

matrices and doing the differentiation), and

$$\Delta n_q = -n_q \sum_{lmn} t_{mn;ql} \frac{n_l(1-n_m)(1-n_n)}{(\epsilon_q + \epsilon_l - \epsilon_m - \epsilon_n)^2} t_{mn;(ql)} + \dots$$

$$+ (1-n_q) \sum_{kln} t_{qn;kl} \frac{n_k n_l (1-n_n)}{(\epsilon_k + \epsilon_l - \epsilon_q - \epsilon_n)^2} \times t_{qn;(kl)} + \dots \quad (\text{A13})$$

With the above equations, we can easily verify that all but the last term of (A10) are of order  $t^3$  and that the last term is  $O(t^2)$ , proving (A2).

In order to demonstrate (A3), we note that the

equation for  $\Delta E(\rho, \epsilon)$  without self-energy terms is

$$\Delta E(\rho, \epsilon) \text{ no self-energy terms} \\ = \frac{1}{2} \sum_{kl} t_{kl;(kl)} \rho_k \rho_l + \text{hole-hole term and} \\ \text{3-body cluster of } O(t^3) + O(t^4). \quad (\text{A14})$$

Since the zero order  $\rho_k$  is  $n_k$  [see (3.5)], the third-order terms included in (A14) are the same as the corresponding terms in  $\Delta E(n, \epsilon)_{\text{BG}}$ . The third-order self-energy term must therefore be shown to come from the first term on the right in (A14) if the equation is to be proved correct to fourth order. Using  $\rho_k = n_k + \Delta n_k$  and (A13) for  $\Delta n_k$ , we obtain

$$\frac{1}{2} \sum_{kl} t_{kl;(kl)} n_k n_l + \frac{1}{2} \sum_{kl} t_{kl;(kl)} n_k \Delta n_l + \frac{1}{2} \sum_{kl} t_{kl;(kl)} \Delta n_k n_l + O(t^4) \\ = \frac{1}{2} \sum_{kl} t_{kl;(kl)} n_k n_l - \frac{1}{2} \sum_{klmn} t_{mn;kl} \frac{n_k n_l (1-n_m)(1-n_n)}{(\epsilon_k + \epsilon_l - \epsilon_m - \epsilon_n)^2} t_{mn;(kl)} \{ \sum_j (t_{jk;(jk)} + t_{jl;(jl)} - t_{jm;(jm)} - t_{jn;(jn)}) n_j \}. \quad (\text{A15})$$

A rearrangement of terms and a change of summation indices was required to obtain the last term. We have again used the fact that  $\rho_k$  is equal to  $n_k$  in lowest order. The last term above is just the third-order self-energy term in (A8), so that  $\Delta E(\rho, \epsilon)$  without

self-energy terms is indeed equal to  $E(n, \epsilon)_{\text{BG}}$  through third order, proving (A3). There is a difference in fourth order which would lead to an error in the mean energy of nuclear matter estimated to be of the order of 2 MeV.

## Optical Maser Action in C, N, O, S, and Br on Dissociation of Diatomic and Polyatomic Molecules

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This paper reports cw optical-maser action in carbon, nitrogen, oxygen, sulfur, and bromine. The maser action is obtained on dissociation of various diatomic and polyatomic gases. The transitions reported here cover a wavelength range from 8400 to 15 000 Å. The optical-maser action on the carbon lines is obtained on dissociation of CO or CO<sub>2</sub> in a discharge containing CO or CO<sub>2</sub> with either helium or neon. Maser oscillation in nitrogen was obtained from a discharge containing NO or N<sub>2</sub>O with helium or neon. In both the cases above, i.e., in the cases of carbon and nitrogen, the discharges also exhibited maser action on an atomic oxygen line. A discharge containing SF<sub>6</sub> or SF<sub>8</sub> with helium produced maser action in sulfur. And bromine + argon discharge yielded maser oscillation at four separate wavelengths spaced very closely around 8446 Å, which were resolved with a 1-m Jarrell-Ash spectrometer. These four wavelengths in the Br<sub>2</sub>+Ar maser may be of special interest in microwave beat experiments because the separations between them are 3.92, 13.90, 3.78, and 21.60 kMc/sec, respectively. A detailed description of possible dissociation and excitation mechanisms which lead to the above masers is given.

