INTRACAVITY LASER SPECTROSCOPY OF EXCITED MOLECULES

L.N. Sinitsa

Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk
Received January 25, 1997

The investigations into the intracavity laser spectroscopy of excited molecules performed at the Institute of Atmospheric Optics SB RAS are reviewed in the paper. Various ways of the molecule excitation inside a wideband laser cavity are described: by high-temperature heating; in laser-induced plasma; in an electric discharge; in a static electric field, and by resonance optical radiation. Block diagrams of the experimental setups and the investigation results obtained are presented.

In recent years there appeared many experimental and theoretical studies of highly excited vibrational states of small polyatomic molecules (Refs. 1—4 and references therein). These studies have been stimulated by current interest in intramolecular kinetics, photoselective chemistry, and atmospheric optics. The investigation of highly excited vibrational-rotational states has become important in seeking a quantum analog to the classic chaotic motion, classic-to-quantum correspondence, studies of nonlinear resonances and in various applications in the laser chemistry, environmental protection, atmospheric optics, and astrophysics.

Rotational-vibrational lines caused by transitions to excited vibrational states (energy is larger than $7000 \ cm^{-1}$) are very weak, their strengths, as a rule, are 5 to 7 orders of magnitude weaker than line strengths of fundamental bands. Therefore, highly sensitive spectrometers must be used to record these weak bands. Intracavity laser spectrometers, due to their high sensitivity to absorption, become a powerful tool for studying highly excited molecular states.

The method of broad-band Intracavity Laser (ICL) Spectroscopy is in quenching of laser emission at the absorption-line frequencies of the species placed inside a broad-band laser cavity. In this case the laser emission spectrum has sharp dips at the frequencies of absorption lines, which can be recorded with an ordinary spectroscopic instrumentation. In the intracavity laser spectroscopy the laser itself is a nonlinear detector of weak absorption. The laser imitates a multipass absorption cell, but with much greater effective length L_{eff} of the absorbing layer than in an ordinary multipass cell where it is limited by the radiation losses on mirrors. In this case L_{eff} is proportional to the duration t of a continuous generation in the region of an absorption line under study. ICL—spectroscopy was widely used in various applications some of which are described in the monograph.[5] One of the most effective applications of the ICL-spectroscopy is the study of weak molecular spectra caused by transitions to highly excited states. Study of highly excited molecular states was fulfilled

during last 25 years at the laboratory of molecular spectroscopy of the Institute of Atmospheric Optics. The paper summarized these investigations of highly excited molecular states using the intracavity laser spectroscopy technique.

ICL -SPECTROSCOPY OF MOLECULES WITH TEMPERATURE EXCITATION

Traditional absorption spectroscopy under normal conditions (pressure ~ 1 atm, temperature $t = 300$ K, without external fields) allows one to record lines due to the transitions from a relatively low rotational levels of ground vibrational state because only low lying levels have high enough populations at room temperature for recording the transitions. Highly sensitive methods such as ICL-spectroscopy, photoacoustic spectroscopy extend investigation into the region of levels with higher rotational quantum numbers.

The ICL-spectrometers in combination with the effective methods of populating the upper states enable one to investigate transitions not only from high J-levels but from the excited vibrational states as well. As a result of high speed operation and small size of the absorption cell the ICL-spectrometers can be effectively used with excitation of the molecules at high temperature, with electric discharge, high-energy particles, optical pumping and so on, that allows one to obtain information which is inaccessible when using other methods.

The simplest way to populate energy levels with high J and V quantum numbers is heating of molecules. The population of the rotational energy level N_{VJ} with the energy E_J in the case of thermodynamic equilibrium is determined by Boltzmann law

$$N_{VJ} = q_{VJ} \, N_V = (1/Q_R) \, N_V \, q_J \exp{(-E_J/kT)}, \quad (1)$$

where q_{VJ} is the fraction of molecules at the Jth level of the vibrational state V, N_V is the population of the vibrational state with the quantum

number V, q_J is the statistical weight of the rotational level,

$$Q_R = \sum_J q_J \exp\left(- E_J / kT\right) \text{ is the rotational partition}$$

function, k is the Boltzmann constant.

The population of the vibrational state N_V with the energy E_V is

$$N_V = (1 / Q_V)\, N_0\, q_V \exp\left(- E_V / kT\right), \qquad (2)$$

where q_V, Q_V are the statistical weight and the vibrational partition function, respectively.

Population of the molecular energy levels determines the rotation-vibration line strengths and absorption coefficients of a gas

$$K_{VJ} = \frac{1}{8\pi c \nu^2} \left(\alpha_{V'J' \leftarrow V''J''}\right) \Delta N_{V'J' \leftarrow V''J''}\,. \qquad (3)$$

Here $\alpha_{V'J' \leftarrow V''J''}$ is the spectral Einstien coefficient and

$$\Delta N_{V'J' \leftarrow V''J''} = N_{V''J''} - \left(q_{V'J'} / q_{V''J''}\right) N_{V''J''}. \qquad (4)$$

CO$_2$. For example, the harmonic frequencies of CO_2 molecule are $\nu_1 = 1345$ cm^{-1}, $\nu_2 = 667$ cm^{-1}, $\nu_3 = 2361$ cm^{-1}, rotational constant $B_0 \cong 0.390$ cm^{-1}, and the partition functions are[6]:

$$Q_R = \sum_J q_J \exp\left[\frac{- \hbar c\, \nu_R(J)}{kT}\right] \approx \frac{T}{1.12}\,,$$

$$\qquad\qquad (5)$$

$$Q_V = \sum_{V_1} \sum_{V_2^l} \sum_{V_1} q_J \exp\left[\frac{- h c\, \nu_V(V_1,\, V_2^l,\, V_3)}{kT}\right],$$

The temperature increase leads to a redistribution of the population of the molecules, and to an increase in the upper states population. The total partition function $Q_{VR} = Q_V\, Q_R$ changes with increasing temperature in the following way: $291\,(T = 300$ K), $977.6\ (T = 600$ K), $2164\ (T = 900$ K), and $4699.3\ (T = 1200$ K), this leads to a redistribution of the populations of rotational and vibrational states at temperatures 300–1300 K as presented in Fig. 1. At room temperature, the population of the low vibrational states: (00001) for $E_V = 0$, (01101) for $E_V = 667$ cm^{-1}, (10001) for $E_V = 1345$ cm^{-1}, and (00011) for $E_V = 2361.7$ cm^{-1} have the following fraction: 0.95; 0.04; 0.001; 0.00006 of the whole number of molecules. This means that the band strengths for transitions with the same change of the vibrational quantum numbers, from the initial (00011) state, will be five orders of magnitude weaker than those starting from the ground state.

