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THE INTERSTELLAR ABSORPTION LINES OF MOLECULAR ORIGIN

By P. Swings

RECENT observations by W. S. Adams at the Mount Wilson Observatory have brought conclusive evidence of the existence of molecules in interstellar space. Using very high dispersion and fine-grained plates, Adams discovered several sharp, interstellar lines due to CH and CN. It is rather interesting to notice that the conclusive evidence in favour of interstellar molecules came through the detection of sharp lines, whereas some years ago molecules had been considered in an attempt to explain the broad, interstellar features discovered by P. W. Merrill. Because of the importance of this problem, it seems worth while to summarize the various investigations which have recently culminated in Dr. Adams' startling discovery and to describe the present state of the problem of interstellar matter.

For a long time the H and K lines of Ca^+ and the principal lines of Na (D_1, D_2 and the ultraviolet pair) remained the only observed stationary lines. In 1934, Merrill (1) reported the discovery of four interstellar lines in the yellow and red regions of the spectrum; the wave lengths of these lines are λλ5780.4, 5796.9, 6283.9 and 6613.9; instead of being narrow and sharp, they are somewhat widened and have rather diffuse edges; no identification was found for these lines (2). Since the ultimate lines of all the abundant atoms and ions are now thoroughly known and since none of them coincides with any of Merrill's lines, H. N. Russell (3), in his George Darwin Lecture of 1935, suggested that they may rather be molecular bands; the fuzzy character of the lines adds some weight to this hypothesis. Russell concludes: "If the temperature of the gas is low enough—more precisely if the rotation of the molecules is little excited—only a few of the band lines observed at room temperature might appear."

This suggestion was developed by the author in 1936 (4). Assuming that the distribution on the rotational levels of the molecules is mainly due to selective absorption between these levels, and adopting a distribution of stars similar to the one considered by A. S. Eddington (5) in his discussion of interstellar ionization, the order of magnitude of the "equivalent temperatures T_λ" (6) was determined for the rotational levels. For a given molecule, we actually have to determine the equivalent temperatures corresponding to the pure rotational levels; the rotational lines are always in the far infra-red, depending upon the moment of inertia I of the molecule. For example, for CO_2 ($I = 70.10^{-40}$g.cm.$^{+2}$), the first ten rotational lines go from about 10,000μ to 1000μ. The equivalent temperature turns out to be very low and for $\lambda = 1000\mu$, it is only 0.5°K.

In order to get some idea of the maximum width of a molecular band, the molecule of CO_2 was considered and a Boltzmann distribution was computed for $T_\lambda = 10°K$, $T_\lambda = 5°K$ and $T_\lambda = 3.2°K$. The calculation shows that the number of observable rotational lines must be very small; for $T = 3.2°K$, which is still much too high, only the first three or four rotational lines would appear in the bands, which means that the widths of these bands would be less than 6 or 7 cm.$^{-1}$, or approximately 2A near λ6000; the edges must be diffuse. This was of the type observed by Merrill; in any case, it removed the objection that Merrill's lines, though fuzzy, are not broad enough to be of molecular origin (7).

These considerations had been applied to the example of the CO_2 molecule because a coincidence of wave-length had been observed between two of Merrill's lines and two calculated rotatory-oscillation bands of CO_2. This was, of course, a purely tentative identification, intended to illustrate the general problem; it could be verified by searching for the two stronger CO_2-bands at λλ7820-7833 characteristic of the Venus spectrum. Subsequent observations by Merrill (8) and also theoretical considerations (9) showed that the coincidence was probably accidental.

When we consider the populations of the rotational levels, two cases are possible, depending upon the existence or the absence of an electric dipole in the normal electronic state of the molecule. In the first case (CH, CN, etc.), there are strong, selective transitions between the rotational levels (pure rotation spectrum), whereas in the second (H_2, O_2, N_2, . . .), these transitions are forbidden. But, owing to the very low density of interstellar matter, it was suggested that even a symmetrical molecule without electric dipole, may be able to emit these "forbidden" low-frequency radiations because they occur faster than the exchanges of collisional processes. Hence a low temperature for the distribution of the rotational quantum numbers is appropriate in most cases; this point will be considered further on. It was also suggested that, once the identifications are certain, the determination of the intensities of the rotational lines will give a direct measure of the temperatures corresponding to the actual distribution on the rotational levels.

