where their direct presence may not be so obvious.

At the resolutions employed in the comet West observations, the $^{12}\text{C}_2$ Q and $^{12}\text{C}^{13}\text{C}$ P triplets are blended. Spectrum synthesis would allow the $^{12}\text{C}^{13}\text{C}$ contribution to be extracted. We employ a similar method on the flame spectrum at this resolution; we measure the equivalent width of the blend and estimate the Q -branch contribution by requiring that the corrected P triplet give the ratio $^{12}\text{C}/^{13}\text{C} = 89$. Then, we assume the same mix of Q and P lines except for a reduction of Q relative to P in the comet arising from the higher vibrational temperature. We obtain $^{12}\text{C}/^{13}\text{C} = 60 \pm 15$. The lower resolution spectrum gives a very similar result: $^{12}\text{C}/^{13}\text{C} = 50 \pm 15$. We assume that $^{12}\text{C}_2$ and $^{12}\text{C}^{13}\text{C}$ are excited similarly in the comet and, in particular, that a straight factor of 2 must be applied in the reductions to account for the Λ -type doubling present in $^{12}\text{C}^{13}\text{C}$ but absent from $^{12}\text{C}_2$. We checked that the excitation of the lines is not obviously affected by Fraunhofer lines and that the underlying continuum

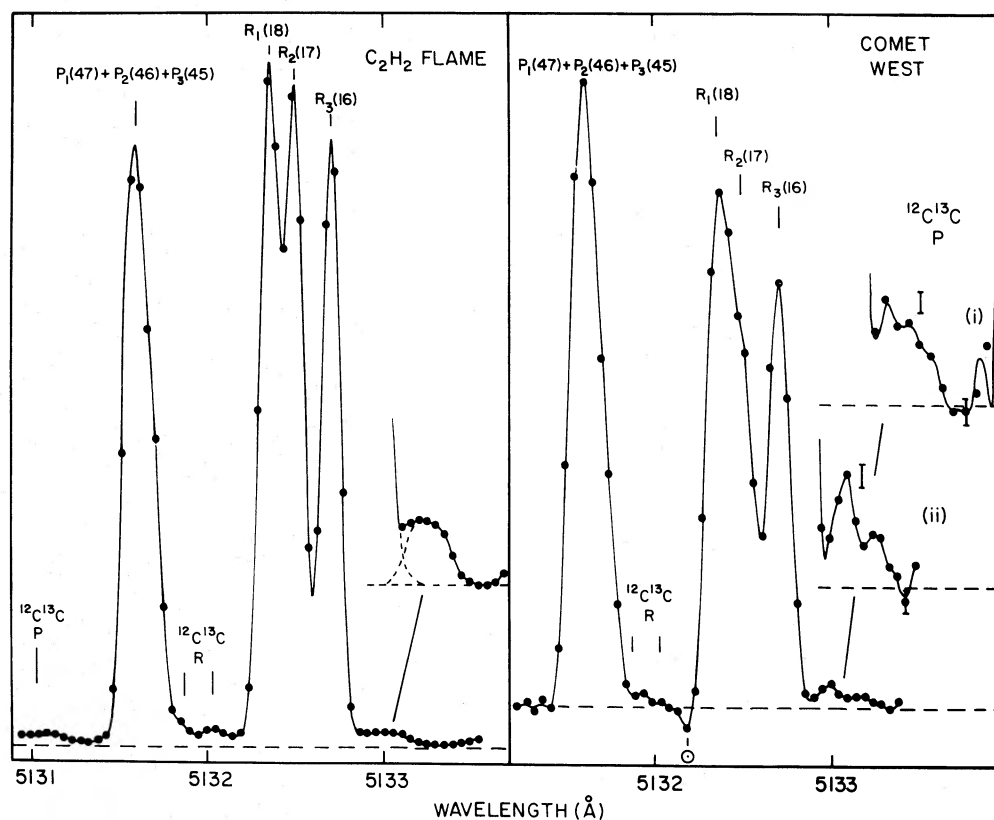


FIG. 7.—High-resolution spectra of comet West and an acetylene flame between 5131 and 5133.4 Å showing weak $^{12}\text{C}^{13}\text{C}$ features. The insets show on an expanded scale ($\times 5$) the $^{12}\text{C}^{13}\text{C}$ $P_1(47) + P_2(46) + P_3(45)$ triplet corresponding to the $^{12}\text{C}_2$ triplet near 5131.6 Å. Inset (ii) corresponds to the full-scale spectrum. Inset (i) is from a slightly lower resolution spectrum. The error bars shown with the insets are estimated from the total comet rate in the continuum and at the peak of the $^{12}\text{C}^{13}\text{C}$ feature.