When temperature increases to 1350 K, the ratios of populations of (00001), (01101), (10001), and (00011) states reach 0.20; 0.20; 0.45; 0.023

(Fig. 1a). This enables one to investigate transitions started from these vibrational states. Redistribution of the population to high rotational quantum numbers J leads to the line strength redistribution (Fig. 1b).
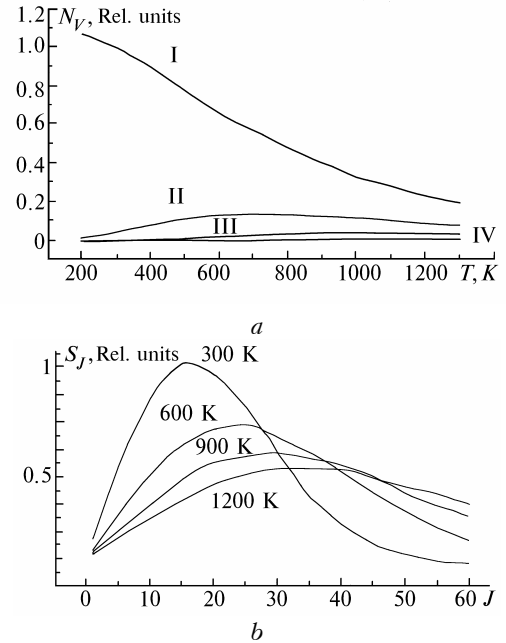

FIG. 1. Population of CO_2 vibrational states as function of temperature (I − (00001), II − (01101), III − (10001) and IV − (00011)) (a); Redistribution of rotational line strengths inside the CO_2 band at temperatures 300 ... 1200 K (b).

The (20032) ← (00001) CO_2 band origin ($\nu_0 = 9517$ cm^{-1}) is located near high frequency border of a Nd glass laser. Due to the vibration anharmonicity the sequences of transition with $\Delta V_1 = 2$, $\Delta V_2 = 0$, $\Delta V_3 = 3$, starting from the first excited vibration states are situated in the range of a Nd-glass laser emission. These transitions were recorded using a Nd-glass and a F-color center LiF-laser ICL-spectrometers. The populations of the excited states were increased by heating of the 1-m long absorption cell to temperature up to 1350 K.

Special absorption cells were designed for ICL-spectroscopy of molecules with temperature excitation. A high-temperature quartz cell was used for temperature excitation up to 1300 K. The Windows of the absorption cell was heated up to 700 K to provide small gradient of temperature along the cell.

The band (20032) ← (00001) was investigated at higher rotational quantum numbers J. Besides, "hot" band discovered earlier in Venus Spectrum [7], was recorded in laboratory conditions. "Hot" bands (22232) ← (02201), (30032) ← (10001), and (20042) ← (00011) were recorded for the first time.

H$_2$O. High temperature spectra of $H_2^{16}O$ in the acetylene flame recorded using a Fourier transform spectrometer in the region up to 6000 cm^{-1} showed

its efficiency for study highly excited rotational levels of ground vibrational states, when it was possible to determine energy of rotational levels with the rotational quantum numbers up to $J = 20$. High temperature spectra of water vapor and its isotopes were investigated using ICL-spectrometers in 8000 to 11000 cm^{-1} region.[9,13] It is interesting to study structure of the rotational states which belong to vibrational state of the second hexade and first decade of the water vapor states in resonance.

Investigations of $H_2^{16}O$, $H_2^{18}O$, D_2O, and HDO molecules were carried out at temperatures 300—1200 K and allowed us to record several thousands new absorption lines.

Using energy structure recorded the inverse spectroscopic task was solved and spectroscopic parameters for the states which belong to the second hexade were determined. These parameters allowed us to calculate energy structure of states with $J \approx 7$ to 11 within an accuracy better than 0.1 cm^{-1}.

Spectra of water vapor are very complicated in the high frequency region. Neighboring lines in the spectrum correspond to transitions with high and low rotational quantum numbers, so the line assignment is a very difficult task in such circumstances. Spectra of $H_2^{16}O$ ($P = 10$ Torr) recorded using an ICL-spectrometer at temperatures of 300 K and 900 K are presented in Fig. 2.
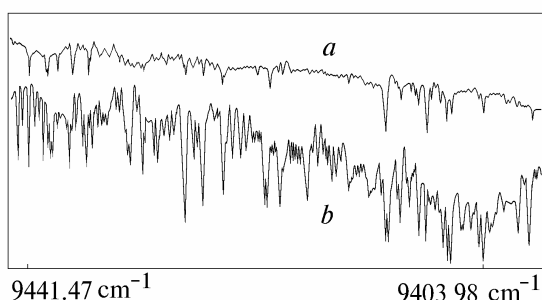

FIG. 2. Spectrum of $H_2^{16}O$ recorded at the temperature 300 K (a) and 900 K (b).