Simultaneously with this paper, Th. Dunham, Jr. and W. S. Adams reported their remarkable observation of interstellar *Ti II*-lines (10). The ground term of *Ti II* is a^4F; but only those transitions which arise from the lowest sub-level, $a^4F_{3/2}$, were observed, whereas the stronger lines arising from the higher sub-levels $a^4F_{5/2,\ 7/2,\ 9/2}$, were absent; $a^4F_{5/2}$ is only 0.012 volt above $^4F_{3/2}$. This important observation gave definite evidence that the forbidden transitions between the sub-levels of ^4F must occur in interstellar space (λλ76μ, 103μ and 59μ). The magnetic dipole probabilities for these transitions are such that the lifetimes of $^4F_{5/2,\ 7/2,\ 9/2}$ are still shorter than the intervals between two collisions or absorptions. Practically all the Ti^+ atoms are in their lowest electronic sub-level. This conclusion concerning atomic levels is similar to the previous suggestion concerning molecular rotational states.

Almost simultaneously, Dunham (11) presented evidence for the presence of interstellar *Ca* I (λ4227) and *K* I (λ7699) and the Mount Wilson observers also recorded several sharp, unidentified interstellar lines at λλ3934.3, 3957.7, 4232.6 and 4300.3A.

At this stage—in 1937—the unidentified interstellar absorption features were:

a) several broad lines between λ5780 and λ6614;

b) four sharp lines in the photographic region.

In 1937, M. N. Saha (12) published the statement that one of Merrill's bands (λ6283) was certainly due to the Na_2 molecule ($^1\Sigma \leftarrow {}^1\Sigma$; $v''=0$, $v'=11$) and that another line (λ5780) might provisionally be attributed to *NaK* ($v''=0$, $v'=5$). This identification was criticized by Swings and Rosenfeld (13) and Eyster (14) for spectroscopic reasons. If Saha's identifications were correct, several other bands of Na_2 and *NaK* should be present and should even be stronger, according to the Franck-Condon diagrams of these two molecules.

The note by Swings and Rosenfeld contains two suggestions which proved to be fruitful later on. The first one concerns the estimation of the molecular abundances in interstellar space; the second deals with the identification of the sharp line λ4300.3 with *CH*. Assuming that the density of radiation in the region of molecular absorption leading to dissociation is identical with black-body radiation at temperature T diluted by the factor δ, the number of diatomic molecules in dissociative equilibrium will be given by the usual formula, except that the numbers of atoms have to be divided by $\sqrt{\delta}$. Applying this, for example, to the *CH*-molecule with $T=10{,}000°K$ and $\delta=5.10^{-15}$, it is found that the number of *CH*-molecules per cubic centimeter is (15)

$$n_{\mathrm{CH}} \sim 10^{-8} n_{\mathrm{C}} n_{\mathrm{H}}.$$

Application to CO_2 and Na_2 shows that the abundance of these molecules is probably much too low to permit detection in interstellar absorption. The molecular abundances were then compared to the atomic abundances. It may safely be assumed that the atomic populations of *H*, *O*, *N* and *C* per cm.^{3} are between 1 and 10^{-3}. Thus, for diatomic compounds such as H_2, (16) *OH*, *CH*, *NH*, O_2, *CO*, *CN*, etc., the numbers of molecules would not be much smaller than the numbers of observed interstellar atoms. In other words, a search for the interstellar bands of *CH*, *OH*, *NH*, *CN*, C_2, . . . seemed most promising. In 1937, only one coincidence was available and it was pointed out by Swings and Rosenfeld (17); they suggested that the sharp interstellar line observed at λ4300.3 may be due to *CH*. The absorption lines of *CH* starting from the two lowest rotational levels of the ground electronic and vibrational state are λ4300.24 and λ4303.86. If the second line were present, it would be blended in an early B-star with OII 4303.82 and this might prevent its detection. In any case (18), "the first would give an interpretation of the interstellar line observed by Dunham; the corresponding absorbing molecules would all be in their lowest level, in complete analogy with the case of Ti^{+}-atoms."