### I. INTRODUCTION

**D**URING a collision of the second kind between an excited atom  $A^*$  and a polyatomic molecule, dissociation of the molecule can take place. In such a reaction, the atom  $A^*$  returns to its ground state, and the dissociation products may end up in their respective ground states or some excited levels depending upon the energy of the excited atom  $A^*$ . In certain cases, dissociation of this kind leads to selective excitation

of atoms to one particular level of the dissociation products. If the lifetimes are suitable, then one obtains optical maser action on a transition belonging to the spectrum of that particular dissociation product. The selective excitation on dissociation of a diatomic or polyatomic molecule requires that the discrepancy between the energy of the excited atom  $A^*$  and that of the dissociation products be small. However, the energy-coincidence requirement is not nearly as stringent as

that required in the case of selective excitation during atom-atom collisions<sup>1,2</sup> of the type predominant in helium-neon optical masers.<sup>3,4</sup> The excitation transfer cross sections obtained in the case of dissociative excitation involving collision between an atom and a polyatomic molecule are comparable to those in the case of atom-atom transfer collisions with much smaller energy discrepancy. There are two reasons for this. First, since we are involved with more than two atoms, there is greater number of degrees of freedom open to each particle. There is usually a large number of repulsive molecular states covering a reasonable energy range (1–2 eV) which terminate in the same levels of the dissociated molecule. This makes the energy-coincidence requirement less stringent. And second, when a polyatomic molecule is involved, a factor which increases the probability of such dissociative excitation process is that the chance of the reaction being reversed when the particles are separating is much smaller than that in case of two atoms.<sup>2</sup> (This is because of the larger number of paths available to the representative particles, so that the probability that they will retrace the original path is smaller.) Thus, even with the additional restriction on the lifetimes of the two maser levels, dissociative excitation promises to be a general way of obtaining optical maser action in a gaseous discharge.

The first successful application of dissociative excitation for obtaining optical maser action in gaseous discharges was to the neon-oxygen and the argon-oxygen masers.<sup>1</sup> In these cases the maser action was produced at 8446 Å corresponding to the  $3p^3P_2-3s^3S_1^0$  transition of atomic oxygen. The excitation mechanisms in these two cases were markedly different although they arose from the same general feature of dissociative excitation. In the case of neon-oxygen maser there was a direct excitation of atoms to the upper maser level  $3p^3P_2$  due to dissociation of oxygen molecules following impact with neon  $1s$  metastable (Paschen notation) atoms. In the argon-oxygen maser, dissociation of  $O_2$  resulted in excitation to metastable states of atomic oxygen which have large electron excitation cross section for the upper maser level.

In this paper we show the generality of the dissociative excitation technique for obtaining optical maser action in gaseous discharges. We report cw oscillation on a number of transitions of carbon, nitrogen, oxygen, sulfur, and bromine attained by dissociation of various diatomic and polyatomic molecules on collisions with helium, neon, or argon metastable atoms. The optical maser action reported here covers a wavelength region from about 8400 to 15 000 Å. In addition to the importance of this technique as a generally applicable

method of obtaining maser oscillation in gaseous discharges, it may be possible to obtain some more information about dissociation energies of various molecules. In particular, in order to explain maser action on dissociation of NO, we were forced to preferentially use one of the two commonly accepted values for the dissociation energy of NO.

In the following, we briefly describe the experimental apparatus used in these investigations and we give the experimental results and discuss each case in detail.

