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Spectra of Comets and the Abundance of CO₂ or Molecules
Containing the CO Group in Comets**

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TRIPLET TRANSITIONS OF NEUTRAL CO IN THE SPECTRA OF COMETS AND THE ABUNDANCE OF CO₂ OR MOLECULES CONTAINING THE CO GROUP IN COMETS

by

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ABSTRACT

The high-dispersion spectra of comet Mrkos (1957 V) taken at Mt. Palomar by J. L. Greenstein and remeasured by A. Woszczyk contain many unidentified weak lines. The possibility that some of these lines belong to transitions between triplet levels of neutral CO molecules is investigated. Their presence would suggest excitation related to the dissociative recombination of a parent containing the CO group, which is first ionized by solar uv. Of 31 CO lines (of the Asundi and Triplet systems), 14 are masked by known or by questionably identified lines as statistically expected. Of the remaining 17, 13 coincide within a few tenths of an Ångström with an unidentified line and 4 do not. These results are contrary to statistical expectations. (Some members of the third positive system of CO, which might be present, have not been included in the figures.)

Although these figures strongly favor the identification proposed, the numbers are not large enough to support entirely the argument of a small statistical probability (0.2%) of the observed state. Also, the rotational structure of the CO bands for the triplet systems needs further investigation.

C. F. Lillie's observations of comet Bennett (1970 II) between 1200 and 1800 Å, especially of the fourth positive system of CO, seem to favor a cometary atmosphere characterized by a large relative abundance of CO₂ and/or molecules containing the CO group. A model outlined for comet Bennett at 0.8 a.u. seems to be approximately consistent with observations. The chemical aspects, however, especially need further consideration. New observations, particularly of the Cameron bands of CO, are needed to settle the questions raised.

I. INTRODUCTION

In his recent studies on the OAO spectra of comet Bennett (1970 II), Lillie noted the similarity of spectral emission features in the 1200- to 1800-Å range not caused by H I, O I, C I, or C II in the comet's

spectrum and those of Venus and Mars, which have essentially CO₂ atmospheres. These emission lines belong to CO. Based on the most straightforward interpretation of OAO data, their intensity would suggest a CO production rate almost 10 times as high as that of H₂O. An alternative, suggested by the

spectral observations of Venus' and Mars' atmospheres, is that besides recombination of atomic carbon and oxygen (which should be unimportant in cometary atmospheres), dissociative recombination of CO_2 ions (or ions of some other molecules containing the CO group produced by solar uv) and excitation in that process may be the cause. Lillie¹ also found, in the same spectra, more hydrogen than could arise from dissociation of OH.

Although CO_2 has been suspected of being a major constituent of cometary gases,^{2,3} detecting it by spectroscopy is difficult. Wehinger and Wyckoff⁴ found that in the innermost parts of comet Kohoutek's (1973 XII) coma CO ions were more abundant than H_2O ions (and those of CH and H_2) by a factor of ≥ 100 . This finding is difficult to explain without assuming a large relative abundance of CO or CO_2 or some other molecule producing CO by dissociation—including dissociative recombination.

The question of interest is whether or not lines due to transitions between two triplet electronic states (or between an upper triplet state and the singlet ground state of CO) occur in cometary spectra. Fluorescence excitation, leading to one of the higher triplet levels, from the ground state is so unlikely that different modes of origin should also be considered. These should include dissociative recombination of the CO_2 ion (or some similar ion) or collisional excitation from the ground state of CO, which would require high electron densities and temperatures.* Even then, an abundance of CO_2 (or some other parent of CO) at least as great as that of water is required, which raises other interesting questions. Because of the many initial states in question, only weak intensities would be expected for such lines in the optical range.

II. OBSERVATIONAL DATA AND THEIR INTERPRETATION

A comparison of observational lists such as those in Richter's⁶ monograph (Appendix, Table VII) and

*The observed isophotes of C_2 and CN emission lines, for example, of comet Bennett (1970 II),⁵ do not indicate any collisional dissociation in the inner coma. This limits the electron flux that can be postulated to $\sim 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$.

Pearse and Gaydon's⁷ laboratory data reveals several coincidences within a few tenths of an Ångström, which is outside statistical expectation. Nevertheless, these results are not convincing^{8,9} particularly because of the inhomogeneity and incompleteness of the cometary and laboratory data.

