LASER SPECTRUM IN NITROUS SULPHIDE

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Nitrous sulphide (N_2S) is identified as a carrier in a previously reported laser. A selection rule is given for the transfer of energy. N_2S is probably a by-product of the combustion of coal.

In 1965, Patel [1] published an article on a cw laser in an N_2-CS_2 system. At that time it was not possible to assign the laser carrier and CS_2 appeared to be excluded because the band origins known for it did not appear to allow this possibility. Since then there have been three attempts to assign the carrier as CS_2 on the basis of more recent spectroscopic data.

Maki [2] first assigned the carrier on the basis of transitions between rotational states of CS_2 ($001 \rightarrow 100$) vibrational transition. Later, Legay-Sommaire [3] achieved a good fit of the spectrum by assuming that the ($02^01 \rightarrow 12^00$) transition in CS_2 comprised the laser. Finally, Maki and Sams [4] used new data and extensive calculations to show that the original assignment was more probable than that of Legay-Sommaire but they pointed out that their work was not direct evidence that CS_2 was the carrier. In addition, they noted that there were not enough lines in the spectrum according to theory.

We have examined the data of Maki and Sams and have used the table of 10^01-00^00 to achieve combinations of the form:

$$\{\nu_R(J) - \nu_P(J)\}/(4J + 2) = B'. \tag{1}$$

The prime stands for upper state. We selected groups of unblended lines at J values near 10, 30, 50 and 100 and calculated B' by eq. (1). We did this to measure the effect of centrigugal distortion in CS_2. In going from $J = 10$ to $J = 100$, the change in B' was only three parts per thousand. In the region $J = 30$ to 40, where Patel's laser was assigned, the change in B' was ≈ 2

parts in ten thousand and therefore negligible.

From the formula for P branch transitions [5] we find that the difference between successive lines J and $J + 2$ is, in the absence of centrifugal distortion:

$$\Delta\nu_P = -2(B' + B'') - 4(J + 1)(B'' - B'). \tag{2}$$

The second term on the right indicates the interaction of vibration and rotation and for quite rigid molecules like CS_2 it is very noticeable. It causes the P branch spacing to increase.

We have employed Maki's rotational constants to calculate P branch spacings at $J = 30$ and it should be 0.503 cm^{-1}. At $J = 40$ it should be 0.526 cm^{-1}. This is a divergence of more than 4% for his assignment of the laser as CS_2 ($00^01 \rightarrow 10^00$).

We did not have B values for Legay-Sommaire's assignment of ($02^01 \rightarrow 12^00$) so we used constants to calculate them [6,7]. We checked these constants by calculating Maki's rotational constants B_{001} and B_{100} exactly, and B_{101} and B_{121} from the tables of Maki and Sams agreed to within one part per thousand. The use of B_{021} and B_{120} in eq. (2) showed that the spacing at $J = 30$ would be 0.505 cm^{-1} and 0.528 cm^{-1} at $J = 40$ in Legay-Sommaire's assignment of ($02^01 \rightarrow 12^00$). This is a divergence of $\approx 4\%$.

We plotted Patel's laser lines on a 10 by 20 inch graph. A tightly stretched 10 mil wire covered every point but one. The sixth line of the ten-line pattern has 0.02 cm^{-1} error. The slope was 0.521 cm^{-1} per line and there was no apparent divergence. This feature of the plot, namely lack of divergence, comprises

direct evidence that the carrier is not carbon disulphide. We will provide additional direct proof later.

From previous work [4] we know that the assignment of this laser to CS_2 cannot be made in a satisfactory fashion. From our work, it appears definitely excluded. It therefore seems logical to inquire whether another carrier could be causing the spectrum. Of known substances, NCS and N_2S are candidates while substances containing only nitrogen and carbon are not because their rotational constants are too large.

NCS has a rotational constant of 0.2036 cm^{-1} [8] and must be considered. We do not know the high frequency stretching vibration but it should be near 2000 cm^{-1}. The low frequency stretching vibration is 715 cm^{-1}. This means that the difference between these two, which would comprise a laser in this substance, would occur above 1000 cm^{-1}. We therefore reject NCS as a candidate. We will add direct proof later.

We refer to N_2S as a known substance even though until now it has not been detected. We clarify this by pointing out that its existence is required by periodic law. It is the analogue of nitrous oxide; it is stable and similarly unreactive. There are other chemical considerations. When CS_2 is added to a stream of active nitrogen, it is consumed at a very high rate [9,10]; and under the conditions where we have observed this laser, no CS_2 survived. It is consumed under conditions where N_2S is a logical product.

