STIMULATED EMISSION FROM MOLECULAR HYDROGEN AND DEUTERIUM IN THE NEAR INFRARED

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Results of investigation of stimulated emission from hydrogen and deuterium molecules or mixtures of them are presented. Stimulated emission from the latter two gases has been obtained for the first time. A mechanism for populating the vibrational levels of the operating levels based on the Franck-Condon principle is discussed in detail for H_2, D_2, and HD molecules. The results are compared with the experiments, which confirm the inversion mechanism.

In a previous paper [1] we reported stimulated emission from molecular hydrogen and discussed a possible inversion mechanism based on the Franck-Condon principle. No reliable assignment to transitions in H_2 was given for the stimulated emission lines. Hence it was desirable to make reliable assignments; to do this it was advisable to obtain laser action in molecular deuterium in addition to making wavelength measurements with increased accuracy. As is well known [2], comparison of the spectra of isotopic molecules allows one to make reliable line assignments.

In the present paper we will only briefly describe the experimental results. Primary attention will be given to the mechanism for populating the vibrational levels of the working states. In this paper we do not analyze the rotational structure of the H_2 and D_2 laser spectra but instead limit ourselves simply to presenting the experimental information on this question.

1. EXPERIMENTAL CONDITIONS AND RESULTS

The experiments were carried out with a pulsed gas laser having high voltage excitation [1]. Stimulated emission at wavelengths less than 1 micron was recorded photographically with a DFS-3 spectrograph having a dispersion of about 1.7 Å/mm¹⁾. The laser spectrum and the calibrating spectrum were photographed in the same diffraction order of the grating, which had 1200 lines/mm. We estimate the accuracy of measurement of the laser wavelengths on the DFS-3 spectrograph to be better than 0.08 Å. Stimulated emission at wavelengths longer than 1 micron was measured with comparatively poorer accuracy, about 10 Å, using a grating monochromator with an imperfect mechanical scanner. An FÉU-22 photomultiplier was used as the detector. The monochromator was also used to investigate the temporal characteristics of the emission; in this case the photomultiplier output signal was displayed along with the current pulse on a DESO-1 dual-beam oscilloscope. The time resolution of the system was determined experimentally by the method discussed in [3] and was about 50 nsec.

Stimulated emission was observed in molecular hydrogen, deuterium, and their mixtures. The results of investigations of the laser spectra are shown in the Table. The wavelengths of three laser lines in hydrogen and two in deuterium were measured with high accuracy on the DSF-3 spectrograph (see the first two columns). For comparison we give in the third column the frequencies of the spontaneously emitted lines as measured by Dieke [4] with the probable errors in hundreds of wave numbers. The differences between our measurements and those of Dieke do not exceed 0.06 Å.

Because of their large rotational constants, the spontaneous emission lines of molecular hydrogen and deuterium are rather widely spaced. Judging by the tables available to us [6] the lines of hydrogen are separated as a rule at intervals greater than 1 Å. This makes possible reliable assignments of the above five laser lines of hydrogen and deuterium to the transitions indicated in the fourth column in the Table. On the left in this

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1) We express our deep appreciation to M. A. Mazing and N. A. Vrublevskaya for kindly letting us use their apparatus and for instructing us in its use.

λ_{air}, Å meas.	ν_{vac}, cm^{-1} meas.	ν_{vac}, cm^{-1} [4]	Transition $2s\sigma\, {}^1\Sigma_g^+(E) \rightarrow 2p\sigma\, {}^1\Sigma_u^+(B)$	
		H_2		
8349.49	11973.49	11973.41	2→1	P (2)
8876.13	11263,08	11263,11	1→0	P (4)
8898.77	11234.43	11234.37	1→0	P (2)
11155 *	8962 *	8956.37	0→0	P (4)
11215 *	8915 *		0→0	—
13050 *	7660 *	7656.73 **	0→1	P (4)
		D_2		
8277.53	12077.58	12077.59	2→0	P (3)
9529.99	10490.31	10490.30	1→0	P (3)
		HD		
9160 *	10914 *		1→0	—