The theoretical treatment of the dissociation equilibrium under interstellar conditions of extreme dilution was only a first approach to the problem; a revised, detailed theoretical investigation of this most interesting case is now required and is planned at the Yerkes Observatory.

At the Astrophysical Symposium on Interstellar Matter, held in Paris in 1937, the molecular problem was discussed in some detail (19). Let us assume that the molecule has a permanent electric dipole and let us compute the equivalent temperatures T_λ for the infra-red regions, where the pure rotation spectrum is located. We easily find the following data:

TABLE I. Equivalent Interstellar Temperatures for $\lambda > 1\mu$

λ	T_λ	λ	T_λ
1μ	414° K	100μ	5.0° K
5μ	81.2	500μ	1.0
10μ	47.0	1000μ	0.54
50μ	9.3	10000μ	0.06

We are trying to find under which conditions will there be an appreciable population on a certain rotational level which can be reached by absorption of wave length λ. For example, when shall we have

$$e^{-\frac{h\nu}{kT_\lambda}} > e^{-1}\,?$$

This requires $\lambda T_\lambda > 1.5$ c.g.s. or $\lambda T_\lambda > 1.5 \times 10^4$ micron-degrees. If we adopt the figures of Table I, we find that between 1μ and $10{,}000\mu$, the product λT_λ is practically constant, around 500 micron-degrees. This means that, whatever λ, the population on the rotational level would be very low and we should thus expect to find practically all the molecules in the lowest rotational level.

The crude character of this treatment is evident, especially because of the method of determining T_λ. It is improbable that T_λ is constant in space and that it behaves as simply and regularly as was assumed for the computation of Table I. It is quite possible that in certain regions of space or of wave-lengths, T_λ is such that λT_λ varies and may become greater than 1.5×10^4.

If, instead of absorptions, the collisions (which are very rare) were responsible for the excitation of molecules in their rotational levels, the excited molecules would almost always have time to fall down to a lower rotational level, with emission of permitted or forbidden lines, depending upon the presence or the absence of an electric dipole. The question is quite similar to the case of the ground sub-levels of ionized titanium discussed by Dunham.

In 1938, C. S. Beals and G. H. Blanchet (20) discussed their observations of a diffuse, broad, symmetrical band, extending from λ4410 to λ4450, which had been noticed previously by Merrill as a vague feature near λ4427. The important work by Beals and Blanchet gave definite evidence in favour of an interstellar origin. This was also confirmed by Miss F. Sherman (21).

The situation had thus become the following: although interstellar molecules had been initially considered for the explanation of fuzzy bands, it now appeared that they would rather give an interpretation of the sharp unidentified lines. The recent observation of new sharp lines by Adams improved the situation considerably. A few months ago, Adams (22) reported the observation of a new faint, sharp line in the spectrum of ζOphiuchi at λ3874.6 and McKellar (23) noticed its coincidence with the R(0) line of the (0, 0) band of *CN* ($^2\Sigma \leftarrow {}^2\Sigma$) at λ3874.61. McKellar also noticed that the sharp line λ3934.3 coincides with the R(0) line of the (9, 0) transition in *NaH* ($^1\Sigma \leftarrow {}^1\Sigma$) at λ3934.29; this identification is subject to doubt (24), and McKellar noted that the other vibrational transitions from (7.0) to (12.0) should be almost as intense as λ3934.3 (9.0). The three molecular identifications would indicate that the molecules were practically all in the lowest rotational vibrational and electronic level.

McKellar suggested that the identification of λ4300.2 with *CH* could be confirmed if the (0.0) transition of the other electronic system $^2\Sigma \leftarrow {}^2\Pi$ were also observed: the corresponding lines of lowest rotational level are λ3886.32, λ3878.7 and λ3890.15, of relative intensities 3, 1, 2 and of combined intensity somewhat less than λ4300.24. The Harvard Announcement Card No. 526 (June 18, 1940) brought the desired observational confirmation. On a high dispersion spectrogram of ζOphiuchi taken on a fine-grained plate, Adams observed the three new lines of *CH* with the expected intensities. McKellar has now determined the best laboratory wave-lengths of the *CH*-lines and the agreement with Adams' interstellar wave-lengths is gratifyingly close (25). McKellar's suggestions, together with Adams' observations, have provided conclusive evidence of the existence of interstellar molecules.