## II. EXPERIMENTAL

The gas mixtures were investigated for maser action in a quartz discharge tube with Brewster angle windows.<sup>5</sup> The tube was 250 cm long and 5-mm i.d. The optical resonator consisted of a pair of near-confocal mirrors spaced about 260 cm apart. The use of external mirror system was preferred primarily because it allows one to investigate corrosive gases like  $SF_6$  and  $Br_2$  without fear or danger of damaging the dielectric coatings of the high-reflectivity mirrors. The mirrors were coated typically for 99% reflection with about 0.5% transmission in the wavelength region being investigated. This experimental system has been described in detail in Ref. 6.

The wavelength measurements were carried out with (1) a 250-mm Bausch & Lomb monochromator and (2) a 1-m Jarrell-Ash spectrometer. The wavelengths were measured in air. The wavelength measurements given in the case of carbon, nitrogen, oxygen, and sulfur are taken with the B & L spectrometer. The bromine-maser wavelengths were measured with the Jarrell-Ash spectrometer, which had a resolution of about 1:390 000 at 8400 Å.

## III. RESULTS AND DISCUSSION

### 1. Carbon

The optical maser action in carbon has been obtained on dissociation of either CO or  $CO_2$  in discharges containing CO or  $CO_2$  with either helium<sup>7</sup> or neon. The gas pressures used were CO or  $CO_2=0.01$  Torr+helium = 2 Torr, and CO or  $CO_2=0.01$  Torr+neon = 1 Torr. The wavelengths at which maser oscillation has been obtained and their possible classifications are given below:

Wavelength measured (air), Å	Possible classification	Gain percent/meter	Power output, mW
10 689	C I $3p^3D_3-3s^3P_2^0$	3	2
14 539	C I $3p^1P_1-3s^1P_1^0$	2	1.

<sup>1</sup> W. R. Bennett, Jr., W. L. Faust, R. A. McFarlane, and C. K. N. Patel, *Phys. Rev. Letters* **8**, 470 (1963).

<sup>2</sup> H. S. W. Massey and E. H. S. Burhop, *Electronic and Ionic Impact Phenomena* (Clarendon Press, Oxford, England, 1952).

<sup>3</sup> A. Javan, W. R. Bennett, Jr., and D. R. Herriott, *Phys. Rev. Letters* **6**, 106 (1961).

<sup>4</sup> A. D. White and J. D. Rigden, *Proc. I.R.E.* **50**, 1697 (1962).

<sup>5</sup> W. W. Rigrod, H. Kogelnik, D. J. Brangaccio, and D. R. Herriott, *J. Appl. Phys.* **33**, 743 (1962).

<sup>6</sup> C. K. N. Patel, *J. Appl. Phys.* **33**, 3194 (1962).

<sup>7</sup> H. A. H. Boote and R. M. Clunie, *Nature* **197**, 173 (1963). They report optical maser action at 1.068 and 1.454  $\mu$  in a CO+He pulsed discharge.

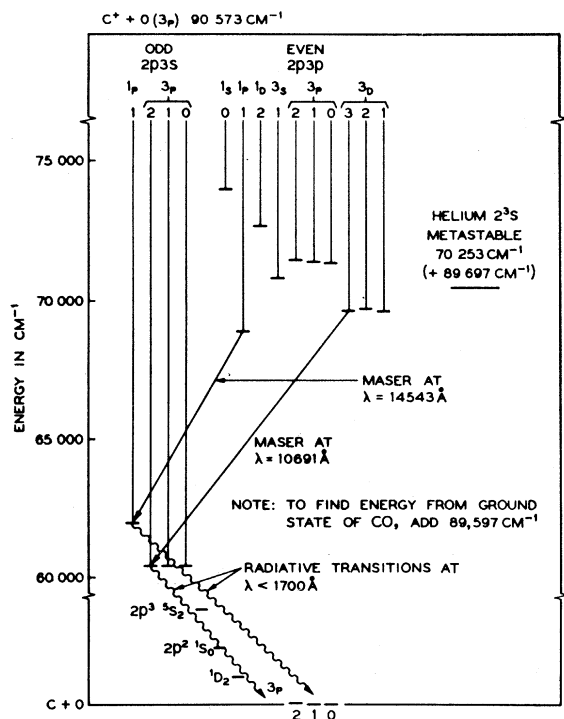
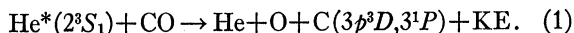


FIG. 1. Energy-level diagram of atomic C.