In this report we compare Woszczyk's¹⁰ list of cometary emission lines (which had been modified, wherever possible, to give the mean between his and Greenstein and Arpigny's¹¹ earlier data) with data from Krupenie's¹² report and with additional data from some of the papers quoted therein.

The spectra of the dusty comet Mrkos (1957 V), measured by Woszczyk,¹⁰ were taken by J. Greenstein with the 200-in Hale telescope on Mt. Palomar when the comet's distance from the sun, R, was $0.564 \pm 0.005 \text{ a.u.}$ and $dR/dt = +34 \text{ km/s}$ ($z = 1.08 \text{ a.u.}$). Greenstein and Arpigny¹¹ measured the plates independently, but they did not include many weak lines considered unidentifiable though probably real. Therefore, only Woszczyk's¹⁰ list was used for this study. Most of his wavelength (λ) values should be accurate to within $0.1 - 0.2 \text{ Å}$, depending on the intensity and profile of the line and the influence of the solar continuum reflected by the comet's dust particles. The wavelengths of the weakest lines should, of course, be less accurate.

Table I contains all CO triplet system bands (the upper level is $d^{3}\Sigma_u^-$) with wavelengths of $5300 - 6500 \text{ Å}$, for which the vibrational quantum number of the lower, v'' , is 0. (For the one transition to $v'' = 1$ in that interval, the Franck Condon factor is of order 10^{-3} .) Merton and Johnson's¹³ and Herman and Herman's¹⁴ data (index M+J or H+H) are given first. NID denotes an unidentified line in Woszczyk's¹⁰ list (index W). The last column gives data on the spectral density, the number of unidentified lines, or lines with questionable identification (?) in Woszczyk's¹⁰ list; d denotes a double line. Following L. Haser's¹⁵ suggestion, a double line is supposed to consist of two approximately equal components 0.8 Å apart (for $\Delta\lambda \geq 1 \text{ Å}$ Woszczyk has evidently counted them as two lines).

Woszczyk's list also covers the shorter wavelength range ($4700 - 5300 \text{ Å}$), which could not be reached by dissociative recombination of CO_2 .* In this range, there are more triplet lines of CO, some of which

*The line width on the plate should be $0.75 - 1 \text{ Å}$ for simple weak emission lines (dispersion 27 Å/mm).

TABLE I
CO TRIPLET - SYSTEM

$v' - v''$	λ_{M+J}	λ_{H+H}	λ_W	$\Delta\lambda$	Int.	Identif.	Lines per Å
6, 0	5307.2		5307.51	+0.3	1	NID	26 1 / 60 Å; (5 d)
	5309.5		5308.68	-0.4 ^a	2d	"	24 NID; (4 d)
	5330.5	5330.5	5330.80	+0.3	2m	"	1 ?; (1 d)
	5351.3	5351.2	5351.22	0.0		"	1NH ₂ ; (0 d)
5, 0	5621.7		5621.27	(0.0) ^a	2d	C ₂ ; NH ₂	41 1 / 55 Å; (9 d)
	5626.0		5625.78	(-0.2)	2; 3	C ₂	17 NiD; (2 d)
	5647.6	5647.6	5648.03	+0.4	1	NID	5 ?; (0 d)
	5670.5	5670.5	5669.80	(+0.3) ^a	0d	NH ₂	
4, 0	5980.7		5981.56	-	2, 0	C ₂	38 1 / 60 Å; (4 d)
	-		-	-	-	-	1 NID; (1 d)
	6010.5	6010.5	6010.4	(+0.1)	1m	C ₂	3 ?; (0 d)
	6037.0	6037.0	6037.12	(+0.1)	2N	NH ₂ , C ₂	
3, 0	6399.0	6401.0	6399.79	-	1n	NH ₂	44 1 / 75 Å; (4 d)
	6403.8		6403.46	-0.3	2	NID	9 NID; (1 d)
	6433.1	6433.1	-	-	-	-	13 ?; (0 d)
	6464.6	6464.6	6464.6	0.0±0.4	1d	NID	

^aRed component $\lambda = 0.4$

could be present in the comet, but, because of chance coincidences with other known emissions, their presence cannot be established with certainty. We note again the difficulties arising from the solar Fraunhofer lines in the dust continuum, which should increase with decreasing wavelength.