*Wavelength measured to an accuracy of about 10 Å.
**Calculated from energy level tables [5].

column we indicate the band and on the right the rotational transition. The wavelength of the hydrogen lines indicated by asterisks were not measured with sufficient accuracy and for them therefore we give only a tentative assignment[2]. In mixtures of equal amounts of hydrogen and deuterium we observed an extremely weak laser line which did not belong to the stimulated emission spectrum of either molecular hydrogen or deuterium. The predominant component of this mixture was HD (46%HD, 27%H_2 and 27%D_2). The wavelength of this line was measured with an accuracy of about 10 Å and it lies within the limits of the 1 → 0 band of the E → B electronic transition of the HD molecule. The Table indicates the proposed assignment of this line to a transition of the HD molecule. It should be noted that the firmly identified laser lines in both hydrogen and deuterium belong to the same transition, namely E → B and that the laser emission occurs from the lower vibrational levels of the E state to the lower vibrational levels of the B state. This is also true for the laser lines whose wavelengths we were not able to measure with sufficient accuracy.

It should also be mentioned that laser action was observed in H_2 and in the isotopic molecule D_2 on analogous transitions. This further confirms the validity of the assignments given.

A typical oscillogram of the laser pulse in molecular hydrogen is shown in Fig. 1. The shape of the laser pulse is approximately triangular and has a half-width of about 0.2 μsec. Its displacement with respect to the beginning of the current pulse is about 0.4 μsec. When the current pulse length is increased the half-width and displacement of the laser pulse do not change. The shape and relative position of the current pulse and the laser pulse are the same for the various transitions and do not depend on the hydrogen pressure or on the voltage. The displacement of the laser pulse with respect to the current pulse decreases when the diameter of the discharge tube is decreased.

FIG. 1. Stimulated emission pulse in molecular hydrogen at 11215 Å (above) and the current pulse (below). The time markers are 0.05 μsec apart.

For comparison we show in Fig. 2 oscillograms of laser pulses and of the spontaneous emission in the laser lines when the cavity mir-

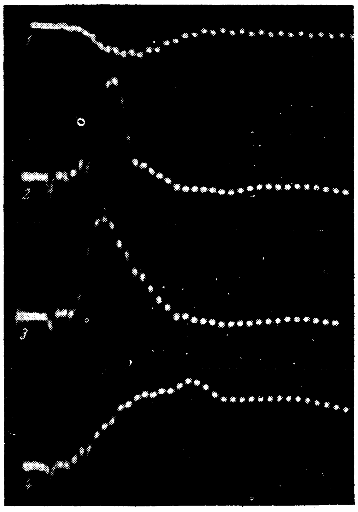

FIG. 2. The stimulated emission pulses (2) and the spontaneous (3) emission at 8899 Å, the spontaneous emission (4) in the H_α line, and the current pulse (1). The time markers are 0.05 μsec apart.

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[2] The wavelengths of these lines were determined somewhat more carefully than in [1].

rors were removed; we also show the spontaneous emission of the atomic hydrogen line H_α. The spontaneous emission pulse differs from that of the stimulated emission only in having a somewhat larger half-width, ~0.35 μsec, due to the slower fall-off. Analysis of the oscillograms shows that the duration of the spontaneous emission pulses from the molecular lines does not exceed the duration of the current pulse. However, the pulse of the atomic hydrogen H_α line has a duration of ~3.5 μsec. Oscillograms of the stimulated emission from deuterium have exactly the same appearance as for molecular hydrogen.

The dependence of the stimulated emission intensity from molecular hydrogen and deuterium on pressure is shown in Fig. 3. The maximum intensity for each curve is taken as unity. The optimum pressure for hydrogen is ~2.5 torr and for deuterium is somewhat larger, about 3.5 torr.