Assignment of high temperature spectra in 8000 ... 9500 cm^{-1} was performed when spectrum recorded using an ICL-spectrometer was compared with the calculated ones. The combination difference method was used to do this with the energy of a level being determined using 2 or 3 lines corresponding, in the spectrum, to different molecular transitions. Line assignment was tested using temperature dependence of water vapor lines which is determined by the expression[8]:

$$S = C_1 \frac{N_J}{Q_V Q_R} \exp\left(\frac{-\hbar c E''}{kT}\right) \left[1 - \exp\left(\frac{-\hbar c \nu}{kT}\right)\right], \quad (6)$$

where C_1 is the coefficient which includes all the temperature independent factors, $Q_R \sim T^{3/2}$, the vibration partition function of H_2O is

$$Q_V = \Pi_{i=1}^3 \left[1 - \exp\left(\frac{-\hbar c \nu_i}{kT}\right)\right]^{-1}, \quad (7)$$

High temperature absorption spectra of water vapor allow one to get information on thousands new excited states and to improve assignment of lines from the (111) vibrational state.

ICL-SPECTROSCOPY OF MOLECULES IN A LASER SPARK

The use of high temperature furnaces and burners makes it possible to obtain an equilibrium Boltzmann distribution of molecules over energy levels but such heaters provide relatively not very high temperatures from 1000—2000 K. At the same time laser radiation being focused on a target can produce a rapid heating of the surrounding medium up to several thousands K. The investigations of molecules excited in a laser spark were carried with the intracavity laser spectrometers based on Nd-glass laser. The radiation of a CO_2 laser emitting 1 s duration pulses of 5 J energy was focused on a target placed 5—10 mm off the axis of a neodymium glass laser resonator (Fig. 3).
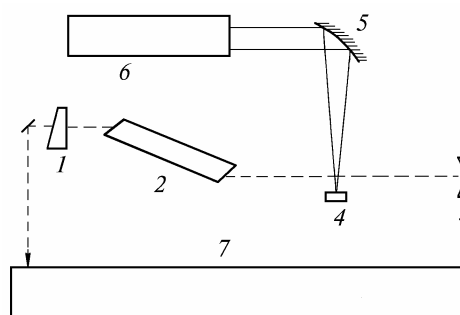

FIG. 3. Block-diagram of a ICL-spectrometer for study of laser spark spectra: the cavity mirrors (1, 3), the active element (2), the target (4), the spherical mirror (5), CO_2-laser (6), and the polychromator (7).

Samples made from metals, graphite and organic substances were used as targets. Focused CO_2 laser radiation produces a plasma. The expanding plasma thermally excites the surrounding air on the axis of the ICL-spectrometer. The neodymium glass laser of the ICL-spectrometer is synchronized with the CO_2 laser. Because of a spectral memory effect in the ICL-spectrometer, the dip existing in the spectrum at the very beginning of a laser pulse remains unchanged to the pulse end, thus allowing one to record the weak induced absorption.

When the laser radiation is focused onto an organic target there appear spectral lines in the ICL-spectrum (more than 200 lines within the interval of 100 cm^{-1} wide) which mainly belong to the vapor of the target substance. Large values of the absorption coefficients of the observed lines ($\sim 10^{-3}$ cm^{-1}) clearly

demonstrate the possibility of making an analysis of the target surface with high concentration sensitivity using the ICL -method.

   In the case of a metal target there appear not so many lines in the ICL-spectrum and they are less intense. Analysis has shown that the ICL-spectrum mainly contains the water vapor absorption lines due to the transitions between the upper vibrational-rotational states (Fig. 4).
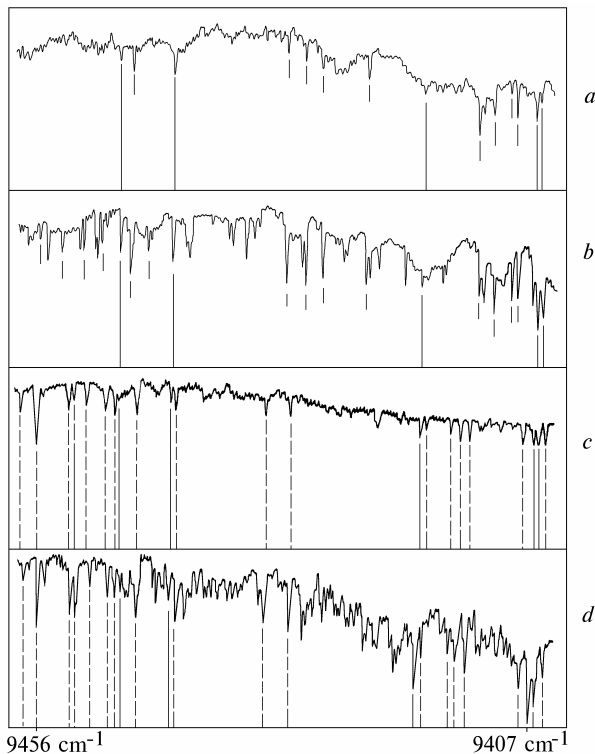

9456 cm^{-1} 9407 cm^{-1}

FIG. 4. The water vapor spectra obtained using an ICL-spectrometer in 9407 … 9456 cm^{-1} at temperatures 300 K (a) and 600 K (b) and using a laser spark from carbon target (c) and at resonance excitation of H_2O with a ruby-laser radiation (d).

EXCITATION OF MOLECULES IN AN ELECTRIC DISCHARGE

   Electric discharge is an effective tool for molecular excitation. Glow discharge was used in combination with an ICL-spectrometers to investigate electronic spectra of molecules.[10] We used a hollow cathode and one-electrode MW discharge.

Hollow Cathode Discharge Excitation

   Hollow cathode discharge was used to record U-atoms.