Table II presents data for all transitions between 5700 and 6500 Å for the Asundi band systems ($a'^3\Sigma^+ - a''^3\Pi$). The index Kr refers to Krupenie's¹² list. The metastable lower electronic state (the same as for the Triplet system) is connected to the ground state of CO by the Cameron bands near 2000 Å.

Between 5700 and 5200 Å is the 11-0 transition at 5256.2 and 5237.8 Å (the three other lines have not been found in laboratory data). The first line coincides with the blue component of the 1d NID line at 5256.8 Å ($\Delta = 0.2$ Å), whereas the other line has no counterpart. The Franck Condon factor for this transition is only 1.2%, compared with 5.0% for the 11-1 transition. This circumstance is probably partly responsible for the incompleteness of the laboratory

data. Therefore it was not included in Table II. Furthermore, the $v' = 11$ state has a higher energy by several 0.01 eV than the $v' = 6$ state of the d $^3\Delta$, electronic state.

We omitted lines for which the wavelength is given only to 1 Å (two in the Asundi system) for statistical reasons, and the line 5888.7 Å, because of the very high intensity (50 in Woszczyk's scale) of the cometary sodium emission line (whose nearer component is only 1.2 Å away) and because of the proximity of the Doppler-shifted solar sodium D absorption line.* That leaves 31 lines—16 in the Asundi system and 15 in the Triplet system. Eleven of them coincide within about 0.4 Å with a C₂ or NH₂ line, and three coincide with a line of questionable identity according to Woszczyk. (The NH₂ line in the Asundi system near 6275 Å for which the difference is 0.55

*These three cases are indicated by enclosing the wavelength within brackets on first mention.

TABLE II
CO ASUNDI - SYSTEM

$v' - v''$	λ_{Kr}	λ_W	$\Delta\lambda$ (Å)	Int.	Identif.	Lines per Å
11, 1		5745.17	-0.4 ^a	1d	NID	21 1 / 35 Å; (6 d)
	5746.0	5746.49	+ .2 ^a	2d	"	12 NID; (4 d)
	(5761)	5760.81	(-)	0N	NH ₂	4 ?; 0 d
	5769.7	5769.3	(0.0) ^a	1d	"	
	5773.5	5773.71	(+0.2)	1N	" ?	
	5779.6	5778.6	-	21	NID	
9, 0	5855.8	5855.75	-0.1	1LN	NID	14 1 / 30 Å; (2+1?d)
	5869.4	5869.9	+0.5(1?)	2d ?	"	6 NID; (1+1? d)
	5876.2	5875.75	-0.45	1;0?	"	7 ?; (1 d)
	(5888.7)	5889.94	50 D of Na (see text)			
10, 1	6105.2	6105.56	(+0.36)	1; 5	C ₂	22 1 / 35 Å; (7 d)
	6119.0	6118.4	(+0.2) ^a	2d	C ₂ · NH ₂	2 NID; (0 d)
	6127.5	6127.39	-0.1	1	NID	8 ?; 5 d
	6135.0	6135.12	(+0.1)	3	C ₂	
8, 0	6244.7	6244.50	(-0.2)	2dL	NH ₂ ?	15 1 / 40 Å; (7 d)
	6257.8	6257.9	(+0.1)	2m	NH ₂	2 NID; (2 d)
	6275.0	6274.45	(+0.55)	3mN	"	4 ?; 3 d
9, 1	6513.5	6513.17	(+0.3)	2mn	" ? (see text)	25 1 / 45 Å; (2 d)
	(6530)	6530.03	(-)	1N	NID	8 NID; (1 d)
	6551.0	6550.79	-0.2	3n	"	12 ?; 1 d

^aRed or violet component ($\lambda + 0.4$ or $\lambda - 0.4$, respectively).

Å, is a 3-mN line.)^{*} Of the remaining 17 lines, 13 coincide within the same limits with an unidentified line, whereas 4 do not (line 5779 Å in the Asundi system and lines 5980, 6399, and 6433 Å in the Triplet system). For the last three lines the nearest probable counterpart is at least 0.8 Å away toward longer wavelengths.