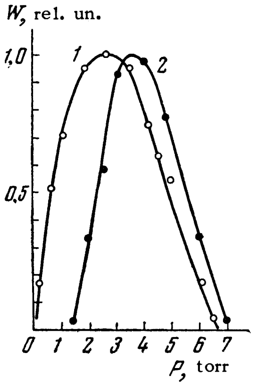

FIG. 3. The dependence of the stimulated emission intensity in molecular hydrogen (curve 1) and deuterium (curve 2) on the pressure (unit intensity for each curve is taken at the maximum): 1 – on the 8899 Å line in molecular hydrogen (voltage 26 kV), 2 – the 9530 Å line in molecular deuterium D_2 (voltage 27 kV).

2. ELECTRONIC STATES AND TRANSITIONS IN THE MOLECULES H_2, D_2, AND HD.

The potential energy curves for the electronic states of interest in the molecule H_2 are shown in Fig. 4. The electronic ground state $(1s\sigma)^2\,{}^1\Sigma_g^+$, which is designated by X, has a potential energy curve which was calculated in [7]. Because of the large vibrational and rotational constants only a few of the lower rotational levels of the un-excited vibrational state $X_{v=0}$ are occupied at room temperature (around 350°K). The population of the upper vibrational levels of the X state may be neglected. Because of the large off-duty factor of the applied discharge pulse, by the beginning of the following current pulse practically all of the molecules are in the lowest state $X_{v=0}$. The equilibrium nuclear separation for the X state is 0.74 Å. The potential energy curve of the lower working state designated by B, is also calculated in [7]. Since it has a larger equilibrium nuclear separation ρ = 1.29 Å, the potential curve of the B state is strongly displaced with respect to the potential curve of the ground state.

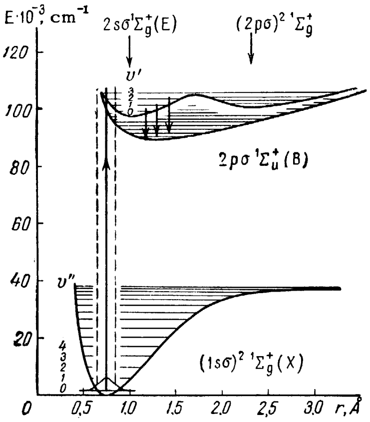

FIG. 4. Potential energy curves for molecular hydrogen (in the lower part of the potential energy curve of the X state we show the square of the vibrational wave function for v = 0).

The potential curve for the upper laser state as calculated in a theoretical paper by Davidson[8] has two minima and is shown in Fig. 4. The experimentally observed system of energy levels, which we have described up to now by the two states $2s\sigma\,{}^1\Sigma_g^+$ (E) and $(2p\sigma)^2\,{}^1\Sigma_g^+$ [9], are treated by Davidson[8] as a single system belonging to the first excited ${}^1\Sigma_g^+$ state. His numerical calculations are in good agreement with the experimental data. The so-called inner minimum has the equilibrium separation 1.01 Å, which is the same as the "experimental" E state. The energy levels of this minimum correspond with the energy levels of the E state. Further, the outer minimum is similar to experimental state $(2p\sigma)^2\,{}^1\Sigma_g^+$. For this reason we follow [8] and call the internal minimum of the first excited ${}^1\Sigma_g^+$ state the E state and the outer minimum a state with two excited electrons $(2p\sigma)^2\,{}^1\Sigma_g^+$.

In treating many questions relating to the population of the working levels, the effect of the outer minimum may be neglected. We will be chiefly interested in the region near the internal minimum, i.e., the E state. Because of the difference in their equilibrium separations the potential energy curve of the E state is displaced with respect to the ground state although it is displaced considerably less than the B state (cf. Fig. 4). One should also recall the existence of the $(2p\pi)^1\pi$ (C) state, which has a different symmetry from the E state, but which is very close to the latter in its fundamental parameters [10]. The electronic energy of the C state is only 20 cm^{-1} less than the energy of the E state. The values of the vibrational and rotational constants are very similar. The equilibrium separations of the C and E states are also nearly the same, viz., 1.033 Å and 1.011 Å. The potential energy curve of the C state calculated for the lower vibrational level from the simple Morse formula almost exactly coincides with the internal minima of the first excited state $^1\Sigma^+$, that is with the E state.

