ISSN 0023-1584, Kinetics and Catalysis, 2007, Vol. 48, No. 2, pp. 183–189. © MAIK "Nauka/Interperiodica" (Russia), 2007.
Original Russian Text © N.M. Rubtsov, G.I. Tsvetkov, V.I. Chernysh, V.V. Azatyan, 2007, published in Kinetika i Kataliz, 2007, Vol. 48, No. 2, pp. 197–204.

# Effects of Reactive Admixtures on the Near-IR Emission Spectra of Hydrogen and Deuterium Oxidation Flames

**N. M. Rubtsov, G. I. Tsvetkov, V. I. Chernysh, and V. V. Azatyan**
*Institute of Structural Macrokinetics and Materials Research Problems, Russian Academy of Sciences,*
*Chernogolovka, Moscow oblast, 142432 Russia*
*e-mail: nmrubtss@mtu-net.ru*

Received December 13, 2006

**Abstract**—The emission spectra of hydrogen–oxygen and hydrogen–air flames at 0.1–1 atm exhibit a system of bands between 852 and 880 nm, which is assigned to the $H_2O_2$ molecule vibrationally excited into the overtone region. This molecule results from the reaction $HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2^{v} + O_2$. The overtone region also contains bands at 670 and 846 nm, which are assigned to the vibrationally excited $HO_2^{\bullet}$ radical. This radical results from the reaction between H and $O_2$. The $HO_2^{\bullet}$ radicals resulting from $H_2$ or $D_2$ combustion inhibited by small amounts of propylene are initially in vibrationally excited states. The role of vibrational deactivation is discussed.

**DOI:** 10.1134/S0023158407020012

The $HO_2^{\bullet}$ radical is one of the main intermediates in the oxidation and combustion of hydrogen-containing compounds [1–4]. In the atmosphere, it is involved in the catalytic cycle resulting in ozone decomposition. The $HO_x$, $OH^{\bullet}$, $H_2O_2$, and $HO_2^{\bullet}$ particles present in the atmosphere and stratosphere result mainly from ozone photolysis followed by the reaction between $O(^1D)$ and water. The atmospheric photodissociation of OH-containing molecules has attracted great attention [5–8]. In particular, there have been studies devoted to the photolysis of OH-containing components by visible light. This process takes place through the vibrational excitation of the O–H bond in the region of overtones whose energy is close to or higher than the dissociation threshold of one of the bonds in the molecule [9].

The postulate of $HO_2^{\bullet}$ formation in the hydrogen flame [10], put forward in the early 1930s, has played an important role in the formation of the theory of branched chain processes. However, although many researchers made numerous attempts to identify this radical directly in the hydrogen flame, this was finally accomplished in 1982 by the laser magnetic resonance (LMR) method [11].

The heat of the recombination reaction between H and $O_2$ is ~44 kcal/mol [12]. Thus, the $HO_2^{\bullet}$ molecule resulting from this reaction contains excess energy, which can be localized on vibrational degrees of freedom (the energy of the electronically excited state of $HO_2^{\bullet}$ is much lower and falls into the near-IR region (~1.4 μm [13]). This energy is sufficient to excite the stretching vibrations of the O–H bond to the $\nu = 4$ overtone, which falls into the visible spectral range. The formation of $HO_2^{\bullet}$ radicals in vibrationally excited states with $\nu > 1$ makes it possible to identify these radicals by measuring their emission in the near-IR region. The vibrational excitation of $H_2O$, $H_2O_2$, and $HO_2^{\bullet}$ into their overtone states can also take place in the combustion of hydrogen and hydrogen-containing compounds and in plasma chemical or photochemical oxidation. The detection of the vibrationally excited $H_2O_2$ and $HO_2^{\bullet}$ species in the overtone region could provide additional information concerning the mechanisms of these processes.

It was reported [14] that a band at 852 nm can be observed for the $H_2O_2$ molecules resulting from the reaction

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 + 33.5\ \text{kcal/mol}. \quad \text{(I)}$$

This band was observed in the study of the flame of the branched-chain oxidation of dichlorosilane [15]. This band was also observed for hydrogen oxidation [16], so it is not impossible that the $HO_2^{\bullet}$ radical makes some contribution to emission in this region.

The domination of the branched-chain mechanism in hydrogen combustion at any pressure shows itself, e.g., as the inhibiting effect of certain small admixtures on all combustion regimes (see, e.g., [17, 18]). Examination of the spectral range of OH overtones during branched-chain oxidation in the presence of an active admixture would provide deeper insight into the inhibition mechanism.

The purpose of this study is to see whether it is possible to identify the overtone bands of the hydroxyl groups of peroxides in the emission spectrum of the hydrogen flame and to study the effects of active admixtures on the intensity of these spectra. Propylene ($C_3H_6$), a strong inhibitor [19], and sulfur hexafluoride ($SF_6$), a weak inhibitor with strong deactivating properties [4], were examined as admixtures. As will be shown below, these inhibitors exert different effects on the spectral composition of emissions.