To compare these results with statistical expectation, we first sum all known and dubiously identified lines, counting double lines as 2 lines, and assuming that each of the 196 components (of 165 lines) covers 1 Å. We are probably exaggerating the influence of

the double lines, to include in a simple way the somewhat greater width of the several dozen lines indexed as m(multiple), n(nebulous), and N(very nebulous). The 196 Å thus found represent 45% of the total interval of 435 Å, so the number of identified and dubious lines (14 out of 31) is exactly as expected. In the remaining 239 Å, we have 81 unidentified lines with 96 components. If we again ascribe 1 Å to each component, 40% of the wavelength interval is covered, whereas 60% (143 Å) is gaps. That is, in 60% of the wavelength interval 4 expected CO lines do not appear, whereas in the 40% covered by unidentified lines 13 appear. If the wavelength intervals were equal, the statistical probabilities of this distribution would be given by the binomial coefficient (17) divided by 2^{17} , or about

^{*}Wavelength differences $\Delta\lambda$ for partially identified lines are shown in brackets.

1%.* Because the two wavelength intervals differ (40 and 60%, respectively), the statistical probability of the observed distribution is smaller yet (0.2%). Thus, the statistics strongly favor the interpretation that most of the CO lines in question are present, but the numbers are not quite large enough for absolute certainty.

We note that for comet Ikeya (1936a), Arpigny¹⁶ lists only 20 lines between 3690 and 3845 Å, all of which are as yet unidentified; 3 of them coincide, within 0.14 Å or less, with known CO lines of the third positive system ($b\ ^3\Sigma^+ - a\ ^3\Pi$). The statistical probability of this happening by chance is obviously small; in this case three out of five weak CO lines in this range are possibly seen. If this identification could be confirmed, their upper levels would require for their excitation, ~1 eV higher energies than the lines considered so far.

The problem of the rotational structure of the CO lines in question remains. In view of the probably quite different excitation conditions,** there is no reason to expect any detailed similarity of the rotational structure with that found in the laboratory. A study analogous to Arpigny's¹⁶ on CN is impossible without a hypothesis about the initial distribution over the rotational states, which in this case should largely determine the rotational structure of the bands.

For the Triplet system the wavelengths of the rotational lines have been published by Gerö and Szabó¹⁷ for the vibrational transitions 3-0, 4-0, 6-0, 7-0, and 9-1 and by Carroll¹⁸ for the vibrational transition 3-0. Their tables show that for most of the heads that Merton and Johnson¹³ and Herman and Herman¹⁴ list, the λ -splitting is too large and the rotational splitting too small to permit a resolution on the Palomar plates of comet Mrkos. Moreover, in some of the tables the exact relation is not clear bet-

ween Herman and Herman's¹⁴ measurements, which generally agree with earlier ones by Merton and Johnson,¹³ and those given by Gerö and Szabó.¹⁷ See, for example, the band R_{13} for the vibrational transition 6-0 (counted as in Krupenie's¹² report). Herman and Herman's¹⁴ value of 18682.1 cm⁻¹ agrees with that of Merton and Johnson¹³ (18682) and with that of an unidentified line in the comet's Palomar spectrum, whereas the branch in question begins in Gerö and Szabó's¹⁷ table where v' is still given as 3) with 18680.5 and further values decrease as J increases.

On the other hand, for the vibrational transitions 3-0, for which Carroll's¹⁸ measurements agree essentially with earlier ones (cf. Gerö and Szabó¹⁷), most of the transitions from $J = 4$ (6464.6 Å) to $J = 8$ (6474.8 Å) of the same branch appear to be present in the comet's spectrum. Three of them ($J = 4, 5$, and 8) coincide within a quarter of an Ångström with an unidentified line in the cometary spectra; a fourth ($J = 6$) coincides approximately with a NH₂ line (intensity 2d); and a fifth ($J = 7$) is in the immediate vicinity of a solar absorption line, such that the continuous background is probably disturbed. Carroll's intensity values for the 3-0 transition appear to indicate a distribution over the various bands and the J values rather different from those pertaining to earlier measurements by Merton and Johnson¹³ and Herman and Herman.¹⁴ More band heads in Gerö and Szabó's¹⁷ list coincide with NID or known lines in Woszczyk's list, for instance, that of the R_2 band in the 6-0 transition (in Gerö and Szabó 3-0) at 18754.6 cm⁻¹ ($J = 2$), or rather the four lines between 18754.3 ($J = 1$) and 18753.1 ($J = 4$) together with a 2m NID line at 18753.7 cm⁻¹ (5330.8 Å) and similarly, the head (at $J = 3$) of the R_{32} band at 18794.6 cm⁻¹, with the NID line of intensity 1 also at 18794.6 cm⁻¹ (5319.2 Å). However, these cases are not convincing enough to warrant any further statement before the original plates are reinspected from this point of view.