Figure 1 shows an energy-level diagram of atomic carbon.<sup>8</sup> The ground state of CO is taken to be 89 700  $\text{cm}^{-1}$  below the ground state of atomic carbon, assuming that in one particular type of dissociation of CO by collision with helium metastables, the oxygen atom is left in its ground state and the carbon atom is an excited state.<sup>9</sup> It can be seen from the energy-level diagram that the  $3p^3D$  and  $3p^1P$  levels are in good coincidence with the  $2^3S_1$  metastables. Thus the excitation process can be written as



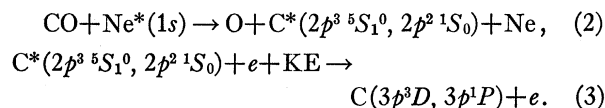
The process described in Eq. (1) is exothermic, and leads to a preferential excitation of the upper maser level in C for the 10 689- and the 14 539-Å transitions. An indirect proof of this process is obtained by looking at the output power at these two wavelengths as a function of time when the rf discharge is pulsed. One notices an increase in the power output in the afterglow which is a characteristic of excitation involving metastable transfer.

In the CO+Ne system the neon 1s metastable states lie much lower than the  $3p^3D$  or the  $3p^1P$  states of carbon assuming the dissociation excitation from CO. Hence, direct excitation of these states on dissociation of CO by an inelastic collision with neon 1s metastable atoms can be ruled out. However, as in the case of the

<sup>8</sup> C. E. Moore, *Atomic Energy Levels* (U. S. Government Printing Office, Washington 25, D. C.).

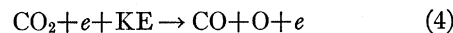
<sup>9</sup> G. Herzberg, *Molecular Spectra and Molecular Structure* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1962), Vol. I.

$\text{O}_2$ -Ar maser,<sup>1</sup> neon metastables can excite the carbon atoms to the  $3p^3S_2^0$  and  $2p^2^1S_0$  metastable states. From these states, then, electron impact can lead to the excitation to the  $3p^3D$  and  $3p^1P$  states of carbon. The processes can be written as



This two-step process is as effective in producing  $3p^3D$  and  $3p^1P$  states as is direct process described in Eq. (1).

The case of maser action in carbon on dissociation of  $\text{CO}_2$  by either helium or neon is much more complex since the dissociation energy of  $\text{CO}_2$  will depend upon the dissociation products and the processes would not have any simple explanation. It is suggested, however, that since maser action is also obtained from CO, processes of the type



are very effective in producing CO in a discharge containing  $\text{CO}_2$ +helium or neon. After a dissociation of this type, the explanation given for the case of CO will be valid even in  $\text{CO}_2$ +helium, neon case. It should be remembered that the maser action in  $\text{CO}_2$  is as strong as that in the CO.