   Strong U-line $\lambda = 591.54$ nm coincides with the spectral region of R6G dye laser, so special ICL-spectrometer on the basis of a broad-band R6G dye laser has been constructed. The spectrometer consists of two parts: i) a laser with a cell inside the cavity and ii) a grating spectrometer for recording laser emission spectra. The scheme of the

spectrometer is presented in Fig. 5. Two variants of the flash lamp pumping of the dye-laser allowed us to increase pulse duration have been tested. In the first variant pumping pulse was formed by two discharge contours. At the first stage the capacitor discharged at minimum lamp voltage. After that, at time delay about 40 μs which is equal to just a half of a leading edge of the pulse, the second contour discharged through controlled discharge device. In this case it is possible to significantly shorten the front of the light pulse and, as a consequence, to reach longer generation (~100 μs). In the second variant, the front of the light pulse has been shortened by a proper choice of the discharging device inductance. As a result, generation duration reached 50 to 100 μs.
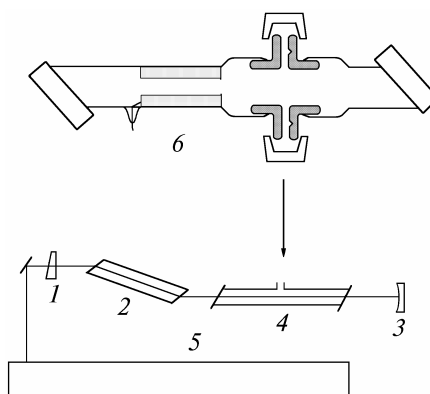

FIG. 5. Block-diagram of the intracavity laser spectrometer with the hollow cathode: the mirrors (1, 3), the active laser media (2), the cell (4), the spectrograph (5), and the hollow cathode (6).

   Integrated over time ICL-spectrum was recorded using a grating spectrograph at a spectral resolution of 0.03 cm^{-1} and at inverse linear dispersion of 0.1 nm/mm.

   Typical pulse duration of the laser was ~80 μs, which provides the threshold absorption sensitivity of an ICL-spectrometer for integral spectral recording as low as 10^{-7} cm^{-1}; that corresponds to a path-length of about 10000 m in traditional spectroscopy with the attenuation of the radiation of 10%.

   The threshold sensitivity of the ICL-spectrometer was estimated from the recorded spectrum. The intensities of the H_2O lines at $\nu = 16907.23$ and 16913.61 cm^{-1} in the absorption spectrum of air (humidity corresponded to 10 Torr of water vapor) which lead to 10 percent dips in the laser emission spectrum are $2.9 \cdot 10^{-5}$ and $2.6 \cdot 10^{-5}$ cm^{-2}atm^{-1}, respectively. The absorption coefficients at the center of these lines under atmospheric conditions are of $1.2 \cdot 10^{-7}$ and $1.1 \cdot 10^{-7}$ cm^{-1} values, which are of the same order of magnitude as the estimates of the threshold sensitivity obtained from the pulse duration.

   The ICL-spectrometer with a hollow—cathode discharge was used to detect U-atoms. The main problem of detecting U was connected with the

technique of elements atomization. To carry out atomization we have designed special hollow cathode (Fig. 5), which permits to place a sample on the internal surface of the cell.

The cathode has 5-mm-thick walls and it is of 50 mm length. As an anode, a hollow cylinder made of stainless steel was used. The buffer gas (Ar) leaked into the cell with a hollow cathode, which was previously evacuated. A discharge current varied from 10 to 50 mA. The U-line in absorption and emission spectrum was investigated under various conditions.

The hollow cathode operates both in a cw mode and in a pulse mode, that is why the investigation of different stage of the hollow cathode discharge could be made. The experimental set up enabled recording of the laser emission spectrum both at a discharge switched on and after its termination every 50 μs. This enabled the possibility of observing the formation of absorption lines in the plasma of the hollow cathode discharge.
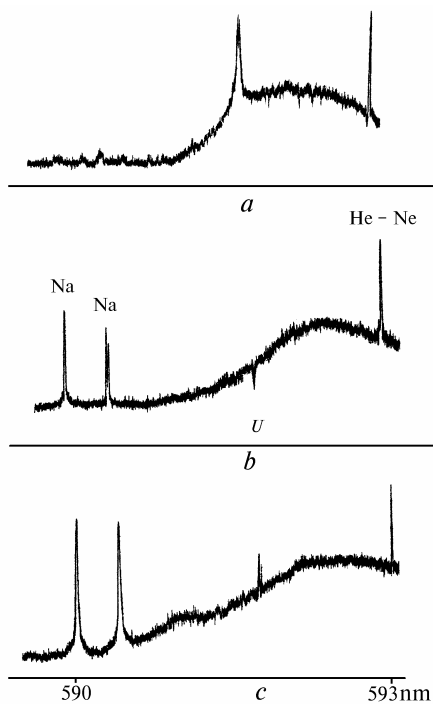

FIG. 6. *Spectra recorded using an ICL - spectrometer with the hollow cathode, a) the hollow cathode is switched on; b, c) the hollow cathode is switched off (reference line of a* He-Ne *laser;* Na*, U lines of a sample).*

In the experimental study of the ICL-spectra using a hollow cathode discharge three peculiarities of spectra formation were revealed.

1) Discharge is switched on. Very strong emission gain line is observed in the ICL-spectrum (Fig. 6a);

2) Discharge is switched off. There are absorption U-lines in the ICL-spectrum (Fig. 6b);

3) Discharge is switched off. There is a combination of the emission and absorption lines in the ICL-spectrum (Fig. 6c).

As follows from this study, the processes in the ICL-spectrometer with a hollow cathode are complicated and it is necessary to carry out special investigation of excitation processes in a hollow cathode.

One-Electrode MW Discharge

To excite a single-electrode discharge plasma inside a laser cavity[12] a high frequency generator with self-excitation was used. The block-diagram of the spectrometer is presented in Fig. 7. Relaxation oscillations were produced in the generator with a series contour at relatively low voltage 1800—3200 V.