III. EXCITATION MECHANISMS

The lowest level of the $a\ ^3\Pi$ terms connects with the singlet ground state of CO by the 0-0 lines of the Cameron system at 2062 Å, which is 6.01 eV above the ground state. A line at about 5308 Å corresponds

*Other ways to determine a numerical value for the statistical probability have been considered. They also lead to values of about 1%. I am greatly indebted to E. Meyer for advice on this matter.

**The electronic transition is faster than any spontaneous change of v or J (rotational quantum number), and also than any change of v or J by collision. This does not apply to the Cameron band system.

to a transition from a level 2.33 eV higher, that is, at 8.34 eV above the ground state;* there is very little solar continuum radiation available for radiative excitations. The lowest a ³II levels (which are common to all the band systems that seem to be present in the optical range) have a lifetime of ≤ 10 ms.

According to investigations presented at the last Goddard symposium on comets (November 1974),¹⁹ the photoelectrons lose their energy so rapidly in the inner part of a comet's coma that their average kinetic energy cannot be high enough to collisionally excite CO molecules to the levels in question.** We assume, therefore, that collisional excitations by electrons are not significant in the appearance of these band systems. The electron temperature that determines dissociative recombination is considered to be about 0.1 or 0.2 eV in the inner parts (such that the rate constants should be of corresponding order or somewhat smaller than under laboratory conditions); it might, however, be larger and the rate constants correspondingly smaller in the outer parts, say beyond 3 × 10⁴ km. Unfortunately, no laboratory data on this temperature dependence are available for the reactions in question.

Lillie's remarks on the general resemblance (due to the high-excitation CO bands) of comet Bennett's uv spectrum (at 0.8 a.u.) at 1200 - 1800 Å, to those of the upper atmospheres of Venus and Mars, suggest CO₂ (or some CO·X), which we shall call CO_p ("parent"), as a major constituent.

The main observational facts, which should be brought into a consistent scheme, are

1. The flux (not due to H I, O I, C I, II) of > 10²⁹ quanta/s inside a coma radius $r \approx 3 \times 10^4$ km.[†]

2. The apparent density dependence of this emission (concluded from the drop beyond $r \approx 3 \times 10^4$ km and the strong dependence on solar distance, R).

*This value is just about the available energy for dissociative recombination of CO₂ ions. The difference between the ionization energy and that required for dissociation of CO₂ is 8.32 eV.

**Compare also the footnote on p. 2 and the estimates for the electron density (~10⁴ cm⁻³ at $r = 10^4$ km) made later.

†According to Lillie's observations the radius of the region, from which most of the emissions in question originate, is about 3 × 10⁴ km. For high-dispersion spectra in the optical range, 1 × 10⁴ km is adequate.

If, say, 20% of the dissociative recombinations lead to the observed emissions in the range 1200-1800 Å (including some from upper triplet state to ground state), and the emission is roughly constant per radial shell (1 cm thick), this means $\geq (5/3) \cdot 10^{20}$ dissociative recombinations per centimeter and second, or $\geq (4/3) \cdot 10^{19}$ cm⁻¹ ster⁻¹ s⁻¹.