The potential energy curves of the isotopic molecules H_2, HD, and D_2 should practically coincide since the potential energy of the molecule depends but weakly on the mass of the nuclei. This is supported in particular by the fact that the electron energies and equilibrium separations of the electronic states X, B, E, and C of all three molecules coincide to within better than 1%[10]. In contrast to the potential energy, the kinetic energy of the molecule does depend on the nuclear masses. Hence the position of the vibrational and rotational levels within the potential energy curves are different for the different isotopes. The heavier the isotope the lower down the energy levels [8].

The ground state in H_2, D_2, and HD is connected with the C and D states by optical transitions. These give rise to the Lyman band ($B \longleftrightarrow X$) and to the Werner band ($C \longleftrightarrow X$) in the vacuum ultraviolet. The dipole transition $E \rightarrow X$ is forbidden because both states are of the same symmetry. The intense electronic transition $E \rightarrow B$ on which laser action is observed occurs in the infrared. The transition $C \rightarrow B$ is forbidden because the parity of both states is the same (see [10] concerning the transitions).

3. POSSIBLE MECHANISM FOR INVERSION BETWEEN VIBRATIONAL LEVELS

Using the H_2 molecule as an example we now consider the population of the upper and lower working states. During the initial moments of the discharge pulse at least, the B and E states are excited from the ground state primarily by collisions with fast electrons

$$H_2(X_0) + e \rightarrow H_2(E_{v'}) + e, \qquad (1)$$

$$H_2(X_0) + e \rightarrow H_2(B_{v''}) + e, \qquad (2)$$

(the subscripts 0 and v denote vibrational levels). The effective cross-sections for excitation of the B and E states by fast electrons (taking into account all of the vibrational rotational levels of each state) have been calculated in [11] using the Born method. At energies of about 100 eV the order of magnitude of these cross-sections is 10^{-17} cm^2, and the cross-section for the B state exceeds that for the E state by a factor 3 or 4. The maximum cross-sections evidently are of the same order of magnitude. If one took only this fact into account it would be hard to understand how population inversion can occur between the vibrational levels. Hence it becomes necessary to explain the mechanism for excitation to individual vibrational-rotational levels in the operating states. However it turns out that the population of the vibrational levels can be discussed independently of the population of the rotational levels. In the present paper we treat the excitation of vibrational levels only; the population of rotational levels will be considered in another publication.[12]

Electronic transitions in the molecule take place according to the Franck-Condon principle[10]. This principle is valid not only for transitions involving the absorption and emission of photons but also for molecular excitation transitions due to electron collision [13]. According to the Franck-Condon principle the large mass of the nuclei prevents the positions and velocities of the nuclei from changing during an electron transition. Only "vertical" transitions are possible on the diagram of the potential energy curves. Hence, when collisions occur between fast electrons and hydrogen molecules in the state $X_{v=0}$, only those vibrational levels of the B and E states which lie within the limits of the vertical band are populated (cf. Fig. 4). The potential energy curves of the E and X states are such that in the processes of the type (1) only the lower vibrational levels of the E state (having vibrational numbers $v' = 0, 1, 2$) are populated. Because of the large displacement of the potential energy curve of the B state (the lower state of the laser transition) relative to the ground states, the vertical band intersects vibrational levels with $v'' \geq 3$. Excitation of the lower vibrational levels $v'' = 0, 1$ and 2 by direct electron collisions from the ground state by processes (2) are very unlikely, since this violates the Franck-Condon principle. However the shapes of the potential energy curves of the B and E states are the same and hence there should be a rather large probability for transitions between the states $E_{v'}$ ($v' = 0, 1, 2$) and $B_{v''}$ ($v'' = 0, 1, 2$). Because of the difference in the excitation probabilities for the states by processes (1) and (2), it is possible to establish inversion between them; when the conditions for oscillation are satisfied laser action will occur. The corresponding transitions are indicated by the arrows in Fig. 4. During the course of the discharge pulse and the laser action, the working levels may be populated not only by the processes (1) and (2) but also by other means; this can lead to a decrease in the rate of population in the upper working level and to the cessation of laser action. This explains the pulsating character of the laser action.