of scattered sunlight does not contain significant absorption at the $^{12}\text{C}^{13}\text{C}$ lines and the continuum points. These checks and the measurement uncertainties seem to preclude a ratio as high as the terrestrial ratio $^{12}\text{C}/^{13}\text{C} = 89$. However, we cannot exclude a weak unidentified line underlying the measured line. Moreover, our spectra of other potentially useful regions are of insufficient quality to provide a check on the ^{13}C excess in comet West. Therefore, we urge that our result *not* be taken as evidence that the $^{12}\text{C}/^{13}\text{C}$ ratio in comets is closer to the interstellar than to the solar system value. The key point is that we have demonstrated that the 0–0 band is a potential source of an accurate $^{12}\text{C}/^{13}\text{C}$ ratio for bright comets.

Unfortunately, our spectra centered at 5134.6 and 5136.3 Å are not of sufficient quality to confirm the $^{12}\text{C}/^{13}\text{C}$ determination. The spectrum at 5134.6 Å (Fig. 9) has a rather low signal-to-noise ratio and the baseline is not well defined. The peak signal in the $^{12}\text{C}_2$ emission lines is approximately equal to the continuum signal in the first region, centered at 5132 Å. The $^{12}\text{C}^{13}\text{C}$ P -branch triplet is seen with evidence also of the triplet $R_1(18)$, $R_2(17)$, and $R_3(16)$. In this region, the $^{12}\text{C}^{13}\text{C}$ P lines appear to be free of blending with weak $^{12}\text{C}_2$ lines, and also, the continuum is well defined to

the red. Hence, this region is a prime candidate for reobservation in the next bright comet. In Figure 9, the $^{12}\text{C}_2$ $R_2(16)$ appears anomalously weak. Inspection of the solar spectrum at the Doppler-shifted wavelength seen by the comet shows that this line coincides with a strong solar line at 5133.7 Å so that the excitation rate is depressed relative to the rates for the neighbouring $R_1(17)$ and $R_3(15)$ lines. Of course, the same solar line appears in the scattered solar spectrum upon which the emission lines sit.

In the third region (Fig. 10), with a central wavelength of 5136.3 Å, the $^{12}\text{C}^{13}\text{C}$ lines are seen as expected, but again the spectrum is too noisy to permit a $^{12}\text{C}/^{13}\text{C}$ determination. The $^{12}\text{C}^{13}\text{C}$ P lines are approaching the $^{12}\text{C}_2$ R_3 line so that higher resolution will be needed here to effect an adequate separation of the $^{12}\text{C}^{13}\text{C}$ and the $^{12}\text{C}_2$ lines.

The following $^{12}\text{C}^{13}\text{C}$ P -branch triplets were not examined in either the comet or the acetylene flame but would appear to be potential candidates: $N'' = 45$ at 5131.2 Å, $N'' = 43$ at 5138.8 Å, and $N'' = 27$ at 5159.8 Å. This trio and the three illustrated in Figures 7, 9, and 10 are all of the useful $^{12}\text{C}^{13}\text{C}$ P -branch triplets between $N'' = 47$ and $N'' = 26$. For $N'' \leq 25$, the crowding of the $^{12}\text{C}_2$ lines precludes detection of $^{12}\text{C}^{13}\text{C}$ lines except at