## EXPERIMENTAL

Experiments were carried out in a static vacuum apparatus [20] coupled with an OSA-500 multichannel optical spectral analyzer (which is sensitive in the 200–900 nm range). The total pressure was 0.1 to 1 atm, and the temperature was varied between 300 and 800 K. Two different reactors were used. Reactor I was a quartz cylinder 4 cm in diameter and 30 cm in length. It was fitted with a furnace and an initiating source and had removable quartz windows at its ends [20]. The furnace temperature was controlled using a KVA-501 temperature regulator with an accuracy of ±0.5 K. Reactor II was a stainless steel cylinder 16 cm in length and 8 cm in diameter. It had removable covers and organic-glass optical windows. Spark ignition electrodes were placed in the center of the reactor. Ignition was initiated with a spark with an energy of ~0.9 J or with a nichrome coil (eight turns, $d = 0.3$ mm) energized by pulsed voltage from a capacitor battery with a capacitance of 300 μF. From the spark ignition system, a 6-V rectangular pulse was directed to the synchronization input of the optical spectrum analyzer OSA-500. This made it possible to scan spectra starting at a chosen wavelength during ignition and to rule out noise accumulation (the time interval between the spark and the ignition event was no longer than 0.5 ms). The resolving power of the optical system was 0.15 nm per channel. The required number of spectral data accumulations (one accumulation = 500 channels (72 nm); 32 ms) were saved in the computer memory of the OSA-500 instrument. The active element of OSA-500 was cooled in a thermostat to 223 K. This significantly extended the signal storage time before signal "readout" by the electron beam. The spectrum addition and multiplication function made it possible to reliably record emission lines in the specified spectral range.

The surface of reactor I was washed with hydrofluoric acid. Stoichiometric mixtures of $H_2$ ($D_2$) and $O_2$ and mixtures consisting of 16.5 or 33% hydrogen and air were examined. The amount of an admixture was varied between 0 and 8%. The emission from the flame was focused with a collimator (fluorite; focal length, 7 cm) on the entrance slit of the optical device. The lower ignition limit was determined by the admission method [4], and combustion kinetics was controlled by luminescence measurements. Emission from the electronically excited radical $OH^{\bullet}$ ($A^2\Sigma^+$) at $\lambda = 306$ nm was measured using an interference filter ($\Delta\lambda = 25$ nm) and an FEU-71 photomultiplier (spectral sensitivity range, 200–600 nm). The emission bands arising from combined transitions in $H_2O$ (823 nm) and $H_2O_2$ (852 nm) [15, 16] were recorded using an MDR-3 monochromator and an FEU-62 photomultiplier (spectral sensitivity range, 600–1300 nm). The signal from FEU-71 was directed to the synchronization input and then to one of the inputs of an S9-8 dual-trace memory oscilloscope operating in the leading mode. The signal from FEU-62 was fed to the other input of the S9-8 oscilloscope. During combustion, along with recording the emission from $OH^{\bullet}$ ($A^2\Sigma^+$), we measured emission around 1.4 μm ($OH^{\bullet}$, $\nu = 2$) using an MDR-3 monochromator (grating with 300 grooves per millimeter, silicon filter). The spectral width of the slit was ~0.005 μm. The monochromator was calibrated against the characteristic absorption bands of chloroform as described in [17]. The emission measurement system consisted of an FD-10 photodiode; a preamplifier; and U3-29, V6-9, and U2-8 amplifiers connected in series. The signal from the last amplifier was directed to an S9-8 oscilloscope. The variable signal was recorded by modulating the emission with a mechanical shutter operating at a frequency of 3300 Hz. The modulation envelope represented the time variation of the chemiluminescence intensity.

The reactor was pumped to $2 \times 10^{-3}$ Torr. The gas pressure in the reaction zone was measured with VDG-1 and VIP-2 vacuum gages. $H_2$, $D_2$, $O_2$, $SF_6$, and $C_3H_6$ were reagent grade.

## RESULTS AND DISCUSSION

### *Emission Spectra of the Branched-Chain Hydrogen and Deuterium Oxidation Flames*

Figure 1 shows emission intensity data for the spark-initiated combustion of stoichiometric hydrogen–oxygen and deuterium–oxygen mixtures in reactor I in the presence and in the absence of the above admixtures in the spectral range of 820 to 860 nm. In this spectral range, the $2D_2 + O_2$ mixture does not emit light (curve *1*). The emission spectrum of the $2H_2 + O_2$ mixture at 100 Torr (curve *2*) contains bands at 823, 846, and 852 nm. The bands at 823 and 852 nm are due to the $H_2O$ and $H_2O_2$ molecules, respectively [14, 16]. The assignment of the 852 nm band to $H_2O_2$ [14, 16] is based on the fact that there are no bands assignable to $H_2O$ in the 840–892 nm range [21]. Comparison of curves *1* and *2* suggests that the molecule emitting at 846 nm contains hydrogen atoms. The literature contains no information concerning the assignment of the 846 nm band.

Figure 2 (curve *3*) shows the emission spectrum of the $2H_2 + O_2$ mixture in the 630–670 nm range obtained under the same conditions. This spectrum