The mechanism for stimulated emission in the molecules HD and D_2 is essentially the same as in H_2. However there are certain differences related to the isotopic displacements of the energy levels of the first two molecules below the corresponding levels in molecular hydrogen. There is a large displacement observed for the molecule D_2. Hence the conditions for excitation of the vibrational levels of the three molecules are different; moreover there are different Franck-Condon factors for the vibrational transitions $E_{v'} \rightarrow B_{v''}$. The largest differences should be observed between the stimulated emission spectra of molecular hydrogen and deuterium.

The mechanism proposed above for stimulated emission in molecules of H_2 and D_2 is in agreement with the experimental results. According to this mechanism, stimulated emission in deuterium and hydrogen should be and is observed on the same electronic transition, viz., $E \rightarrow B$. In both molecules stimulated emission is observed from the lower vibrational levels of the E state ($v' = 0, 1, 2$) to the lower vibrational levels of the B state ($v'' = 0, 1$) and simultaneously on those transitions which should occur according to the Franck-Condon principle and are indicated in Fig. 4 by the arrows. The assignments of the laser lines in H_2 and HD given in the Table (although the line wavelengths were measured rather crudely) also agree with the proposed inversion mechanism. One should underline the great value of experiments with isotopic molecules since they allow one to make more reliable assignments of laser lines in molecular transitions. Moreover such experiments provide additional experimental and theoretical data on the excitation of the vibrational and rotational levels of the working states of the molecules.

We now briefly consider the effect on the stimulated emission of perturbations experienced by the E state ([4,8,9]) and also the effect of the interaction between the E and C states. These perturbations are caused by the interaction of the energy levels of the inner and outer minima of the potential curve of the first excited state ${}^1\Sigma_g^+$. The perturbation gives rise to a change in the intensities of individual lines which directly effects the intensity of the stimulated emission. The strongest perturbation occurs for the vibrational level $v' = 2$ of the E state of the hydrogen molecule. It is possible that this explains the rather weak stimulated emission in the band $E_{v'=2} \rightarrow B_{v''=1}$ of the hydrogen molecule. However, a more detailed study of this question is necessary.

Because of the energy resonance and the very exact coincidence of the potential energy curves of the E and C states there may be a transfer of the excitation energy. This transfer could occur either due to collisions of the molecule or to collisions of the molecules with electrons. We do not exclude the possibility that population of the E state under our conditions is due to energy transfer of excitation from the C states. Such a cascade process for populating the E state must be considered along with the direct mechanism for population of the ground state. On the other hand it is also possible to have energy transfer from the E to the C state. Because of the near coincidence of the potential energy curves of the E and C states, in both this and the previous case the Franck-Condon principle remains in force just as in the direct excitation mechanism.

In conclusion we note that the assignment of the laser lines in hydrogen and deuterium, given in the present article, is in general not subject to doubt. It is desirable, however, to increase the accuracy of measurement of certain of the wavelengths of the laser lines in hydrogen and hydrogen and deuterium mixtures with the goal of making the assignments more precise.

The inversion mechanism which was proposed in [1] and considered more extensively here for inverting the populations of the vibrational levels of the E and B states of molecular hydrogen and deuterium is based only on the very general Franck-Condon principle and should have wide applicability. This point of view should also be used in considering the excitation of vibrational levels in molecular nitrogen and in carbon dioxide [14] as well as in other molecular systems.

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