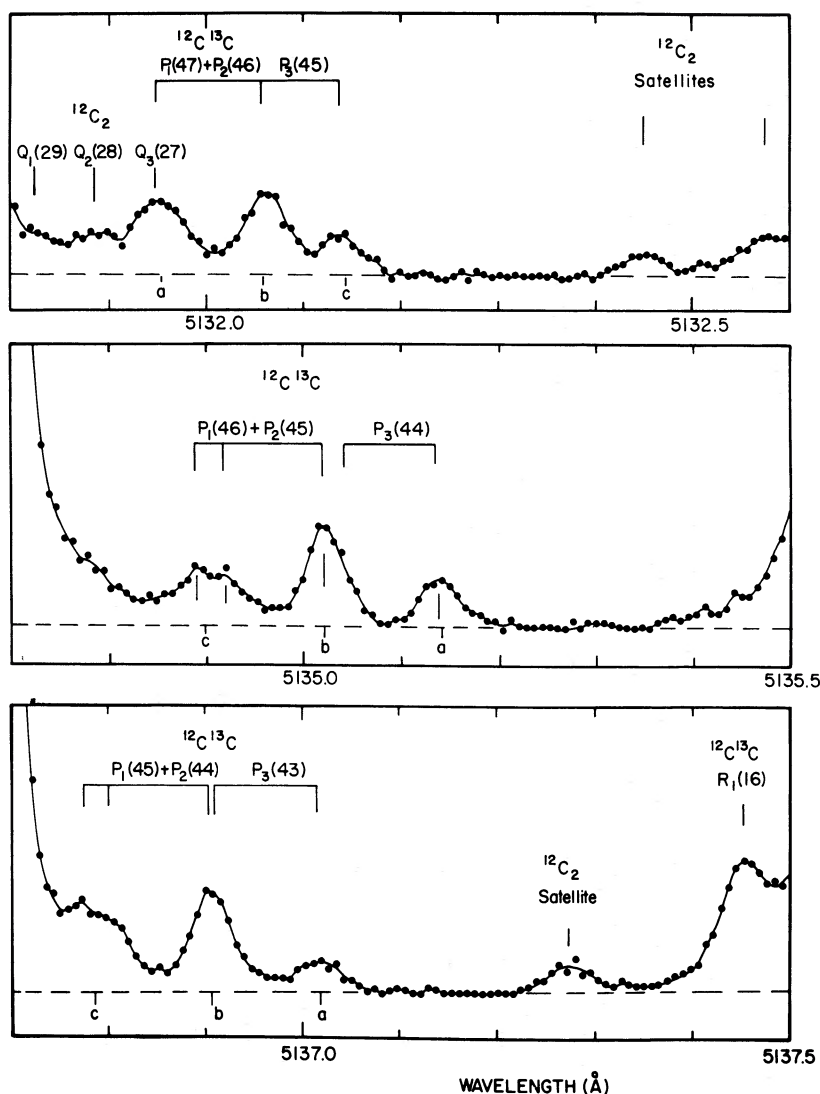


FIG. 8.—High-resolution spectra of an acetylene flame showing three $^{12}\text{C}^{13}\text{C}$ P -branch triplets, which are resolved into three principal components (a , b , and c), and weak $^{12}\text{C}_2$ lines of either the Q or satellite branches

very high resolution. For $N'' \geq 48$, these P -branch lines of the 0-0 band are overlapped by the 1-1 band, and again detection of $^{12}\text{C}^{13}\text{C}$ lines will require high resolution. We shall not review in detail the potentially detectable $^{12}\text{C}^{13}\text{C}$ lines. Several are good candidates, especially at a resolution somewhat higher than 0.1 Å.

The high-resolution spectra may also provide interesting information on the relative line intensities.² As noted earlier (see Fig. 9) the intensity of a line is reduced when a deep Fraunhofer line is Doppler shifted into coincidence with one of the principal transitions feeding the upper level. A comparison of the acetylene flame and comet spectra in Figures 7 and 10 shows that the $R_2(15)$ and $R_2(17)$ lines in the comet are about 20% weaker than the adjacent R_1 and R_3 lines. The apparent anomaly may reflect the coincidence of the $R_2(11)$ and $R_2(13)$ lines with strong Fraunhofer lines. Thanks to the domi-

nance of the P - and R -branches, the rotational structure is almost completely separable into two noncommunicating ladders corresponding to even $J''/\text{odd } J'$ and