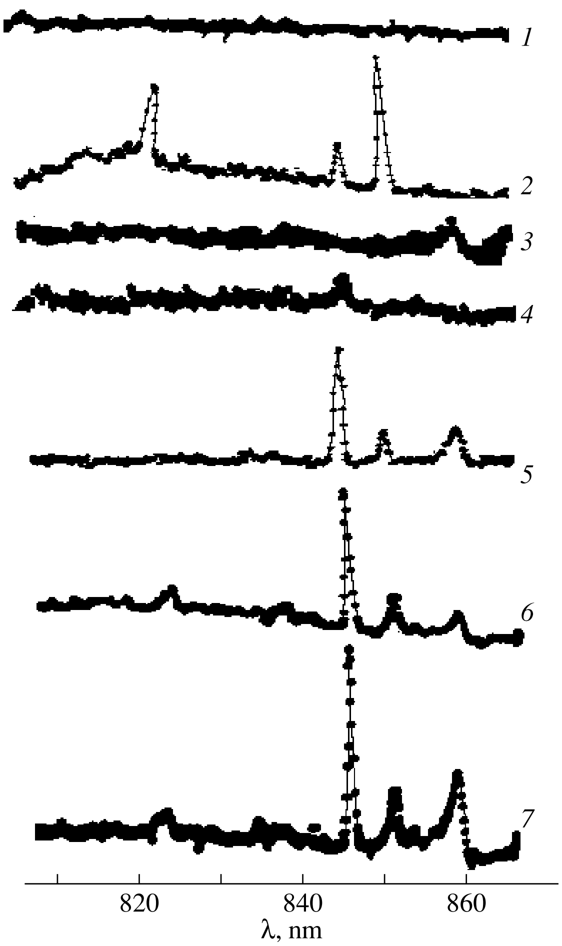

**Fig. 1.** Emission spectra of the flames of stoichiometric mixtures of (*2*, *6*, *7*) hydrogen, (*1*, *4*, *5*) deuterium, and (*3*–*7*) propylene with oxygen in the 810–860 nm range at $T$ = 300 K and $P$ = 100 Torr (spark initiation): (*1*) $2D_2 + O_2$, (*2*) $2H_2 + O_2$, (*3*) 3% $C_3H_6 + O_2$, (*4*) 1% $C_3H_6 + 2D_2 + O_2$, (*5*) 2% $C_3H_6 + 2D_2 + O_2$, (*6*) 1.5% $C_3H_6 + 2H_2 + O_2$, and (*7*) 3% $C_3H_6 + 2H_2 + O_2$.

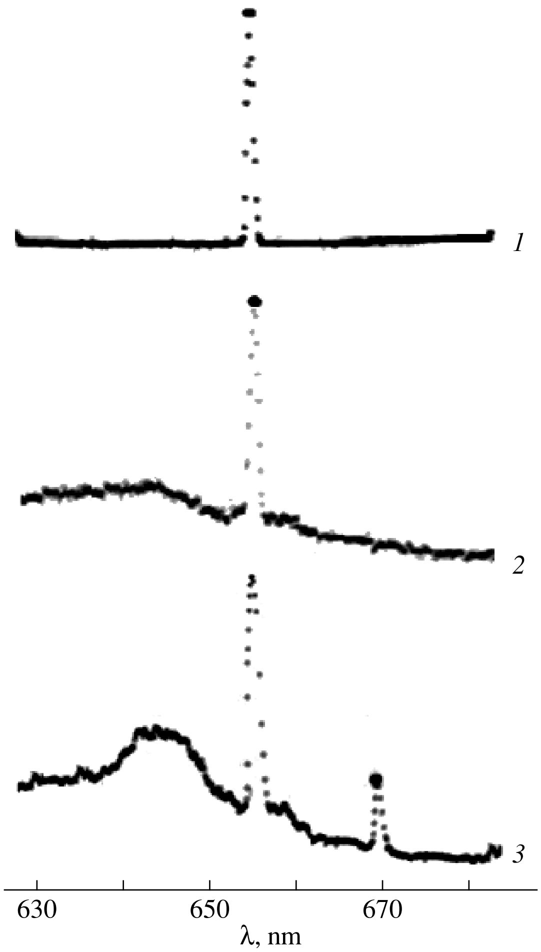

**Fig. 2.** Emission spectra of the flames of stoichiometric mixtures of hydrogen and deuterium in the 630–680 nm range at $T$ = 300 K and $P$ = 100 Torr (spark initiation): (*1*) pure $H_2$, (*2*) $2D_2 + O_2$, and (*3*) $2H_2 + O_2$.

contains two bands. The band at 656 nm is due to the excited hydrogen atoms (656.3 nm) [12], which form in the spark discharge. This is confirmed by the emission spectrum of the spark in pure hydrogen (curve *1*). The excited deuterium atom gives rise to a band at 656.1 nm [12] (Fig. 2, curve *2*). However, the spectrum of the hydrogen flame contains a band at 670 nm due to molecules containing hydrogen and oxygen atoms. Again, the literature contains no information concerning the assignment of the 670 nm band.

In reactor II, we investigated stoichiometric hydrogen–oxygen and deuterium–oxygen mixtures spark-ignited at 230 Torr and mixtures consisting of 16.5 or 33% hydrogen and air ignited at atmospheric pressure (Fig. 3). The data obtained with this reactor are similar to the above data for the bands at 670, 846, and 852 nm. Reducing the proportion of hydrogen in the mixture eliminates the 846 nm band (curve *4*). As can be seen in Fig. 3, some ten bands adjoin the 852 nm band on its long-wavelength side ($\Delta\lambda \approx 45$ cm$^{-1}$). These bands are affected by the admixtures in the same way as the 852 nm band, so they can tentatively be assigned to $H_2O_2$. These bands occur at 852.1, 856.9, 860.0, 863.4, 866.7, 870.0, 872.4, 876.0, 881.4, and 886.0 nm.