## 2. Nitrogen

Radio-frequency discharges containing 0.03 Torr of either NO or  $\text{N}_2\text{O}$ , with either 2 Torr of helium or 1 Torr

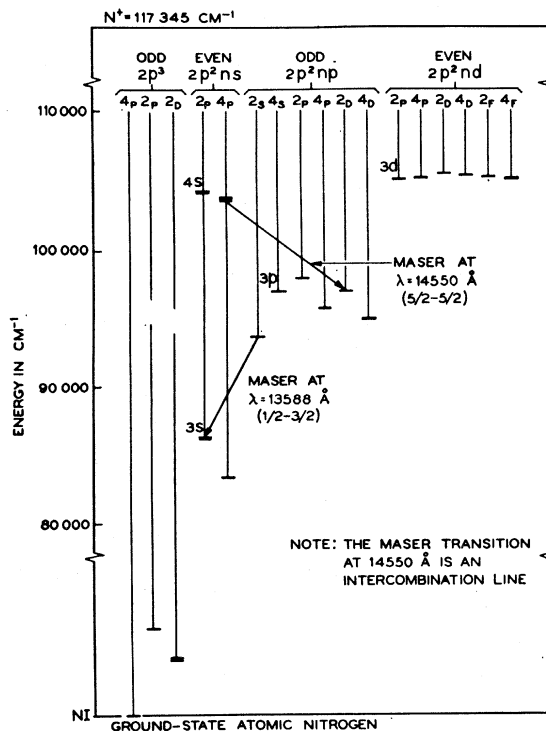


FIG. 2. Energy-level diagram of atomic N.

of neon have exhibited optical maser action on two atomic transitions of nitrogen. These transitions are listed below with possible classification:

Wavelength (Å)	Possible classification
13 583	N I $3p^2S_{1/2}^0 - 3s^2P_{3/2}$
14 544	N I $4s^4P_{6/2} - 3p^2D_{5/2}^0$ .

It should be noted that the maser transition at 14 544 Å is about 96 kMc/sec from the 14 539-Å transition in carbon and may be of interest for photo-heating experiments.

Figure 2 shows the energy-level diagram of atomic nitrogen.<sup>8</sup> In the case of dissociation from NO, the ground state of NO would be 52 300 cm<sup>-1</sup> below the ground state of nitrogen.<sup>9</sup> There is one more commonly accepted value of the dissociation energy of NO which is 42670 cm<sup>-1</sup>. However, this lower value has been discarded here since it would lead to direct excitation of the lower maser level on collision of NO with neon 1s metastable states. With the higher value of the  $D_0(\text{NO})$ , the  $2^3S_1$  metastable stable states lie less than 1-2 eV above the upper maser levels, suggesting possibility of selective excitation of these levels by collision of NO with helium  $2^3S_1$  metastables. Further, it is of interest to note that the transition at 14 544 Å is an inter-combination line connecting a level of spin multiplicity of 4 to a level of spin multiplicity of 2.

In case of maser action in nitrogen from a NO+neon discharge, a two-step excitation involving excitation of the  $2p^3^2P$  and  $2p^3^2D$  metastable states of nitrogen is suggested.

Again, the maser action in N<sub>2</sub>O+He or Ne discharge cannot be explained very easily since it will involve a four-body collision in case there is a preferential dissociation on collision with either a helium or a neon metastable atom.

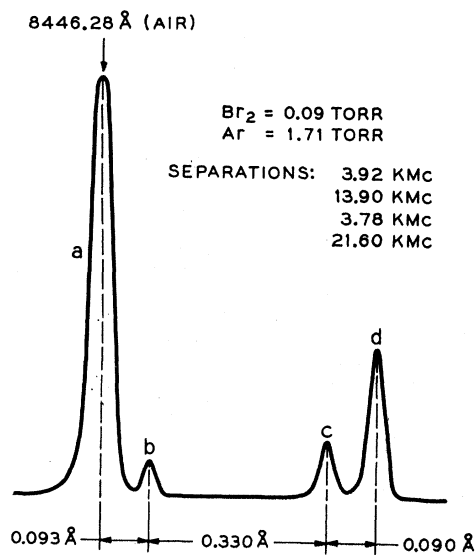


FIG. 3. Spectrometer trace of output from a Br<sub>2</sub>+Ar optical maser, showing four distinct transitions.