² Nieuwpoort and Bleekrode (1969) discussed an intensity alternation seen in the emission lines of the 0-0 band P -branch produced in a low-pressure oxyacetylene flame. They proposed that the alternation reflects a population distortion caused by collision-induced transition between the $d^3\Pi_g$ state and $b^3\Sigma_g^-$ and $c^3\Sigma_g^+$. Our flame spectra appear to confirm their observation of an intensity alternation when intensities are judged by the peak of the $P_1 + P_2$ blend. At high resolution, the doublets with the higher peaks are noticeably narrower. The equivalent widths of the lines do not show the alternation, and adjacent lines have identical equivalent widths to within the measurement errors of a few percent. Meinel and Messerle (1968) investigated the "high-pressure" Swan system bands and also failed to find an intensity alternation. The alternation of peak (not integrated) intensity reflects the alternations in the Λ -type doubling expected for a homonuclear molecule with zero nuclear spin (Bleekrode 1977).

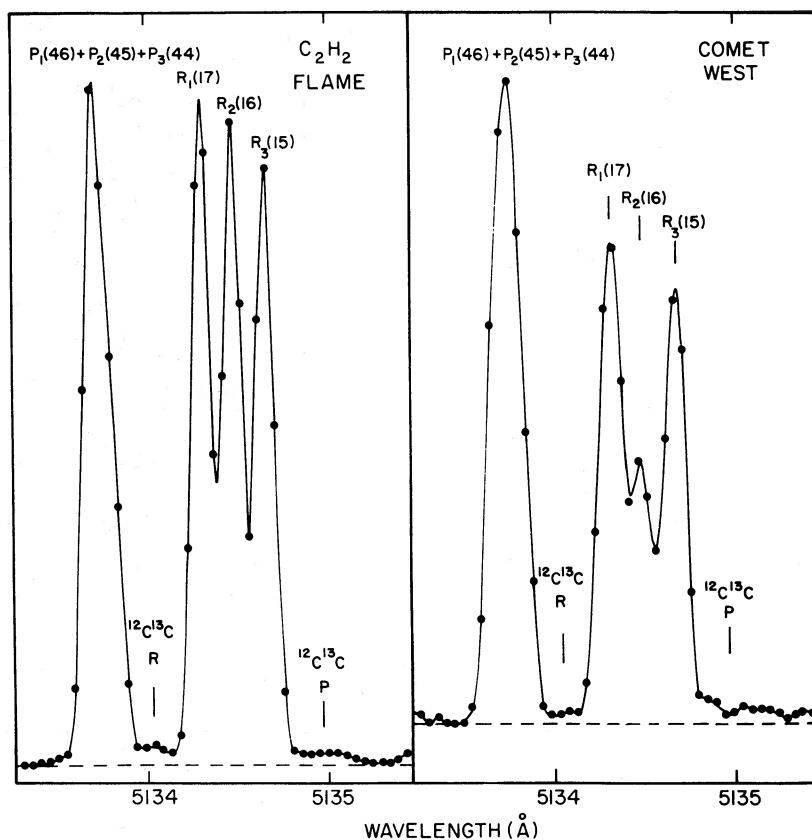


FIG. 9.—High-resolution spectra of comet West and an acetylene flame between 5133.5 and 5135.5 Å

odd J'' /even J'' . Then, the strong absorption line coincident with $R_2(1)$ will affect neighboring even J'' R and P lines but not the adjacent odd J'' lines. At very low J'' , satellite and Q -branch lines couple the odd and even $J''(J')$ levels.

In Figure 6, $P_3(28)$ appears anomalously weak relative to the blend of $P_1(30)$ and $P_2(29)$; note the intensity ratio of the blend $P_1(27)$, $P_1(26)$, and $P_3(1)$ to $P_3(25)$ is within a few percent of the predicted ratio (Fig. 11). The reduced intensity of $P_3(28)$ is not obviously attributable to the influence of Fraunhofer lines on radiative excitation out of $^3\Pi_0$ ($v'' = 0$, $J'' = 28$) and adjacent levels.