Figure 4 shows the plots of the wave numbers of the strongest overtone bands of the hydroxyl group of the water, $H_2O_2$, and $HONO_2$ molecules versus the number of the vibrational level, which are derived from earlier reported data [6, 22, 23] ($\nu_1$ and $\delta$ are, respectively, the wave numbers of the asymmetric stretching and bending vibrations of OH). The overtones of the OH stretches in the $H_2O_2$ and $HONO_2$ molecules occur at smaller wave numbers because the $\nu_1$ value is smaller for these molecules than for $H_2O$. Obviously, this situation will also be observed for combined overtone vibrations $n\nu_1 + \delta$ since $\delta(H_2O) > \delta(H_2O_2)$ [22]. Thus, the bands at 852, 846, and 670 nm are likely due to combined OH vibrations in a molecule containing a peroxide group. A portion of the absorption spectrum

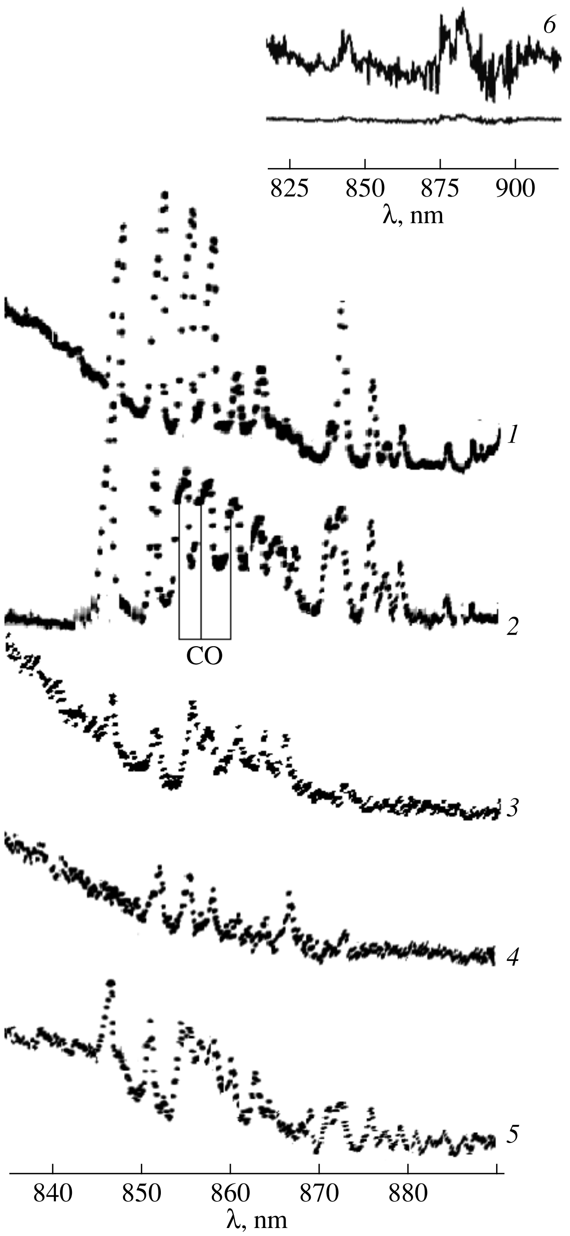

**Fig. 3.** (*1*–*5*) Emission spectra of the spark-initiated flames of stoichiometric mixtures: (*1*) $H_2$–$O_2$ (230 Torr), (*2*) $H_2$–$O_2$ in the presence of 2.7% $C_3H_6$ (230 Torr), (*3*) 33% $H_2$ in air (1 atm), (*4*) 16% $H_2$ in air (1 atm), and (*5*) 16% $H_2$ in air + 2.5% $C_3H_6$ (1 atm). (*6*) Portion of the overtone spectrum of $HONO_2$ [19].

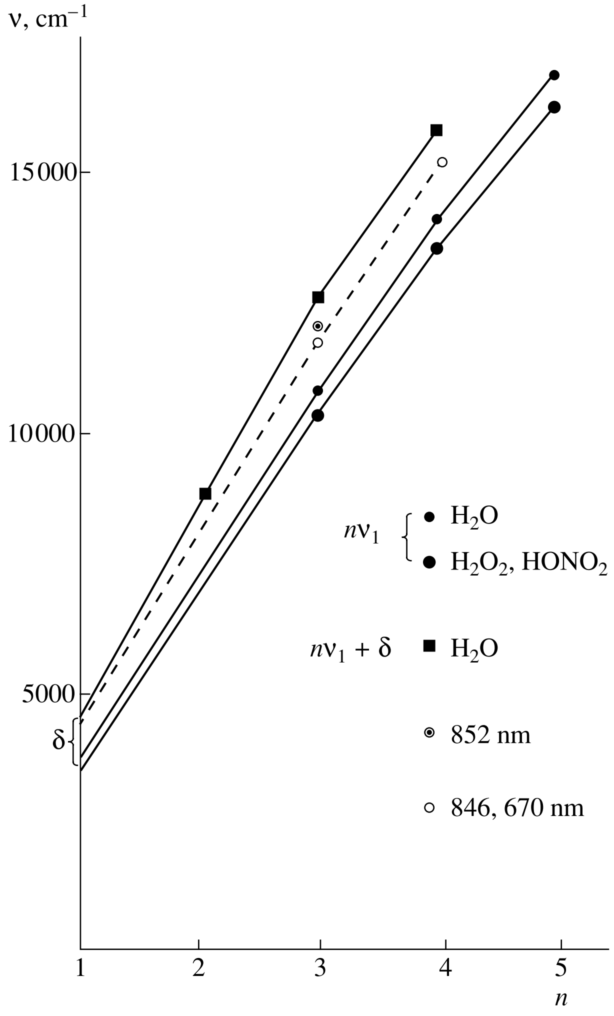

**Fig. 4.** The wave number of the vibrational transition in the hydroxyl group as a function of the vibrational quantum number for $H_2O$, $H_2O_2$, and $HONO_2$.