The Raman spectrum of N_2 shows a band 2331 cm^{-1} from the exciting line. The addition of an oxygen atom to this molecule causes the N–N stretching frequency to drop to 2223 cm^{-1}. The low frequency stretch of N_2O is at 1285 cm^{-1}. The substitution of sulphur for oxygen in this molecule will cause both stretching frequencies to decrease, which is easy to see, but we know from normal coordinate theory that all comparable vibrations must decrease. Thus in going from $N_2O(001 \rightarrow 100)$ to $N_2S(001 \rightarrow 100)$ the frequency should decrease, which it evidently does.

In nitrous oxide the N–N bond length is 1.1282 Å and the N–O bond length is 1.1842 Å. In nitric oxide (NO) the bond length is 1.1508 Å and in nitric sulphide (NS) it is 1.4938 Å. The substitution of sulphur for oxygen causes an increase in bond length of 0.343 Å. We estimate a slight change in N–N bond is going from N_2O to N_2S. Thus the tentative structure for N_2S is:

$$r_{xy} = 1.13 \text{ Å}, \qquad r_{yz} = 1.527 \text{ Å}.$$

We calculate from the estimates that B_{000} for N_2S is 0.227 cm^{-1}. Previous experience leads us to expect 0.23 cm^{-1} as an upper limit with 0.21 cm^{-1} very possible as the true value of B_{000}.

We are confident that the rotational constant of N_2S will not be greatly different from our calculations of it. Four times B_{000} for this molecule should occur near 27 GHz.

With N_2S as a carrier, it is easy to understand why its laser lines would be equally spaced: the vibrational frequencies of N_2 and N_2S differ by ≈ 300 cm^{-1} and so N_2S requires a great deal of rotational energy to resonate with the nitrogen pump. This additional energy causes the molecule to distort as a result of the comparative ease in deforming the N–S bond.

Molecules like CS_2 and CO_2 conform to Bose–Einstein statistics and as a result genuine combinations of wavefunctions can take place only between states of the same parity. Other combinations cannot exist.

To see this, we write P(1 → 2) instead of P(2), P(3 → 4) instead of P(4) and so forth. Instead of R(0) it would be R(1 → 0), etc. If we used parentheses only, it would imply pure rotational transition. The addition of the P or R implies rovibrational transition. The first quantum number designates the rotational state of the upper laser level and the second the lower laser level rotational number. It is clear from this notation that the upper laser level has only odd parity states and the lower laser level has only even parity states. The upper laser level is antisymmetric, therefore odd and can combine only with odd rotational states. No other states exist.

Maki and Sams are incorrect in stating that the intensities of Patel's laser lines are erratic. Every intensity alternates. True, there are two which are exceptionally strong, but between these two there are six others which alternate two to one. This laser carrier shows nitrogen statistics.

The rotational states of the antisymmetric stretch of CS_2 all have the same parity and like CO_2 cannot distinguish the parity states of nitrogen which are in the ratio of two even to one odd. Patel's laser carrier is unequivocally not CS_2.

On the basis of our analysis thus far, we put forward the following postulate:

> In collision, energy transfer is allowed between states of the same parity and forbidden between states of opposite parity.

With this postulate, it is easy to imagine the mechanism of the laser: the N_2S molecules extract energy from nitrogen at a rate which is slow compared to rotational relaxation of N_2. This means that the rotational distribution of N_2 is unperturbed and the carrier molecules always experience an environment where even states of nitrogen are twice the abundance of odd states. Individual molecules collide and, if parity considerations allow it, receive energy. Thereafter they transit to the upper laser level where they *instantly* experience the laser field and are compelled to give up the stored energy before another collision can occur. This explains the alternating intensity pattern because the even states of N_2S are pumped at twice the rate of the odd states.

The carrier of this laser is unequivocally not the NCS radical. Although NCS has odd and even rotational states, each has ($+$) and ($-$) parity because of lambda doubling. The same is true for the angular momentum states of CS_2.

By elimination and consideration of chemical and physical properties, we have achieved the identification of N_2S. But there are other sulphides in our laser system. The prolonged addition of CS_2 to active nitrogen results in precipitation. The precipitate begins blue, turns green, then black with increasing thickness.

It is possible that the color is due to trapped NS and NS_2 in a matrix of N_2S_5 and other sulphides.

Nitrous sulphide is not reactive toward charcoal, soda lime or steel wool which comprise our chemical trap. It readily passes through pump oil. It has a distinct and not unpleasant odor. Experience thus far makes us believe that those familiar with the combustion of coal can recognize it.

References

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