Other sharp lines observed by Adams are: λ3579.04 (unidentified), λ3745.33 (fairly prominent, unidentified) and λ3874.02. This last line is probably the R(1) transition of *CN*; it is less conspicuous than the R(0) line at λ3874.62. The difference between the rotational levels is 0.00042 volt; the observation of Adams would thus mean that a certain proportion of *CN*-molecules are on the rotational level 1 at 0.00042 volt. This behaviour may be understood by the foregoing considerations, and the evidence in favour of the existence of interstellar *CN*-molecules is, on the whole, quite satisfactory.

Now, if *CH* and *CN* are considered as being definitely present in interstellar space, there is a great probability that other hydrides, such as *NH* and *OH* and possibly also the carbon molecule C_2, may also be found. The lines of *NH* and *OH*, which may be expected, lie in the observable ultraviolet region; the heats of dissociation of these two molecules are of the same order as that of *CH* and we may expect an abundance of *NH* and *OH* similar to or even greater than that of *CH*. The strongest interstellar line of *NH* should be λ3357.8 and that of *OH*, λ3078.4.

We may wonder whether there is still some hope that interstellar gaseous molecules may also be responsible for broader lines, such as those observed by Merrill or perhaps even for a wide band such as that investigated by Beals and Blanchet. Molecules may give rise to broader lines or even to bands in the following cases:

(*a*) if certain equivalent temperatures T_λ are higher than the values of Table I (for example, if the infra-red radiation of the stars and of the interstellar particles in certain spectral regions is larger than was assumed in Table I; or if a region of space is richer in stars or dust; or in regions nearer to the stars, etc.);

(*b*) if, due to peculiar processes (for example, dissociation of more complex molecules, especially of solid particles), the molecules keep a certain rotational energy and if the transitions to lower rotational levels are unusually strongly forbidden;

(*c*) if the probability of the forbidden transitions between two rotational levels is so extremely small that the "populating processes" exceed the "emission processes."

The molecular hypothesis should not be altogether abandoned for the broad lines, although the prospects are not too hopeful (26).

Another possibility suggested by Merrill (27) and also considered by Beals (20) and others is that these bands would be due to solid particles at the very low interstellar temperature: there is a strong correlation between the intensities of the broad lines and the colour excesses attributed to small diffracting, interstellar particles.

The widths of the absorption bands of a solid are essentially due to the termal agitation and to the broadening of the levels of each constituent (atom or molecule) owing to the interactions of neighbouring particles. In order to explain relatively narrow bands, the required assumptions for solids are a low temperature and weak interactions between the constituents. The first requirement is fulfilled in interstellar space. The second enables us to exclude the metals in the crystalline state (conductors) and the crystals with ionic lattice. In both cases, the interactions are strong and give rise to broad bands, even at very low temperatures. On the other hand, weak interactions are present in molecular crystals and in amorphous metals; hence, these are two possibilities which may lead to satisfactory identifications (28).

If we adopt for interstellar space relative abundances similar to those of stellar atmospheres, we may expect crystals of light elements (solid hydrogen, solid oxygen, ice, CO_2, etc., or mixtures of them). The spectra of such solids at very low temperatures should exhibit great similarities to those of the corresponding atoms or molecules as vapours at high pressure or as liquids, although the influence of the crystalline lattice should be manifest also. But experimental work is completely lacking in this field of optics and is much needed. It should start with the investigation of the absorption spectrum of solid hydrogen at a temperature of about 3°K. Incidentally, the absorption spectrum of solid oxygen has been investigated by Victor Henri (29); the strongest absorption band is at λ5795.7 and it will be recalled that Merrill observed a band at λ5796.9. Although this may be a chance coincidence, it is worthwhile to point it out.

The amorphous metals have also a conspicuous interest. Such solids are obtained by condensation at low temperatures and are favoured by small dimensions. It seems probable that part of the small interstellar "metallic" particles are in the amorphous state. They are insulators and their electric properties are fairly well known; unfortunately almost nothing is known regarding their optical properties and laboratory work in this field of optics is also urgently needed. The collaboration of cryoscopy and astrophysics will almost certainly be profitable in the future.