Edge of pulses was 1—2 μs with the pulse duration 6 to 400 μs. Repetition rate of the generation was 0.5 to 50 Hz. Energy of pulses at the carrier frequency 52 MHz is absorbed by the discharge plasma. High value of peak power of 0.5—10 W was achieved in the experiment.
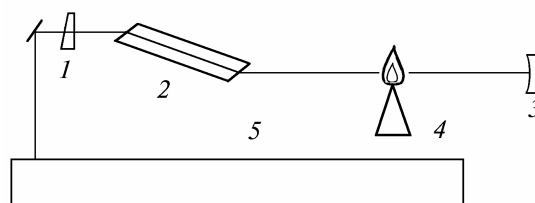

FIG. 7. *Optical arrangement of the intracavity laser spectrometer with the plasma inside the cavity, 1,3 are the mirrors, 2 is the active laser medium, 4 is the plasma source.*

These stable wide-band pulses enable one to obtain AM one-electrode discharge for excitation of plasma of different forms (one-channel, multi-channel, diffuse plasma, etc.) at low and atmospheric pressure. If pressure of the gas decreases, the threshold of the non-equilibrium plasma initiation increases, that allows one to excite the samples more effectively. Estimation shows that electron temperature can achieve 3000—10000 K and ion temperature T_i was 400—1500 K which are sufficient for ionization of highly excited samples such as Ti, W.

Nd-glass laser has been used as a laser source. Spectral range of a non-dispersive ICL-spectrometer was 9360—9480 cm^{-1}, pulse duration was 1 ms which provided detection limit as low as $3 \cdot 10^{-9}$ cm^{-1}. Spectra were recorded using a grating polychromator with the spectral resolution 0.02 cm^{-1}.

In the experiment there were recorded spectra of metal samples as well as of different salts and oxides. The spectra contain thousands of new lines. Examples of the spectra are presented in Fig. 8. The spectra contain not only absorption lines but emission lines also since in a broad-band laser the condition

the gain coefficient = the cavity losses

is valid in a wide spectral region and any absorption line (emission line) of absorption coefficient (gain coefficient) more than $3 \cdot 10^{-9}$ cm^{-1} appears as a sharp dip (peak) in the lasing spectrum.

Experiments showed that the combination of an ICL-spectrometer with a one-electrode discharge plasma is an effective tool for investigation of highly excited atoms and molecules.
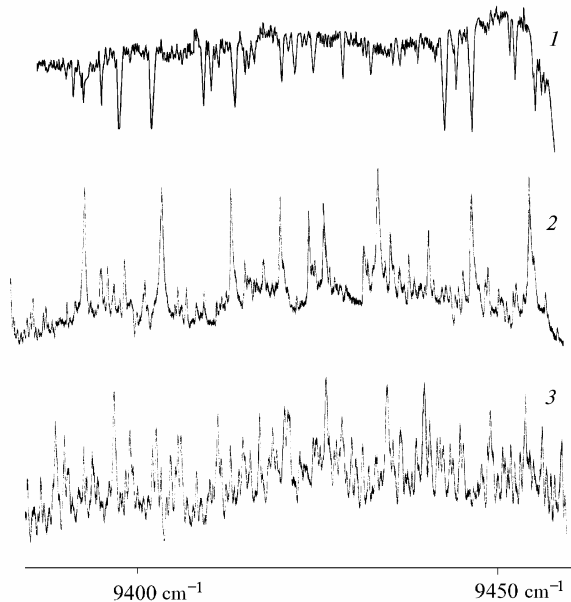

FIG. 8.   ICL-spectrum with Pd *(a),* W *(b), and* Fe *(c) in plasma.*

ICL SPECTROSCOPY WITH A RESONANCE LASER EXCITATION

In the above section we have analyzed some nonresonance methods of excitation.   Much more efficient populating of the upper vibrational states of molecules can be achieved using a resonance optical excitation when the laser radiation frequency coincides with that of the transition $V''J'' \rightarrow V'J'$ (Ref. 9, 13). In this case the laser radiation excites the molecules from the rotational level J'' of the lower vibrational state V'' to the rotational level J' of the upper vibrational state V' (Fig. 9). Molecular collisions result in relaxation of the molecular ensemble to a Boltzmann equilibrium distribution over rotational levels at a rate $1/\tau_R$. The vibrational relaxation of the molecules takes place at a rate $1/\tau_V$, where τ_R and τ_V are time constants of the rotational and vibrational relaxation, respectively.

Formation of a dip in the ICL-spectrum at the resonance optical excitation is determined by the duration τ_P of the laser resonance pumping, rotational relaxation time τ_R, vibrational relaxation time τ_V and by the duration of spectrometer laser pulse τ_L. The rotational relaxation time is of the order of 10^{-11} s, while that of the vibrational one is $^\sim 10^{-6}$ s. The use of an ICL-spectrometer with the

optical excitation can be efficient if high sensitivity of measurements is assured, that is why the duration of the spectrometer laser pulse must be 10^{-4} to 10^{-3} s; this exceeds the rotational and vibrational relaxation times of molecules.   There are three cases determined by the relationship between the relaxation times and laser pulse duration.
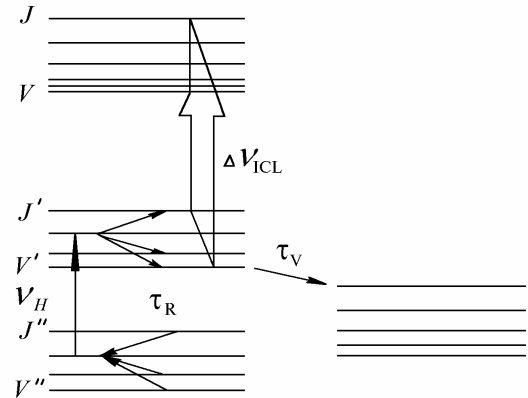

FIG. 9.   Molecular transitions in the ICL - spectroscopy with resonance optical excitation.

A. In the case of a short pumping pulse $(\tau_P \ll \tau_R)$ the Boltzmann distribution of the rotational energy levels is not achieved, so only the molecules that are at the energy level J'' rise to a higher energy levels.

The number of such molecules is proportional to

$$N_1(\tau_P) = (q/2) \, N_0 \, [1 - \exp (U/U_S^R)], \qquad (8)$$

where $U = \int\limits_0^{\tau_P} I \mathrm{d}t$, I is the intensity of laser radiation, U_S^R is the saturation energy of the rotational-vibrational transition, N_0 is the number density of molecules and q is the statistical weight of the level.