In Figures 7, 9, and 10, the ratio of the P triplet to the R_3 line is consistent with an excitation temperature of 3000–3500 K. However, the ratio of $P_2(2)$ [or $P_1(3)$] to $P_3(25)$ corresponds to the low excitation temperature of 1400 K. These low P lines and also the Q -branch lines (Fig. 6) suggest that the lowest rotational levels in $v'' = 0$ are overpopulated relative to the higher levels. The excellence of the fit to the 1–0 band profile with an assumption of a single excitation temperature suggests that the anomalous overpopulation of low levels is restricted to the few lowest rotational levels.

When thorough coverage of the spectrum at high resolution is available, it may be possible to detect differences between lines arising from $^3\Pi_0$, $^3\Pi_1$, and $^3\Pi_2$. The rate for spontaneous emission in the $a^3\Pi_u-X^1\Sigma_g^+$ transition is highest for $^3\Pi_1$ at low J and for $^3\Pi_0$ and $^3\Pi_2$ at high J . Radiative excitation in the Swan (and Ballik-Ramsay) systems couples $^3\Pi_0$, $^3\Pi_1$, and $^3\Pi_2$ through the weak satellite branches. We may expect the Ω -related differences in the $a-X$ rate to produce a correlated intensity difference in the Swan bands provided that spontaneous emission occurs faster than the transfer rate between the $\Omega = 0, 1$, and 2 levels of $a^3\Pi_u$. For example, at $J'' \sim 15$, approximately 200 excitations are needed before a $^3\Pi_1$ to $^3\Pi_0$ or $^3\Pi_2$ transfer is effected. This time scale of about 200 $R_{ad}^{-1} \sim 700$ s is considerably shorter than the expected radiative lifetimes of the low vibrational levels (Table 2). Hence, it is unlikely that the $a-X$ transition can be held accountable for the anomalously low intensity of $R_2(15)$ and $R_2(17)$. However, as discussed earlier, intercombination transitions involving excited states might reduce the effective time scale for a triplet-to-singlet conversion. The search for the $a-X$ related intensity effects should concentrate on the higher members of a

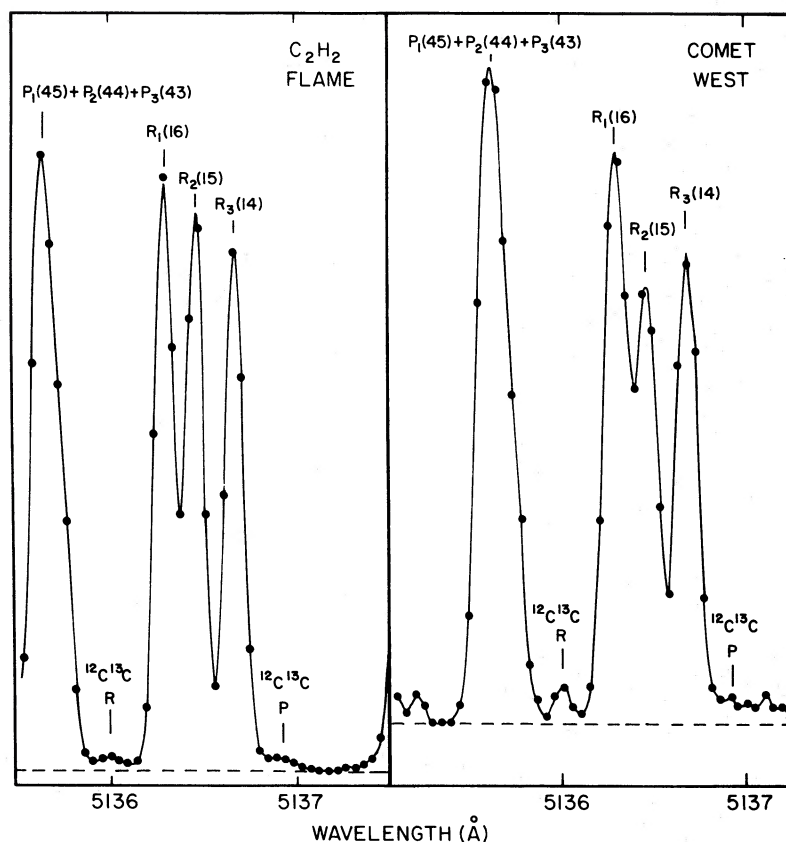


FIG. 10.—High-resolution spectra of comet West and an acetylene flame between 5135.0 and 5137.2 Å

vibrational sequence, say $v'' \gtrsim 3$. This search might look first at lines away from the band origin because the strength of the satellite to main branches for low rotational levels is quite high, and the intensity differences may be erased. Certainly, Figures 7 and 11 show the initial members of the *P*- and *Q*-branches having intensities consistent with their line strengths.

