Evidence for the Presence of CH_2 Molecules in Comets

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The structure of the λ4050 group in comets appears to be incompatible with the assumption of a diatomic emitter. Rather, the structure is in conformity with that expected for a ⊥ band of a nearly symmetric top molecule if the moment of inertia about the top axis is approximately 0.35×10^{-40} g cm^2. Such a small value is possible only for a slightly bent XH_2 molecule with X = C, N, or O. For CH_2 and NH_2^+ a ⊥ band is to be expected in the region 4500–4000A. Of these two possibilities CH_2 is the most likely. Since the CH radicals observed in the comets must necessarily be formed from saturated hydrocarbons by successive photodecompositions one should indeed expect to find the spectra of intermediate molecules that lie in the accessible region.

WHILE most of the prominent features of the spectra of comets have been identified as due to the diatomic molecules C_2, CN, CH, NH, OH, CO^+, N_2^+, and CH^+, there is one group of lines or bands in the region 4050A which up to now has resisted all attempts at identification.[1] This group is reproduced from a spectrogram obtained by Swings in Fig. 1.[2] The suggestion put forward by Swings[1] that this group is due to the NH^+ molecule, which is about the only reasonable diatomic molecule left, has much to recommend itself but there are certain difficulties (see below) which it seems difficult to overcome. Therefore the possibility of a polyatomic molecule as the emitter of these bands suggests itself.

The structure of the λ4050 group supplies indeed a strong argument for a polyatomic and against a diatomic emitter: there is one outstanding series of bands whose three most conspicuous members have the wave-lengths[3] 4074.2, 4051.5, and 4019.4A. The second of these is the most intense. In trying to interpret this series as due to a diatomic molecule one may consider it either as a $\Delta v = 0$ sequence or as a progression ($v' =$ const.) of a band system. However, if it were the latter one would have to assume a vibrational quantum of the order of 160 cm^{-1} which is much too small for any molecule that is at all likely to be abundant in a comet. But if it is the $\Delta v = 0$ sequence of a band system, then the $0-0$ band, which might be either 4074.2 or 4019.4, is not the most intense band. This fact is easily seen to be incompatible with the facts that no other sequences have been observed and that the bands in the observed series are rather close together: On the basis of the Franck-Condon principle the small intensity of the $0-0$ band compared to the $1-1$ band means that the internuclear distance in the upper state is rather different from that in the lower. But in such a case the other sequences (with $\Delta v \neq 0$) should have intensities quite comparable to that of the $\Delta v = 0$ sequence, which is not the case. Moreover, the vibrational frequencies in the upper and lower states should be rather different and consequently there should be a wide spacing of the bands in the sequences, which is also not the case. These appear to be serious discrepancies and suggest very strongly that the λ4050 group is not emitted by a neutral or ionized *diatomic* molecule.

The structure of the λ4050 group is indeed very much like that of a perpendicular band of a *polyatomic symmetric top molecule*. Such a band (compare Fig. 13, Dennison[4]) consists of a series

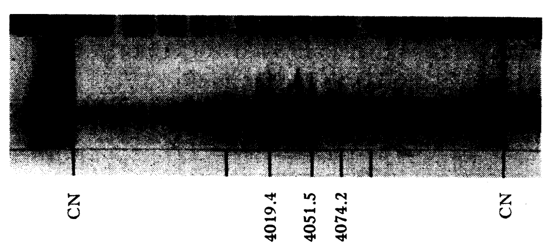


FIG. 1. λ4050 group in comets after Swings, Elvey, and Babcock (reference 1).

[1] See P. Swings, C. T. Elvey, and H. W. Babcock, Astrophys. J. **94**, 320 (1941); P. Swings, Astrophys. J. **95**, 270 (1942).

[2] I am greatly indebted to Dr. Swings for supplying this spectrogram.

[3] These are the wave-lengths recently obtained by Swings (private communication).

[4] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

of strong line-like Q branches which are equidistant when the moment of inertia about the top axis is the same in the upper and lower states but which would converge to longer or shorter wave-lengths if the moment of inertia in the upper state is smaller or larger, respectively, than in the lower. The maximum of intensity is at the center of this series. This is just what is observed in the $\lambda4050$ group of comets.

The observed average separation of the line-like Q branches, that is, the average separation of successive lines in the most prominent series of the $\lambda4050$ group, is 160 cm^{-1}. This corresponds to a moment of inertia about the top axis of 0.35×10^{-40} g cm^2. Such a small moment of inertia (smaller even than that of the diatomic hydrogen molecule) is possible only for a slightly bent XH_2 molecule where X may be C, N, or O. In such a molecule the moment of inertia about an axis parallel to the line $H-H$ may be very small if the $H-X-H$ angle is sufficiently large. Since the other two moments of inertia are large compared to the one just considered and almost of the same magnitude the molecule would be approximately a prolate symmetrical top.

Of the three possibilities CH_2, NH_2, or OH_2 (or corresponding ionized molecules), CH_2 seems to be by far the most likely emitter since according to Mulliken[5] on the basis of its electronic structure CH_2 is expected to have a resonance transition[6] in just the region 4000–4500A. A more detailed consideration shows that this predicted CH_2 band system should consist of $\perp$ bands if the $H-C-H$ angle is large and if the molecule is approximately a prolate symmetric top. Also, since the electron jump occurs between nonbonding orbitals the geometrical structure should be about the same in the upper as in the lower state, that is, according to the Franck-Condon principle, the $0-0$ band should have a much greater intensity than any other band.