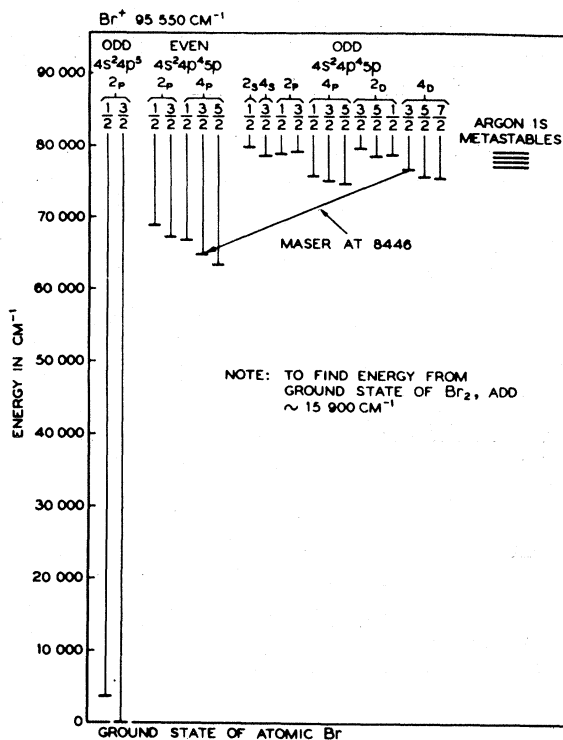
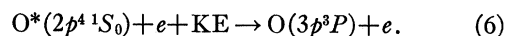
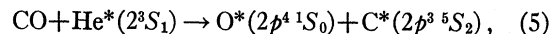


FIG. 4. Energy-level diagram of atomic bromine.

### 3. Oxygen

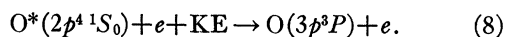
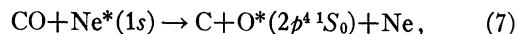
Optical maser action in O<sub>2</sub>+Ne and in O<sub>2</sub>+Ar discharges has been reported earlier.<sup>1</sup> The maser action takes place at 8446 Å, corresponding to the  $3p^3P_2 - 3s^3S_1^0$  transition of oxygen. We have found that in the discharges containing CO, CO<sub>2</sub>+He, Ne or NO, N<sub>2</sub>O+He, Ne, at essentially the same pressures as those described for maser action in carbon and in nitrogen, respectively, optical maser action also takes place on the  $3p^3P_2 - 3s^3S_1^0$  transition of atomic oxygen. It should be remarked that the maser output obtained here in oxygen is at least as strong as that obtained from the O<sub>2</sub>+Ne or O<sub>2</sub>+Ar discharges.

In a CO+helium discharge, we earlier saw the processes involved in obtaining maser oscillations in carbon. For the maser oscillation in oxygen, in the same discharge, a two-step excitation is conceivably involved:



This type of two-step process also helps the maser oscillation in carbon as explained in Eq. (3).

In a CO+neon discharge, maser oscillation in oxygen requires the same sort of two-step excitation as in the case of carbon in the same discharge:



It should be noted that the process of Eq. (7) is going on at the same time as the process of Eq. (2). Also the process described in Eq. (8) is the same as that described in the Ref. 1 (Eq. 4).

In the CO<sub>2</sub>+helium, neon discharge, the explanation for maser action follows the same arguments as given earlier when we explained the maser action in C from a CO<sub>2</sub>+He, Ne discharge.

In Ref. 1 it was reported that the maser action in oxygen was taking place on the  $3p^3P_2-3s^3S_1^0$  transition and that, although as seen from the fluorescence data there should have been enough optical gain at the  $3p^3P_1-3s^3S_1^0$  transition, no maser action was obtained. Also, it was noticed in the same reference that the maser action at the  $3p^3P_2-3s^3S_1^0$  transition did not take place on the peak of the fluorescence line but was about 2 kMc/sec away on the shorter wavelength side. These two discrepancies were explained by postulating an unidentified absorption line of O<sub>3</sub> in the vicinity of these transitions. We attempted to obtain maser oscillation on the  $3p^3P_1-3s^3S_1^0$  transition assuming that in a CO+He discharge, there would be less O<sub>3</sub> formation. However, these efforts were unsuccessful.