of $HONO_2$ in the ν(OH) = 3.4 overtone region [23] is presented in Fig. 3 (curve *6*). In this spectrum, the bands at 877 and 883 nm were assigned [23] to the *3* combination and the band at 845 nm was assigned to the *3* combination. By analogy, the bands at 852 and 670 nm in Fig. 3 (curves *1*, *2*) are assignable to the $3\nu_1 + \nu(N{=}O)$ combination, while the band at 846 nm has no analogues. Note that the procedure described above does not allow the $3\nu_1$ band for $H_2O_2$ to be recorded because the spectral sensitivity of the OSA-500 instrument is limited by λ = 900 nm on the long-wavelength side.

With reactor II, it is possible to record the combined bands of $H_2O$ around 697 and 723 nm for the spark-ignited stoichiometric $H_2 + O_2$ mixture at 200 Torr. Thus, the above procedure allows one to record all expected overtone bands of the hydroxyl group in the given wavelength range.

It was found that the intensity of the 852 nm band, which is due to $H_2O_2$, is much reduced by adding 2% $SF_6$, while the 846 and 670 nm bands persist up to 7% $SF_6$. The extinction effect of $SF_6$ is unlikely to be selective, since the separation between the bands at 852 and 846 nm is 85 cm$^{-1}$, which is smaller than $kT$. Furthermore, the intensity of these bands is as low as the noise level in the self-ignition reaction at 733 K. This possibly indicates that these bands are due to one chemical compound other than $H_2O_2$. This is also indicated by the fact that the 846 nm band is missing from the spectra of hydrogen-depleted mixtures, while the bands at 852–870 nm are reliably recorded (Fig. 3, curve *4*). Note that if vibrationally excited molecules of hydrogen peroxide result from reaction (I), there will be insufficient energy for the excitation of the next OH overtone in $H_2O_2$, so this overtone will not be observed in the spectrum. Indeed, we were unable to record the $4\nu_1$ band of hydrogen peroxide (755 nm [22]). However, the recording of bands in this spectral range is complicated by the fact that this range is very close to the doublet due to potassium, whose traces are always present in glasses [24] and give rise to very strong emission lines as compared to the OH overtones.

Energy sufficient for the excitation of the 670 nm band is released in the reaction $H + O_2 \longrightarrow HO_2^\bullet$. Therefore, the 846 and 670 nm bands can tentatively be assigned to combined transition in the OH group of the $HO_2$ radical. A study devoted to calculation of the vibrational levels of the $HO_2^\bullet$ radical [25] predicted the existence of high-lying combined levels in $HO_2^\bullet$ around 850 nm (which have not been observed as yet). Furthermore, the energies of the low-lying levels calculated using the same algorithm are in good agreement with experimental data. This can be viewed as an argument in favor of our assignment. The wave functions of the excited states containing a significant contribution from the bending vibrations of OOH were also considered [25]. The wave numbers for the high-lying levels (0, *x*, 0) and (1, *x*, 0), where $x = 6$–8, are reported to be 11 377, 11 607, 11 840, and 11 790 $cm^{-1}$ [25]. These values are similar to the values measured in this study. Thus, it is possible that the 846 nm band is not assignable to the frequency combinations considered in the analysis of Fig. 4. Further studies are required for correct assignment of the spectral transitions.

Note that, of the $H_2O$ overtones between 640 and 900 nm, only an emission band at 823 nm is observed in the experiments in reactor I. As is noted above, the bands at 697 and 723 nm [22] are observed only during the combustion if stoichiometric hydrogen–oxygen mixtures in reactor II. The overtone excitation can be due the exothermic reaction

$$H + O_2 + M \longrightarrow HO_2^\bullet + M. \qquad \text{(II)}$$

In the case of $M = H_2O$, the heat of reaction (II) is 47 kcal/mol [14, 26, 27], which is sufficient for the excitation of the $H_2O$ molecule in the overtone region. Thus, the absence of emission at 697 and 723 nm in reactor I, in which the heat-transfer conditions are better than in reactor II, characterizes the specific features of energy distribution in reaction (II), indicating that a significant part of the released energy remains in the vibrational degrees of freedom of the hydroxyl radical.

With reactor I, the $OH^\bullet$ ($A^2\Sigma^+$) chemiluminescence peak time is equal to the $H_2O_2$ emission and $\lambda = 846$ nm emission peak times, as well as to the time at which the buildup rate of the luminescence of $H_2O$ in the states $3\nu_1 + \delta$ and $2\nu_1$ (1.41 μm) reaches its maximum (Fig. 5). The finding that the intensity peaks of the emission bands at 823, 852, and 846 nm are separated in time is further evidence that the bands at 852 and 846 nm are not due to the $H_2O$ molecule and is in agreement with earlier findings [16].