Pulse duration in the laser ICL-spectrometer is long in comparison with the relaxation times $(\tau_L \gg \tau_V)$ and $(\tau_L \gg \tau_R)$. So, the Boltzmann distribution of the rotational energy levels is achieved and the population of the excited vibrational state N_1 will decrease according to the exponential law

$$N_1(t) = N_1(\tau_P) \exp (- \, t/\tau_V). \qquad (9)$$

B. In the case of a pump pulse of intermediate duration $(\tau_R \leq \tau_P \ll \tau_V)$ the Boltzmann distribution of population over energy levels is achieved during the laser pump pulse that leads to an increase of population of the excited vibrational state

$$N_1(\tau_P) = (N_0/2) \, [1 - \exp (- \, U/U_S)], \qquad (10)$$

where U_S is the saturation energy of the vibrational transition.

C. In the case of long excitation pulses $(\tau_P \gg \tau_V)$ the fast vibrational relaxation (in comparison with pumping pulse duration) leads to continuous decrease of the population of the excited vibration state and to redistribution of the molecules over the vibration states.

When the laser pumping pulse has a rectangular profile the population of the exited vibration states will be

$$N_1(t) = \frac{N_0}{2} \frac{\beta}{\beta + 1}, \qquad t < \tau_P, \qquad (11)$$

$$N_1(t) = \frac{N_0}{2} \frac{\beta}{\beta + 1} \exp\left(\frac{-t}{\tau_V}\right), \qquad t \geq \tau_P, \qquad (12)$$

where $\beta = I/I_S$, I is the intensity of the laser pumping radiation, $I_S = \hbar\nu/2\sigma\tau_V$ is the saturation intensity when absorption coefficient decreases by 2 times, $\hbar$ is the Plank constant, ν is the frequency of a pump laser radiation, and σ is the cross-section of absorption. In that case the population of excited upper energy levels during pump pulse will be constant and will be determined by power density of the laser radiation. When the pump radiation terminates the population of the excited vibration state decreases in according with the exponential law.

The populating excited vibrational state V_1 aleviates the absorption from the rotational energy levels of that state and absorption coefficient is proportional to the population of these vibrational-rotational levels.

If the start of laser generation in an ICL-spectrometer coincides with the end of the excitation pulse, the dip formation in an ICL -spectrum is formed in the same way. The absorption coefficient decreases following an exponential law

$$K(t) = K_0 \exp(-t/\tau_V) \qquad (13)$$

where K_0 is different for the moment of the end of excitation (in the former case after the establishment of Boltzmann distribution over rotational levels).

It that case the ICL-spectrum is described by the expression:

$$J(\nu, t) = J(\nu, 0) \exp\left[\int_0^t c\, K_0 \exp(-t/\tau_V)\, dt\right] =$$

$$= J(\nu, 0) \exp\{-c\, K_0\, \tau_V [1 - (t/\tau_V)]\}. \qquad (14)$$

Dip depth increases during $t' = 2\tau_V$ after the pumping pulse and tends to $c\, K_0\, \tau_V$. The so-called "spectral memory" of the ICL-spectrometer takes place in the case of instantaneous disappearing of the absorption when the dip does not disappear at a moment but only during time delay about 0.1 s.

If the beginning of the laser radiation coincides with the beginning of excitation pulse the dip formation in the ICL-spectrum in cases *A*, *B* and *C* is described by the same expression. In the case *C*

(long exciting pulses $(\tau_P \ll \tau_V)$) the formation of the dip in the ICL-spectrum can be divided into two stages. The former occurs at a constant absorption coefficient during the exciting pulse and the second occurs at the exponentially decreasing absorption after the exciting pulse terminates. Thus the ICL-spectrum in this case can be described as

$$J(\nu, t) = J(\nu, 0) \exp[-c\, K_0\, \tau_P] \times$$

$$\times \exp\{-c\, K_0\, \tau_P [1 - \exp(-t'/\tau_V)]\}, \qquad (15)$$

where t' is counted from the moment of the laser excitation termination.

ICL - spectroscopy with the resonance optical excitation is characterized by the following features:

— high sensitivity of an ICL-spectrometer need not high population of an intermediate level and high power of radiation;

— wide spectral region of the spectrometer allows one to record the entire vibration band, due to transitions both from the state V' populated with the resonance radiation and from the lower states populated due to vibrational relaxation.

Experiments on studying the water vapor absorption spectrum at resonance excitation with ruby laser radiation have been carried out using a neodymium ICL-spectrometer, Fig. 10. Using an photoacoustic cell the radiation of a ruby laser was tuned at the transitions $5_{-4} - 4_{-3}$ of the $\nu_1 + 3\nu_3$ band of $H_2^{16}O$. The line width of the ruby laser emission was 0.02 cm^{-1} and the pulse of the neodymium glass laser was about 200 µs. The power density of the ruby laser radiation inside the absorption cell was about 800 kW/cm^2.
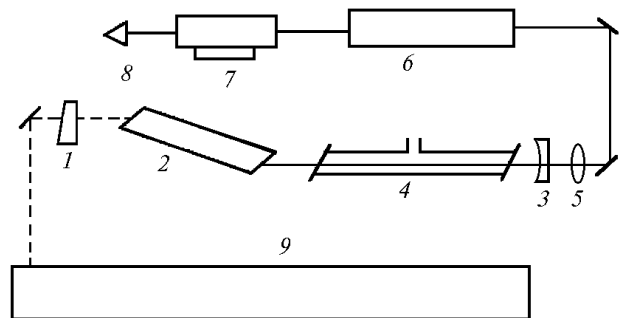
FIG. 10. Block-diagram of an ICL-spectrometer for resonance optical excitation study. 1, 3 are the cavity mirrors, 2 is the active element, 4 is the cell with gas under study, 5 is the lens, 6 is the ruby laser, 7 is the photoacoustic detector, 8 is the laser energy meter, 9 is the polychromator.