V. CONCLUDING REMARKS

Our analysis of the C_2 Swan $\Delta v = -1$ sequence provides an excitation temperature, $T_{\text{exc}} = 3500$ K, for comet West at $r_H = 0.78$ AU that is considerably cooler than the vibrational temperature predicted by two recent calculations describing cometary C_2 molecules bathed in sunlight. The observed and predicted temperatures may be forced into agreement by increasing the electronic transition moment for the $a-X$ intercombination transition to $|R_e|^2 \sim 10^{-4}$. However, our estimates of this transition moment indicate $|R_e|^2 \sim 10^{-7}$, leaving the observed vibrational temperature unexplained. We have suggested that intercombination transitions involving excited states may be important in the singlet-triplet conversions and influence the vibrational temperature achieved in the $a^3\Pi_u$ state. This suggestion cannot yet

be tested thoroughly because estimates of the transition probabilities are unavailable. We would hope that ab initio calculations for C_2 could be extended to the $a-X$, $d-c$, $c-X$, and other transitions.

With the advent of a new generation of detectors in fast high-resolution spectrometers, cometary spectroscopy offers new challenge. Important observational problems include a complete specification of the population across the electronic and vibronic structure as a comet changes its heliocentric distance. Observations close to the nucleus may reveal the nonequilibrium populations created as C_2 is released by parent molecules. Observations near the outer limit of the zone inhabited by C_2 may reveal selectivity in the destruction of C_2 . Between these inner and outer zones, the C_2 molecule is predicted on present assumptions to attain a statistical equilibrium condition set uniquely by the comet's heliocentric distance. If observations of several comets reveal that the relation between the excitation temperatures and the heliocentric distance is not the same for all comets, the basic assumptions must be doubted and new questions answered: Are collisional processes significant for some comets? Is the cometary cloud truly optically thin to C_2 line radiation? Is statistical equilibrium rapidly achieved?

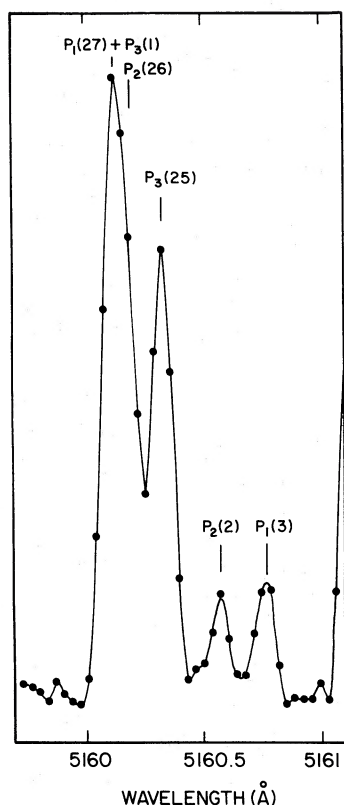


FIG. 11.—A high-resolution spectrum of comet West between 5159.6 and 5161.0 Å

This study has demonstrated that high-resolution spectra of the 0-0 Swan band will provide an accurate determination of the $^{12}\text{C}/^{13}\text{C}$ ratio. The spectral resolution should, if possible, slightly exceed that employed on comet West; the higher resolution would provide better defined $^{12}\text{C}^{13}\text{C}$ lines and key continuum points. As the quality of cometary spectra improves, the analysis must keep pace. In particular, the statistical equilibrium calculations should be extended to include the detailed Fraunhofer spectrum and the rotational structure. If possible, the $^{12}\text{C}/^{13}\text{C}$ determination should be confirmed using another molecule or another C_2 transition.

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A. C. DANKS: European Southern Observatory, Casilla 16317, Santiago 9, Chile

D. L. LAMBERT: Department of Astronomy, University of Texas, Austin, TX 78712