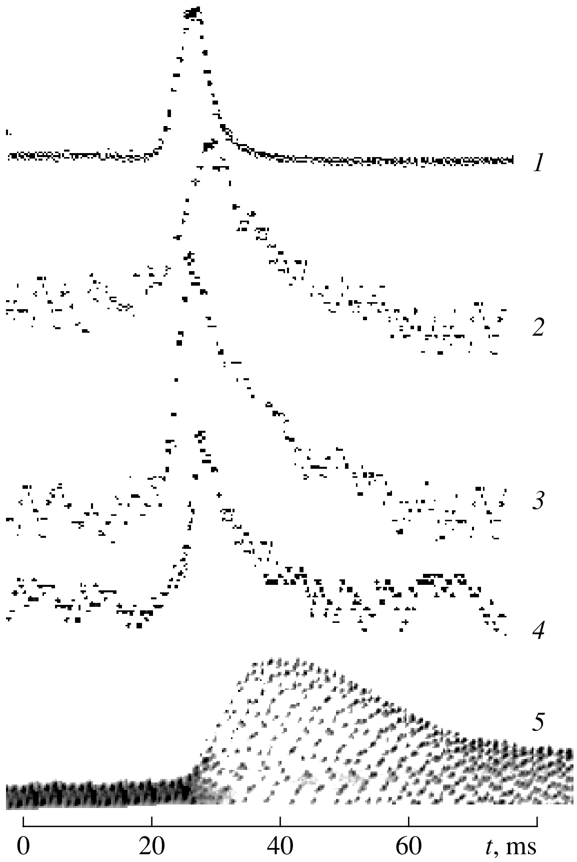

**Fig. 5.** Kinetics of luminescence at $\lambda$ = (*1*) 306 nm, (*2*) 823 nm, (*3*) 846 nm, (*4*) 852 nm, and (*5*) 1.41 μm ($T$ = 300 K, $P$ = 100 Torr, spark initiation).

Note that the observed $H_2O(v)$, $HO_2^\bullet(v)$, and $H_2O_2(v)$ species cannot result from a thermal process involving no chain reaction. Indeed, the flame temperature reported for the stoichiometric hydrogen–air mixture (see, e.g., [4]) is 2050 K at atmospheric pressure. At thermodynamic equilibrium, the concentration of water vapor in the reaction product under these conditions far exceeds the equilibrium concentrations of $H_2$ and $O_2$ molecules and the $HO_2^\bullet$ and $H_2O_2$ concentrations are too low to be detected in our experiments. At the same time, as is demonstrated above (see, e.g., Figs. 1 and 3), detectable amounts of excited $HO_2^\bullet$ and $H_2O_2$ result from combustion. Therefore, the amounts of vibrationally excited species $H_2O_2(v)$ and $HO_2^\bullet(v)$ that

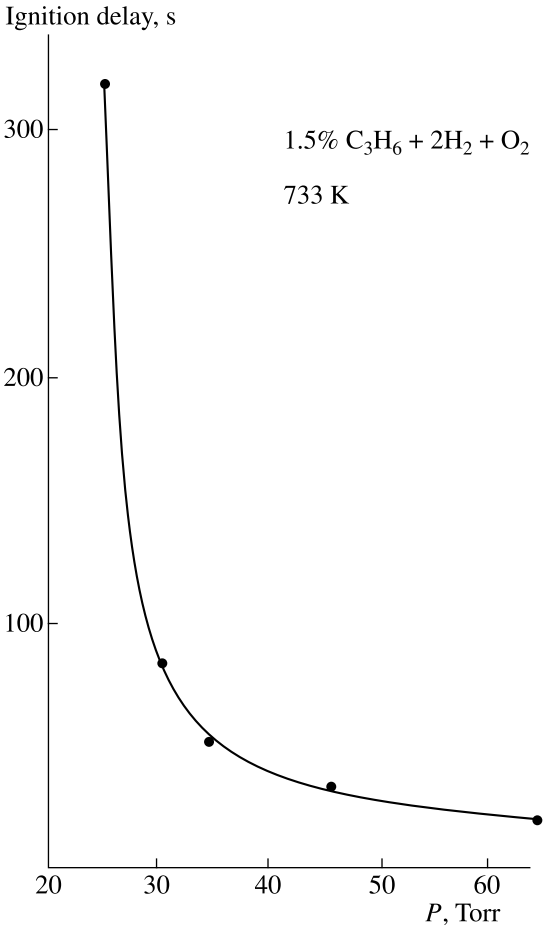

**Fig. 6.** Ignition delay as a function of total pressure for the 1.5% $C_3H_6 + 2H_2 + O_2$ mixture at $T = 733$ K.

result from the exothermic reactions are much greater than the equilibrium amounts of these species.

### *Emission Spectra Arising from Hydrogen and Deuterium Oxidation in the Presence of $C_3H_6$*

Figure 6 plots the self-ignition delay $\tau$ as a function of the total gas pressure for the stoichiometric $H_2 + O_2$ mixture containing 1.5% $C_3H_6$. The inhibited self-ignition limit under the conditions examined ($\tau \longrightarrow \infty$) is 29 Torr. The lower self-ignition limit for the propylene-free stoichiometric mixture is 1.5 Torr, indicating the high inhibiting efficiency of $C_3H_6$ in hydrogen oxidation [19].