The saturation power density of the H_2O molecule J_P is equal to 180 MW/cm^2, that leads to population of the 103 vibrational state of $2\cdot10^{-3}$ from the population of the ground state and close to population of the 010 state of H_2O. Such population enabled to record "hot" transitions from 010 state using high sensitive spectrometers.

As a result, there were recorded many absorption lines in the ICL-spectrum induced by ruby laser

radiation when highly excited water vapor states up to 14400 cm^{-1} were populated. Water vapor spectrum recorded with the resonance optical excitation is presented in Fig. 4d.

Comparison made between the spectra obtained at the resonance optical excitation and excitation in the flame induced by CO_2 laser in graphite and metal target (Fig. 4c) shows that strong lines coincide.

There are more lines observed when the resonance optical excitation is performed when resonantly exiting with ruby laser than at nonresonance excitation.

Coincidence of the lines at resonant and nonresonant excitation shows that the population of excited vibrational states and energy transfer to the lower states takes place though the same levels.

As a result there were recorded many absorption lines in the ICL-spectrum due to the transitions from excited states of H_2O molecules. The comparison made between the spectra obtained at resonance and nonresonance optical excitation shows that in both cases the energy transfer takes place through the same energy levels.

ELECTRIC FIELD-INDUCED ABSORPTION

Transitions of unpolar molecules (like H_2) forbidden by selection rules becomes active when a perturbation decreases the symmetry of an electron shell. The molecular electric dipole moment can be induced by an external electric field. In this case the expression for an integral absorption coefficient A was formulated by Condon[14]

$$A = \frac{8\,\pi^3\,\nu\,Nl}{\hbar c} \int \psi_n^* \, P_a \, \psi_{n'} \, d\tau, \qquad (16)$$

Here $P_a = \alpha_a E_a$ is the component of the dipole moment along the optical vector, E_a and α_a are the component of the electric field and of the molecular polarizability in the same direction, n, n' are the set of quantum numbers for the initial and final states of the transition, l is the path length, $\hbar$ is Plank constant, c is the speed of light, ν is the transition frequency, and N is the number of molecules in the initial state.

The vibrational-rotational spectrum induced by an electric field is determined by selection rules similar to Raman scattering ($\Delta J = 0 \pm 2$), and consists of $Q(\Delta J = 0)$, $S(\Delta J = 2)$ and $O(\Delta J = -2)$ branches. Pure rotational lines $S_0(1) - S_0(3)$, the lines of the fundamental band $Q_1(0) - Q_1(5)$, $S_1(0) - S_1(3)$; $O_1(2) - O_1(4)$, and the lines of the $2 - 0$ band $Q_2(0) - Q_2(2)$, induced by an electric field, have recently been detected.[15–17]

The absorption spectra induced by an electric field can be effectively studied using the technique of intracavity laser spectroscopy, which enables one to record weak absorption spectra in small cells

containing the gas under study. The absorption lines $S_2(4)$ and $S_2(5)$ which are in the range of the Nd - glass laser emission have absorption coefficients of $2 \cdot 10^{-6}$ cm^{-1} and $4 \cdot 10^{-7}$ m^{-1}, respectively, (for an electric field of 70 000 V/cm). The low hydrogen breakdown voltage requires the use of high gas pressures, therefore, collision line broadening becomes an important factor in the measurements since the ICL-spectrometer has high sensitivity to the selective absorption only. As was demonstrated experimentally, at pressures up to 20 atm, the halfwidth of H_2 lines due to Dicke collision narrowing remains below 0.2 cm^{-1}, so that the limitation on the absorption selectivity does not play any role.[16]

The induced absorption spectrum of the hydrogen molecule was studied using the ICL-spectrometer with a Nd-glass and F_2^-:LiF lasers in Ref. 18–20. The resonator cavity of the multimode laser is formed by two mirrors (1) and (6) and a prism (5) (Fig. 11).

To obtain long quasicontinuous generation within the luminescence wing at frequencies below 9100 cm^{-1} the laser cavity contains two active Nd elements (2) and (4) each 160 mm long, pumped at 4000 J each. By varying the element-to-element triggering delay a 200 ms duration of laser generation was achieved. It corresponded to an ICL-spectrometer threshold sensitivity of $4 \cdot 10^{-7}$ cm^{-1} when integrated over time ICL-spectrum was recorded. The laser radiation spectrum was recorded using a monochromator (7) with a spectral resolution of 0.08 cm^{-1}, and an error of 0.05 cm^{-1} in the measurement of the line center position.

To study the hydrogen absorption spectra induced by an external electric field a special high-pressure cell (3) was designed and constructed, with the capacitor plates positioned within it. The steel plates (12), 30 cm long, 4 cm wide, and 1 cm thick, were polished. Plate edges and corners, as well as every other metal edge within the cell, were rounded to prevent electric breakdown, and the surfaces were coated with chromium. The plates were inserted into a special Plexiglas holder (11), and the entire construction was placed within a 1-cm thick metal housing of the cell (10). The breakdown voltage on the surface of the insulating materials separating the plates under the condition of a high-pressure gas atmosphere was lower than the same voltage in the case without insulation. Therefore the holder had special cavities cut into it to increase the pathway along the dielectric surface up to 3 cm. The distance between the plates was 4 mm. Cell windows, each 15-mm thick, were positioned at the Brewster angle to the optical axis to exclude parasitic selection.