Thus, not only the position but also the structure of the $\lambda4050$ group is in agreement with the prediction for CH_2. No resonance transition of the observed type and wave-length is expected for NH_2 nor for OH_2, but NH_2^+ will have a similar transition. However, CH_2 is much more likely to be the emitter of bands observed only near the nucleus of comets than is NH_2^+. Bands of other ionized molecules are all observable much farther away from the nucleus (see also below).

It is particularly significant that the occurrence of CH_2 bands in cometary nuclei might well have been expected even if it had not been suggested by the structure of the $\lambda4050$ group. The CH molecules observed in comets must be produced from some saturated hydrocarbon molecules such as CH_4, C_2H_6, C_2H_4 by photo-dissociation. Certainly the CH molecules are not the only products of such photo-dissociations. It appears certain that also CH_3 and CH_2 are formed, possibly as intermediaries in the formation of CH. While a CH_3 spectrum would lie outside the accessible region a spectrum of CH_2 should occur. It is therefore really not surprising that the structure of the $\lambda4050$ group leads independently to CH_2 as its emitter. It is very satisfactory indeed that the emission of the $\lambda4050$ group is restricted to the nucleus of the comet since on their way further out the gases released from the nucleus are more and more dissociated. It is also in agreement with this interpretation that, according to Swings[7] and McKellar,[7] the $\lambda4050$ group is relatively much stronger than the CH bands at greater heliocentric distances.

The observed NH in comets very probably results from NH_3, and in the photo-dissociation of the latter also NH_2 and NH_2^+ might occur. But the production of NH_2^+ requires radiation of much shorter wave-length than that of CH_2, and therefore NH_2^+ is very probably much less abundant than CH_2.

From the moment of inertia given above and assuming the same CH distances as in CH_4 one obtains an $H-C-H$ angle of about 140°. This value appears rather high since from valence theory values between 90° and 120° might be expected. However, reliable predictions on the basis of valence theory are very difficult to obtain and therefore the large angle does not appear to

[5] R. S. Mulliken, Paper at the Conference on Interstellar Lines held at the Yerkes Observatory (June, 1941). (See P. Ledoux, Pop. Astronom. **49**, 413 (1941).)

[6] All diatomic spectra observed in comets are resonance transitions; that is, have as their lower state the ground state of the molecule.

[7] Private communication.

be a serious argument against the proposed interpretation of the λ4050 group.[7a]

On the basis of the H—C—H angle 140° and the C—H distance 1.09A the two moments of inertia I_B and I_C of CH_2 about the two principal axes perpendicular to the top axis are found to be approximately 3.9 and 4.2×10^{-40} g cm², respectively. Thus the parameter $\rho=(I_A/I_B)$ is 0.086. Nielsen[8] has given calculated spectra for plane asymmetric top molecules with various ρ values. From his Fig. 3 it is seen that for $\rho=0.08$ the structure just begins to assume the typical form of a ⊥ band of a symmetric top molecule. The figure shows also that the deviations from a smooth series in the λ4050 group (see Fig. 1) and the other features of the λ4050 group may well be explained as due to the deviation from the symmetric top particularly if it is realized that Nielsen's spectra are drawn for $I_C=20\times10^{-40}$ instead of $I_C=4.2\times10^{-40}$ g cm². The influence of non-uniform intensity distribution of the exciting solar radiation as discussed by Swings[9] for CN must also be considered.

[7a] Note added in proof: Professor Mulliken has called my attention to a paper by Vogel [J. Chem. Phys. 4, 581 (1936)] in which it is shown that, on the basis of the Heitler-London-Pauling-Slater valence theory one can only say that the angle in CH_2 is probably intermediate between 90° and 180°.

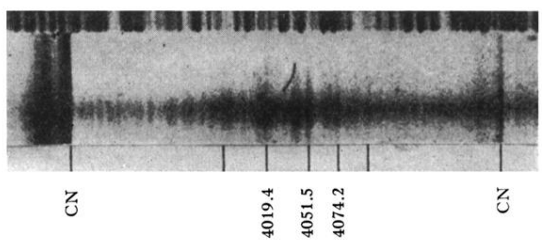
[8] H. H. Nielsen, Phys. Rev. 38, 1432 (1931).

The writer expects to carry out experiments in the near future with a view to reproducing the λ4050 group in the laboratory. Various reasons may of course make it impossible to observe the CH_2 spectrum in electric discharges or other light sources. In that event one would have to wait for opportunities for taking cometary spectra with higher dispersion in order to settle definitely the identification of the λ4050 group and, if CH_2 is the emitter, in order to obtain more definite information about the structure of the CH_2 molecule.

I wish to thank Dr. P. Swings and Professor R. S. Mulliken for helpful correspondence.

Note added August 19, 1942: Since the above was written, the writer has been able to produce the λ4050 group in the laboratory in a discharge through rapidly streaming CH_4. The conditions of excitation in the laboratory strongly support the assumption that the group is due to CH_2. A somewhat more extended note about these observations including a spectrogram has been submitted to the *Astrophysical Journal.*

[9] P. Swings, Lick Obs. Bull. No. 508 (1941).



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