Figure 1 (curve *3*) shows the emission spectrum for the initiated ignition of 3% $C_3H_6$ in $O_2$. This spectrum differs from the spectra observed during $H_2 + O_2$ combustion (Fig. 1, curve *2*; Fig. 3, curve *3*). The characteristic ignition time in this case is much longer than the same time for the $H_2 + O_2$ mixtures. Since the band at 859 nm (Fig. 1, curve *3*) is not observed in hydrogen combustion, it is not assignable to molecules containing an OH group. This band should be assigned to the $a'^3\Sigma \longrightarrow a^3\Pi$ transition in CO [28]. Note that the ignition of a $C_3H_6$–$O_2$ mixture containing more than 2.7% $C_3H_6$ can be initiated under our conditions only with a spark (0.9 J).

It is clear from Fig. 1 (curves *6*, *7*) that, in the presence of propylene, the relative intensity of the 846 nm band ($J_{846}$) is higher than the intensity of the 852 nm band ($J_{852}$). The reverse situation ($J_{852} > J_{846}$) is observed for the ignition of the propylene-free mixture (Fig. 1, curve *2*). The same relationship between the band intensities is observed for mixtures in which hydrogen is replaced with deuterium (Fig. 1, curves *4*, *5*) and is independent of the initiation technique. In the ignition of the pure $2D_2 + O_2$ mixture, there is no emission in this wavelength range. The redistribution of emission intensity between the 846 and 852 nm bands in the presence of propylene is reproducible and is independent of the order of runs involving and not involving propylene.

As is noted above, the combustion of the $C_3H_6 + O_2$ mixtures containing less than 2.7% $C_3H_6$ and no hydrogen can be initiated neither with a hot coil nor with a spark under the conditions examined. Observation of the band at 846 and 852 nm in the mixtures containing deuterium in place of hydrogen suggests that the band due to $H_2O_2$ and the band that we assigned to $HO_2^{\bullet}$ arise only from the deuterium-promoted oxidation of the hydrocarbon. Therefore, these bands arise from the reaction between propylene and the active sites of deuterium combustion. The finding that the 846 nm band is missing from the spectra of the flames of lean hydrogen–air mixtures and appears in the presence of propylene (Fig. 3, curves *4*, *5*) provides independent evidence that the reaction involving propylene yields $HO_2^{\bullet}$.

Thus, if the assignment of the 846 nm band to the $3\nu_1 + \delta\,(HO_2^{\bullet})$ overtone is assumed to be correct on the strength of the above arguments, the increase in the intensity of this band can be ascribed to the buildup of the vibrationally excited $HO_2^{\bullet}$ species in the presence of propylene, as was done in a previous study [11].

There has been a report on the mechanism of the effect of propylene on hydrogen combustion [29]. The $C_3H_6$ molecule adds a H atom without overcoming any significant energy barrier. This is followed by the generation of a hydroperoxyl radical:

$$H + C_3H_6 + (M) \longrightarrow C_3H_7^{\bullet} + (M),$$

$$C_3H_7^{\bullet} + O_2 \longrightarrow C_3H_7O_2^{*},$$

$$C_3H_7O_2^{*} \longrightarrow C_3H_6 + HO_2^{\bullet}.$$

This inhibition mechanism was verified experimentally by using the EPR and LMR methods [11]. According to LMR data, the introduction of a small amount of the hydrocarbon into a steady-state hydrogen flame causes a buildup of hydroperoxyl radicals in the combustion zone. However, the question as to whether the hydroperoxyl radicals are in an overtone excited state was not raised in that study. It can be assumed that the energy released in the last reaction is sufficient to excite the $HO_2^{\cdot}$ radical into the region of overtones. Indeed, the overall heat of the above three reactions is 44 kcal/mol [12]. The alkyl peroxy radical $C_3H_7O_2^*$ decomposes, having no time for deactivation. After its decomposition, part of the excitation energy resides in the vibrational degrees of freedom of the $HO_2^{\cdot}$ radical. Possibly, this is not the only hydroperoxyl radical excitation pathway in hydrocarbon oxidation.

For the oxidation of deuterium in the presence of propylene, the most likely sequence of reactions is similar to that presented above:

$$D + C_3H_6 + (M) \longrightarrow C_3H_6D^{\cdot} + (M),$$

$$C_3H_6D^{\cdot} + O_2 \longrightarrow C_3H_6DO_2^*,$$

$$C_3H_6DO_2^* \longrightarrow C_3H_5D + HO_2^{\cdot}.$$

Thus, a system of emission bands between 852 and 880 nm is observed for hydrogen–oxygen and hydrogen–air mixtures. These bands are assigned to the $H_2O_2$ molecule excited into the overtone energy range. This molecule results from the reaction $HO_2^{\cdot} + HO_2^{\cdot} \longrightarrow H_2O_2^{v} + O_2$. Bands at 670 and 846 nm are also observed in the overtone range, which are assigned to the vibrationally excited radical $HO_2^{\cdot}$ resulting from the $H + O_2$ reaction. Hydrogen combustion inhibited by small admixtures of propylene also yields vibrationally excited $HO_2^{\cdot}$ radicals.

## ACKNOWLEDGMENTS

This study was supported by Russian Foundation for Basic Research (project no. 05-03-33050), the Civil Research and Development Foundation (grant no. RUE1-2686-MO-05), and INTAS (grant no. 05-1000005-7664').