An important factor for obtaining high strength of the electric field is careful cleaning of the surfaces. Electrodes were artificially "aged" by raising the voltage to the above-breakdown level, to produce such a breakdown for a short time, after which the electrodes were recleaned and washed.
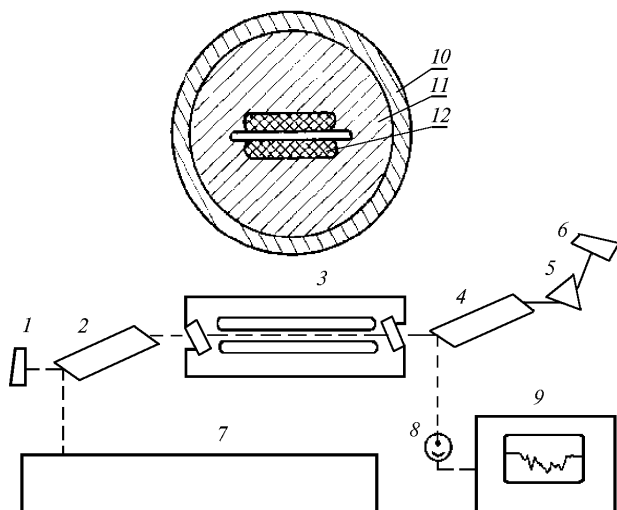
FIG. 11. Block-diagram of the experimental set-up: cavity mirrors (1, 6), active elements (2, 4), high-pressure cell with the capacitor plates 12 (3), prism (5), spectrograph (7), photodetector (8), oscilloscope (9), steel body (10), insulator (11).

This procedure significantly increased the breakdown voltage, and hence, the attainable electric field strength. Such breakdowns burn out minor inhomogeneities and high points from the electrode surfaces. The cell design provides the ability to turn the electrodes at 90° angle to produce electric fields both parallel and perpendicular to the polarization of the laser radiation. Such a cell can work at gas pressures up to 20 atm and capacitor voltages up to 50 kV, thus providing electric field as high as 125 000 V/cm.

The $S_2(4)$ and $S_2(5)$ hydrogen lines at $P = 20$ atm were recorded using laser radiation polarized parallel to the applied external electric field at $E = 125.000$ V/cm.[19] The positions of the line centers were determined relative to water vapor lines from the spectrum of atmospheric air in the laser cavity between the cell with hydrogen and the resonator mirrors. Low intensity of the recorded lines (their absorption coefficients only slightly exceeded the spectrometer threshold sensitivity) does not allow studying their dependence on either the electric field strength or pressure. Transition frequencies at zero pressure were determined using line shift coefficients for the 2—0 band of H_2 ($\delta = 0.004$ cm^{-1} atm^{-1}): $S_2(4) = 9092.34$ cm^{-1}, $S_2(5) = 9215.31$ cm^{-1}.

Using the rotational level energies for the lower vibrational state of the transition, we determined the upper level energies at $V = 2$: $E_2(6) = 10261.14$ cm^{-1}, and $E_2(7) = 10955.50$ cm^{-1}, i.e., the levels of the H_2 molecule having the highest measured rotational energies. The spectroscopic constants of the vibrational state $V = 2$, including the L-constant, were determined from the measured frequencies. Mean polarizability of the 2—0 transition was determined from $Q_2(0)$, $Q_2(1)$, and $Q_2(2)$

absorption lines.[20]   The mean polarizability is equal to $\alpha_{20} = 0.0176$ Å^3.

CONCLUSION

Developed scheme of the excitation of molecules and results obtained show an efficiency of ICL-spectroscopy method for highly excited molecular states study. Spectroscopic information obtained for highly excited vibrational-rotational states allows one to make a basis for solving inverse spectroscopic task of determination of the intramolecular potential function, dipole moment function as well as for testing new methods of description of the molecular energy structure in the region of high excitation.

REFERENCES

1. B.R. Henry, *Vibrational Spectra and Structure* (Elsevier, New York, 1981), p. 10.
2. M.L. Sage, Adv. Chem. Phys. **47**, 293 (1981).
3. M.S. Child and L. Halonen, Adv. Chem. Phys. **57**, 1 (1984).
4. V.I. Starikov, S.A. Tashkun, and Vl.G. Tyuterev, J. Mol. Spectrosc. **151**, 130 (1992).
5. S.F. Luk'yanenko, M.M. Makogon, and L.N. Sinitsa, *Intracavity Laser Spectroscopy* (Nauka, Novosibirsk, 1985), 121 pp.
6. O.V. Achasov, N.N. Kudrjavtsev, S.S. Novikov, et al., *Diagnostics of Nonequilibrium State Distribution in Molecular Lasers*, (Nauka i Technika, Minsk, 1985), 207 pp.
7. J.-J.Mandin, J. Mol. Spectrosc. **67**, 301 (1977).
8. S. Saliman and R.K. Hanson, J. Quant. Spectrosc. Radiat. Transfer. **30**, 1 (1983).
9. L.N. Sinitsa, "*High sensitive laser spectroscopy of high vibration-rotational molecular states,*" Doct. Phys.-Math. Sci. Dissert., Tomsk (1988).
10. P.I. Stepanov, "*Study of electronic spectra of ZrO, ZrN, TiO, and TiN by intracavity laser spectroscopy,*" Cand. Phys.-Math. Sci. Dissert., Moscow (1984).
11. L.N. Sinitsa and V.I. Serdyukov, Proc. SPIE **2619**, 276—279 (1995).
12. Yu. Poplavskii, V.I. Serdyukov, L.N. Sinitsa, and A.S. Tobolkin, Proc. SPIE **2619**, 280—282 (1995).
13. L.N. Sinitsa, Atmos. Oceanic Opt. **8**, Nos. 1—2, 80—92 (1995).
14. E.U. Condon, Phys. Rev. **41**, 759 (1932).
15. W.J. Boyd, P.J. Brannon, and W.M. Bailar, Appl. Phys. Lett. **16**, 135 (1970).
16. H.L. Buijs and H.P. Gush, Can. J. Phys. **49**, 2366 (1971).
17. P.J. Brannon, C.H. Church, and C.W. Peters, J. Mol. Spectrosc. **27**, 44 (1963).
18. V.P. Kochanov, V.I. Serdyukov, and L.N. Sinitsa, Optica Acta. **32**, 1273 (1985).
19. L.N. Sinitsa and G.A. Vandysheva, Atm. Opt. **3**, No. 4, 320—324 (1990).
20. G.A. Vandysheva, V.N. Savel'ev, and L.N. Sinitsa, Atm. Opt. **3**, No. 4, 325—328 (1990).