We tentatively choose (wherever feasible, we shall prefer values given as full or half powers of 10)

$$\frac{Q_{CO}}{4\pi v} = 10^{24.5} \text{ cm}^{-1} \text{ ster}^{-1} \quad \text{and}$$

$$\frac{Q_{H_2O}}{4\pi v} = 10^{24} \text{ cm}^{-1} \text{ ster}^{-1},$$

which, with $v = 10^{4.5}$ cm/s, correspond to $Q_{CO_p} = 10^{30.1}$ and $Q_{H_2O} = 10^{29.6}$ mol/s (approximately as observed). Note that in this model the kinetic mean free path for diatomic or larger molecules in the coma becomes comparable or equal to r at that distance, where

$$\frac{Q/4\pi v}{r} \approx 10^{14.0} \text{ cm}^{-2},$$

or at 10^{10.5} cm (cf. Ref. 20). For the CO_p the photoionization rate used is 0.5×10^{-5} s⁻¹ (0.8 a.u.).* For H₂O the photoionization rate assumed is $\leq 10^{-6.1}$ s⁻¹. With this assumption, the total number of molecules out to the distance r from the nucleus becomes $4\pi r \cdot Q/4\pi v \approx 5 \times 10^{34}$ for $r = 10^4$ km, where the number densities are 10^{6.5} (CO_p) and 10⁶ cm⁻³ (H₂O). At that distance the electron balance (assuming radial symmetry) is

$$\alpha \frac{Q}{4\pi v} \frac{\text{ionizations}}{\text{cm} \cdot \text{ster} \cdot \text{s}} = r^2 n_1 n_e \beta + \frac{d}{dr} (r^2 n_e v_{pl}),$$

*This rather high value was chosen first because of a suggestion made by C. Lillie in 1975. During the final drafting of this report, K. W. Michel²¹ and W. F. Huebner²² provided new data, which make it seem unlikely that the rate given could be even roughly valid for CO₂. However, as Michel noted, other possible parents of CO exist, for which the rate would indeed have the value given above. (This matter will be pursued further in a report with K. W. Michel.)

where β (of order $10^{-7}\text{cm}^3\text{s}^{-1}$, the precise value depending on electron temperature) is the rate constant for dissociative recombination of CO_p ions. Because v is likely to increase slightly with r , and v_{pl} (the plasma velocity), which is $> v$, is likely to increase even more so, the convective term is not very small compared with the first term, especially farther from the sun (varying $\sim R^{-2}$ at small solar distances).

To the extent that the convective term in the last equation can be neglected in first order, that is, when most ionization processes lead to dissociative recombinations,

$$r^2 n_i \cdot n_e \approx \frac{\alpha}{\beta} \frac{Q}{4\pi r^2} \approx 10^{26} \text{cm}^{-4}$$

for $\beta \approx 10^{-7}\text{cm}^3\text{s}^{-1}$, or, at 10^4 km from the nucleus, $n_i \approx n_e = 10^4\text{cm}^{-3}$. The convective term becomes

$$r n_e v_{pl} + r \cdot d(n_e v_{pl})/dr = r n_e v_{pl} \cdot (1 + d \ln(r n_e v_{pl})/d \ln r).$$

For $r = 10^4$ km this justifies the approximation used, because the left-hand term is $> 10^{19}$ ionizations $\text{ster}^{-1} \text{cm}^{-1} \text{s}^{-1}$, which varies with solar distance, at least with the inverse fourth power. It is tempting to ascribe the uv emission drop beyond $r \approx 3 \times 10^4$ km, apart from the exhaustion of the easily ionized component, to the increase of v (due to the decreased mean molecular weight after dissociation and to heating), to increased v_{pl} (due, so to speak, to the electric field*) towards values of order $(kT_e/m_p)^{1/2}$, where the mean free path becomes of order r , and to the resulting different changes with r of the three terms in the continuity equation for the electrons given above. But this matter is not discussed further here.

* $eE = dp_e/n_e dr \approx kT_e d \ln p_e/dr$. For v_{pl} this leads to values of the order of $(kT_e/m)^{1/2}$, the root being essentially the speed of sound of such a plasma with $T_e \gg T_i$. Part of the relatively high "initial" speeds of plasma formations in comets, especially in the rays on the tailward side of the nucleus (which should be essentially parallel to the local magnetic field), do, probably, reflect this sound velocity.

The number of dissociative recombinations of CO_p ions per square centimeter and second becomes $4\pi \cdot 10^9 \text{cm} \cdot 10^{19.2} \text{cm}^{-1} \text{s}^{-1} / \pi \cdot 10^{16} \text{cm}^2 \approx 6 \times 10^{10}$ or 60 kR, which is actually a lower limit. If only a fraction of these (say 20 kR) populates the upper triplet levels and 0.5% of them would lead to each of the ~ 30 individual transitions seen (or masked by known lines) in the optical range, we would have $\geq 10^8$ transitions $\text{cm}^{-2} \text{s}^{-1}$ or 100 R, which appears easily adequate.