## REFERENCES

1. Azatyan, V.V., *Kinet. Katal.*, 1999, vol. 40, no. 2, p. 180 [*Kinet. Catal.* (Engl. Transl.), vol. 40, no. 2, p. 161].
2. Semenov, N.N., *Tsepnye reaktsii* (Chain Reactions), Moscow: Nauka, 1986.
3. Mauss, F., Peters, N., Rogg, B., and Williams, F.A., in *Reduced Kinetic Mechanisms for Applications in Combustion Systems*, Peters, N. and Rogg, B., Eds., Berlin: Springer, 1993.
4. Lewis, B. and von Elbe, G., *Combustion, Flames, and Explosions of Gases*, New York: Academic, 1987.
5. Finlayson-Pitts, B.J. and Pitts, J.N., Jr., *Chemistry of the Upper and Lower Atmosphere*, San Diego: Academic, 2000.
6. Brown, S.S., Wilson, R.W., and Ravishankara, A.R., *J. Phys. Chem. A*, 2000, vol. 104, p. 4976.
7. Fleming, P.R., Li, M., and Rizzo, T.R., *J. Chem. Phys.*, 1991, vol. 94, p. 2425.
8. Kuhn, B. and Rizzo, T.R., *J. Chem. Phys.*, 2000, vol. 112, p. 7461.
9. DeMore, W.B., Howard, C.J., Sander, S.P., Ravishankara, A.R., Golden, D.M., Kolb, C.E., Hampson, R.F., Molina, M.J., and Kurylo, M., *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*, Pasadena: Jet Propulsion Lab., California Inst. of Technology, 1997, vol. 97, p. 4.
10. Hinshelwood, C.N. and Williamson, A.T., *The Reaction between Hydrogen and Oxygen*, New York: Oxford Univ. Press, 1934.
11. Azatyan, V.V., Gaganidze, K.I., Kolesnikov, S.A., and Trubnikov, G.R., *Kinet. Katal.*, 1982, vol. 23, no. 1, p. 244.
12. *Tablitsy fizicheskikh velichin. Spravochnik* (Tabulated Physical Data: A Handbook) Kikoin, I.K., Ed., Moscow: Atomizdat, 1976.
13. Osmann, G., Bunker, P.R., Jensen, P., Buenker, R.J., Gu, J.-P., and Hirsch, G., *J. Mol. Spectrosc.*, 1999, vol. 197, p. 262.
14. Abid, M., Wu, M.S., Liu, J.B., and Ronney, P.D., *Combust. Flame,* 1999, vol. 116, p. 348.
15. Chernysh, V.I., Rubtsov, N.M., and Tsvetkov, G.I., *Mendeleev Commun.*, 2000, p. 143.
16. Azatyan, V.V., Rubtsov, N.M., Tsvetkov, G.I., and Chernysh, V.I., *Zh. Fiz. Khim.*, 2005, vol. 79, no. 3, p. 397 [*Russ. J. Phys. Chem.* (Rngl. Transl.), vol. 79, no. 3, p. 320].
17. Azatyan, V.V., *Usp. Khim.*, 1999, vol. 69, no. 12, p. 22.
18. Azatyan, V.V., Baklanov, D.I., Merzhanov, A.G., et al., *Dokl. Akad. Nauk*, 2001, vol. 376, no. 1, p. 55 [*Dokl.* (Engl. Transl.), vol. 376, no. 1, p. 1].
19. Azatyan, V.V., Kalachev, V.I., and Masalova, V.V., *Zh. Fiz. Khim.*, 2003, vol. 77, no. 8, p. 1432 [*Russ. J. Phys. Chem.* (Engl. Transl.), vol. 77, no. 8, p. 1282].
20. Rubtsov, N.M., Ryzhkov, O.T., and Chernysh, V.I., *Kinet. Katal.*, 1997, vol. 38, no. 4, p. 498 [*Kinet. Catal.* (Engl. Transl.), vol. 38, no. 4, p. 454].
21. Schermaul, R., Learner, R.C.M., Newnham, D.A., Ballard, J., Zobov, N.F., Belmiloud, D., and Tennyson, J., *J. Mol. Spectrosc.*, 2001, vol. 208, p. 43.
22. Hillman, J.J., Jenning, D.E., Olson, W.B., and Goldman, A., *J. Mol. Spectrosc.*, 1986, vol. 117, p. 46.
23. Donaldson, D.J., Orlando, J.J., Amann, S., et al., *J. Phys. Chem. A*, 1998, vol. 102, p. 5171.
24. Azatyan, V.V., Rubtsov, N.M., Tsvetkov, G.I., and Chernysh, V.I., *Kinet. Katal.*, 2006, vol. 47, no. 3, p. 333 [*Kinet. Catal.* (Engl. Transl.), vol. 47, no. 3, p. 327].
25. Barclay, V.J., Dateo, C.E., and Hamilton, P., *J. Chem. Phys.*, 1994, vol. 101, no. 8, p. 6766.
26. Wu, M.-S., Ronney, P.D., Colantonio, R., van Zandt, D., *Combust. Flame*, 1999, vol. 116, p. 387.
27. Wu, M.-S., Liu, J.-B., and Ronney, P.D., *27th Int. Symp. on Combustion*, Pittsburgh, 1998, p. 2543.
28. Pearse, R. and Gaydon, A., *The Identification of Molecular Spectra*, London: Chapman and Hall, 1941.
29. Azatyan, V.V., Borisov, A.A., Merzhanov, A.G., et al., *Fiz. Goreniya Vzryva*, 2005, vol. 41, no. 1, p. 3.