#### 4. Sulfur

In a discharge containing either 0.03 Torr of SF<sub>6</sub> (sulfur hexafluoride) or 0.03 Torr of SF<sub>6</sub> with 2 Torr of helium, two transitions have been observed in maser oscillation. These are given below. Both of them have been identified as transitions of atomic sulfur:

Wavelengths (Å)	Possible classification
10 455	SI $4p^3P_2-4s^3S_1^0$
10 628	SI $4p^1F_3-4s^1D_2^0$ .

We point out here that the 10 455-Å transition of sulfur is the exact analog of the 8446-Å transition of oxygen, which has already been reported in maser oscillation. It is surprising to note that, in a SF<sub>6</sub> discharge, no helium is needed to obtain maser oscillation in sulfur. Addition of helium improves the maser but there is no evidence of any metastable transfer as would be evident from the study of the power output in the afterglow when the rf discharge is pulsed. We will not attempt to explain the maser action in either SF<sub>6</sub> or SF<sub>6</sub>+He because of complicated nature of the SF<sub>6</sub> molecule.

#### 5. Bromine

We have found that in a discharge containing 0.09 Torr of bromine with 1.8 Torr of argon, maser action takes place on four wavelengths spaced very closely around 8446 Å. These wavelengths have been measured

with a 1-m-high resolution grating spectrometer. Figure 3 is a trace from the spectrometer showing the four distinct lines. The wavelengths of the four lines are given below:

Wavelength (Å in air)	Typical power output (μW)
8446.28	740
8446.38	60
8446.70	120
8446.79	300.

We have not yet been able to assign classifications to these maser transitions, but it should be noted that the frequency separation between these lines is about 3.92, 13.9, 3.78, and 21.60 kMc/sec, respectively. These suggest interesting beat experiments. Also, it should be pointed out that the optical maser action in oxygen, as described in the Sec. 3 above, takes place at 8446.33 Å.

In the atomic line spectrum of bromine, there is, however, one transition at 8446.55 Å in air. Figure 4 shows an energy-level diagram of atomic Br.<sup>8</sup> The ground state of Br<sub>2</sub> is about 15 900 cm<sup>-1</sup> below the ground state of atomic bromine.<sup>9</sup> We have shown the 1s metastable states of argon on the same figure. It can be seen that there is a possibility of selective excitation of  $5p^4D$  levels on collisions of Br<sub>2</sub> molecule with argon 1s metastable atoms. The line at 8446.55 Å corresponds to the  $5p^4D_{3/2}-5s^4P_{3/2}$  transition of atomic bromine. Thus, energetically it certainly seems very possible that the 8446.55-Å line should be seen in maser oscillation. Isotope shift and hyperfine splitting can be discarded as possible reasons for explaining the anomalous structure in the line, since these splittings<sup>10</sup> are much smaller than the anomalies seen here. However, there is still a number of possibilities which have to be investigated to determine unequivocally the classification of the above four transitions. The possibility that these lines do not belong to bromine at all but to some other impurity cannot be ruled out entirely.

#### IV. CONCLUSION

We have shown here that the dissociation of various diatomic and polyatomic molecules is a general way of obtaining population inversions in a number of atomic species. However, it may not be construed that the possibilities stop with the descriptions of the schemes given here. There is a large number of schemes still left to be investigated which may lead to population inversion in still a greater number of elements and at a number of interesting wavelengths.

<sup>10</sup> S. Tolansky and S. A. Trivedi, Proc. Roy. Soc. (London) **A175**, 366 (1940).