McDonald Observatory,
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References

(1) *Pub. A.S.P.*, v. 46, p. 206, 1934; see also *Ap. J.*, v. 83, p. 126, 1936; P. W. Merrill and O. C. Wilson, *Ap. J.*, v. 87, p. 9, 1938.
(2) Two other lines were reported later on at λ6203.0 and λ6262.0.
(3) *M.N.*, v. 95, p. 635, 1935.
(4) *Ibid.*, v. 97, p. 212, 1937.
(5) The Internal Constitution of the Stars, 2nd edition, p. 371: 5 per cent. of stars at 18,000°; 10 per cent. at 12,000°; 20 per cent. at 9,000°; 40 per cent. at 6,000° and 25 per cent. at 3,000°.
(6) The equivalent temperature T_λ is such that the actual energy-density for wave-length λ, in interstellar space, is equal to that of equilibrium radiation at temperature T_λ.
(7) For instance, the CO_2-bands, when observed in the laboratory, average about 100 cm.$^{-1}$ in breadth throughout the spectrum.
(8) Private communication.
(9) *Annales d'Astrophysique*, v. 1, p. 39, 1938.
(10) Dunham and Adams, *Pub. A.A.S.*, v. 9, p. 5, 1937; Dunham, *Pub. A.S.P.*, v. 49, p. 26, 1937; *Nature*, v. 139, p. 246, 1937.
(11) *Pub. A.S.P.*, v. 49, p. 26, 1937.
(12) *Nature*, v. 139, p. 840, 1937.
(13) *Ap. J.*, v. 86, p. 483, 1937.
(14) *Ibid.*, v. 86, p. 486, 1937.
(15) If we assume with Struve (*Proc. Nat. Acad. Science*, v. 25, p. 36, 1939) $T = 15{,}000°$ and $\delta = 10^{-16}$, we find $n_{CH} \sim 10^{-7} n_C n_H$. It is interesting to compare this abundance of CH with the recent determinations of atomic abundances by Dunham (*Proc. Amer. Phil. Soc.*, v. 81, p. 277, 1939). Dunham finds per cm.^{3}: $5\times10{-}8$ atom of *Na* I; 4×10^{-11} atom of *Ca* I; 1.4×10^{-7} atom of Ca^+; 1.3×10^{-9} atom of Ti^+. If we take $n_H = 1$ and $n_C = 10^{-2.5}$, we find that n_{CH} is of the same order as n_{Ca}. The identification of interstellar CH-molecules is in agreement with Struve's view regarding interstellar hydrogen atoms on the basis of his observations of H_α emission in many extended regions of the Milky Way.
(16) The H_2 molecules are particularly abundant, but are unobservable, their absorption bands being in the far ultraviolet.

(17) It is evident that this coincidence was found as a result of a systematic discussion of all possible molecules; no other coincidence having been found, the discussion was not published, except for *CH*. See also P. Swings and M. Désirant, *Ciel et Terre*, v. 5, p. 160, 1939.

(18) *Loc. cit.*, p. 485.

(19) *Annales d'Astrophysique*, v. 1, p. 39, 1938.

(20) *M.N.*, v. 98, p. 398, 1938.

(21) *Ap. J.*, v. 90, p. 630, 1939.

(22) Annual Report of the Director of the Mount Wilson Observatory for the year 1938-1939; issued December 15, 1939.

(23) *Pub. A.S.P.*, v. 52, p. 187, 1940.

(24) The theoretical interstellar abundance of *NaH* is much lower than the abundance of *CH* (owing to the lower heat of dissociation of *NaH* and also to the probably lower abundance of *Na*, compared to *C*).

(25) *Pub. A.S.P.*, p. 52, v. 312, 1940.

(26) No clear identification is indicated by a systematic examination.

(27) *Phys. Rev.*, v. 52, p. 761, 1937.

(28) P. Swings and Y. Öhman, *Observatory*, v. 62, p. 150, 1939; P. Swings and M. Désirant, reference 17.

(29) Probably unpublished. Investigations started in Liége (Belgium) in this general direction were interrupted by the war.