Many of the CO_p molecules, which we denote by y , should become CO molecules. With a lifetime of 3×10^5 s (assumed) and a 10^{-7}s^{-1} excitation rate of the 1510 Å line, the quanta produced per second would be 4×10^{28} , which would produce (4/3) y kR. With more reliable figures an upper limit for the CO_p production rate could be derived from the observed brightness of this line.

IV. CONCLUSIONS

Final proof of the concept developed here would require, in addition to further work on the chemistry of CO_p , measuring in future comets the intensity of the Cameron bands, in particular, the fourth positive system of CO (and other bands between 1200 and 1800 Å), and the lines in the optical range discussed above. Furthermore, the emission of CO_2^+ in the optical range and near uv should be studied. Existing high-dispersion spectra of comets might contain valuable information pertaining to the reality of the identifications proposed in this report and should be studied.

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REFERENCES

1. C. F. Lillie, "Ultraviolet Spectronometry of Comet Bennet (1970 II). The 1200 to 1800 Å Region," (to be published), 1976.
2. F. L. Whipple, "A Comet Model. I. The Acceleration of Comet Encke," *Ap. J.* **111**, 375 (1950).
3. F. L. Whipple, "A Comet Model. II. Physical Relations for Comets and Meteors," *Ap. J.* **113**, 464 (1951).
4. P. A. Wehinger and S. Wyckoff, (to be published in *Astrophysical Journal*), 1976.
5. J. Rahe, C. W. McCracken, and B. D. Donn, "Monochromatic and White-Light Observations of Comet Bennett 1969i (1970 II)," *Astron. Astrophys. Suppl.* **23**, 13 (1976).
6. N. B. Richter, **The Nature of Comets** (Methuen and Co., Ltd., London, 1963).
7. R. W. B. Pearse and A. G. Gaydon, **The Identification of Molecular Spectra** (John Wiley & Sons, New York, 1962).
8. E. Treffitz, personal communication, 1975.
9. C. Arpigny, personal communication, 1975.
10. A. Woszczyk, "Le Spectre de la Comète Mrkos (1957d) dans la Région Visible," *Bull. Soc. R. Sci. Liège*, **31**, 396 (1962).
11. J. L. Greenstein and C. Arpigny, "The Visual Region of the Spectrum of Comet Mrkos (1957d) at High Resolution," *Astrophys. J.* **135**, 892 (1962).
12. P. H. Krupenie, "The Band Spectrum of Carbon Monoxide," *N.S.R.D.S. - NBS5* (1966).
13. T. R. Merton and R. C. Johnson, "On the Spectra Associated with Carbon," *Proc. R. Soc. A* **103**, 385 (1923).
14. L. Herman et R. Herman, "Sur le Système de Triplets de la Molécule Neutre de L'Oxyde de Carbone," *J. Phys. Radium (Ser 8)*, **9**, 160 (1948).
15. L. Haser, personal communication, 1975.
16. C. Arpigny, "Spectra of Comets and Their Interpretation," *Ann. Rev. Astron. Astrophys.* **3**, 351 (1965).
17. L. von Gerö and R. Szabo, "The Structure of the Triplet Bands ($d^3\pi \rightarrow a^3\pi$) of Carbon Monoxide," *Ann. Phys. (Ser. 5)*, **35**, 597 (1939).
18. P. K. Carroll, "Structure of the Triplet Bands of CO," *J. Chem. Phys.* **36**, 2861 (1962).
19. M. Shimizu, personal communication to M. K. Wallis and R. S. B. Ong, "Cooling and Recombination Processes in Cometary Plasma," *IAU Colloquium 25, "The Study of Comets," NASA-SP-393 II*, 856 (1976).
20. J. H. Jeans, **Dynamical Theory of Gases**, 4th ed., (Cambridge University Press, London, 1925).
21. K. W. Michel, personal communication, 1975.
22. W. F. Huebner, personal communication, 1975.