INVESTIGATION OF H₂ ABSORPTION SPECTRUM FOR THE "2-0" TRANSITION INDUCED BY ELECTRIC FIELD. I. DETERMINATION OF ENERGY OF THE VIBRATIONAL-ROTATIONAL LEVELS

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Using a highly sensitive intracavity Nd:YAG laser spectrometer the "2-0" transition absorption spectrum of molecular hydrogen, induced by an external electric field, was registered in the 1 μm *range. Energies of the rotational states E_2 (6) and E_2 (7) of the vibrational state $V = 2$ were determined at* 10261.14 *and* 10955.50 cm^{-1}, *respectively.*

Detailed knowledge of the structure of the vibrational-rotational levels of hydrogen molecules is essential to understand many of the physical and chemical properties of that di-atomic molecule, to monitor its atmospheric content and to control various technological processes. To observe molecular hydrogen in astrophysical bodies one needs to know exact frequencies of transitions from low vibrational to high rotational levels.[1,2] Since H₂ is the simplest molecule, and computation of its energy structure is possible "ab initio", it presents an interesting object for testing theoretical calculation schemes.

An H₂ molecule does not possess any dipole electric moment because of its symmetrical electric charge distribution; therefore it is not active in the IR spectral range, and does not have any allowed absorption spectra in its ground electronic state. Its energy structure is studied using the Raman scattering spectra, the electronic emission spectra of hydrogen in electric discharges, and its quadrupole spectra.[4–9] The highest accuracy of measurement is achieved for very weak transitions due to the molecular quadrupole moment, which are recorded in the IR spectral range (the intensity of the strongest line of its fundamental band $S_1(1)$ amounts to $9 \cdot 10^{-7}$ cm$^{-2} \cdot$ atm^{-1}).[7]

Because of low molecular mass the rotational constant for hydrogen is very high ($B_0 = 59$ cm^{-1}), its rotational levels are spaced far from each other, and the occupancy of levels needed for recording is provided for three or four lower rotational levels only; it is therefore extremely difficult to study higher rotational levels of this molecule. Practically all the availably studies of the vibrational-rotational energy structure of H₂, conducted in the IR range, are reduced to recording energy transitions from lower levels of $J \leq 3$.

ELECTRIC FIELD-INDUCED ABSORPTION BY H₂

Transitions of the H₂ molecule electric dipole, prohibited by selection rules, are possible by means of a perturbation lowering of the symmetry of am electron shell. The molecular electric dipole moment can be induced by an external electric field. The expression for an Integral absorption coefficient A of light (its electric vector oriented in the a direction with respect to the direction of the applied field) was formulated by Condon:[10]

$$A = \frac{8\pi^3 \nu N l}{hc} \left| \int \psi_n^{\bullet} \; P_a \psi_{n'} \; d\tau \right|^2 .$$

Here $P_a = \alpha_a E_a$ is the component of the dipole moment along the optical vector; E_a is the component of electric field along the optical vector; α_a is 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; h is Planck's constant; c is the speed of light; γ is the transition frequency; N is the number of molecules in the initial state per unit volume of the medium.

Similar to Raman scattering, the vibrational-rotational spectrum induced by the electric field is subjected to selection rules ($\Delta J = 0\pm2$), and consists of $Q(\Delta J = 0)$, $S(\Delta J = 2)$, and $O(\Delta J = −2)$ branches. The purely rotational lines $S_0(1) − S_0(3)$;[11] the lines of the fundamental band $Q_1(0) − Q_1(5)$; $S_1(0) − S_1(3)$; $O_1(2) − O_1(4)$,[12–13] and the lines of the 2–0 band $Q_2(0) − Q_2(2)$.[13] Induced by an electric field, have been detected thus far.

The vibrational-rotational absorption, induced by the external electric field and estimated with the molecular polarizability dependence on intranuclear distance[14] taken into account, is characterized by coefficients of $2 \cdot 10^{-6}$ cm^{-1} and $4 \cdot 10^{-7}$ cm^{-1}, respectively, (for an electric field intensity 70000 V/cm) at the centers of the absorption lines $S_2(4)$ and $S_2(5)$ which fall into the emission range of the Nd:YAG laser. The absorption spectra induced by the electric field can be effectively studied using the technique of intracavlty (IC) laser spectroscopy, which permits one to record weak absorption spectra in small cells containing the

gas under study. The low hydrogen breakdown voltage requires using high gas pressures; therefore, collision line broadening becomes an important factor in the measurements since the IC spectrometer displays high sensitivity to selective absorption only. As demonstrated by experiments, at pressures up to 20 atm, the halfwidth of H_2 lines due to Dickett's collision narrowing remains below 0.2 cm^{-1}, so that the limitation on the absorption selectivity is met.[12]

EXPERIMENT

The induced absorption spectrum of a hydrogen molecule was studied using the IC spectrometer with a Nd:YAG laser, described in detail in Ref. 15. The resonator cavity of the multimode laser is formed by two mirrors 1 and 6 and prism 5 (Fig. 1).
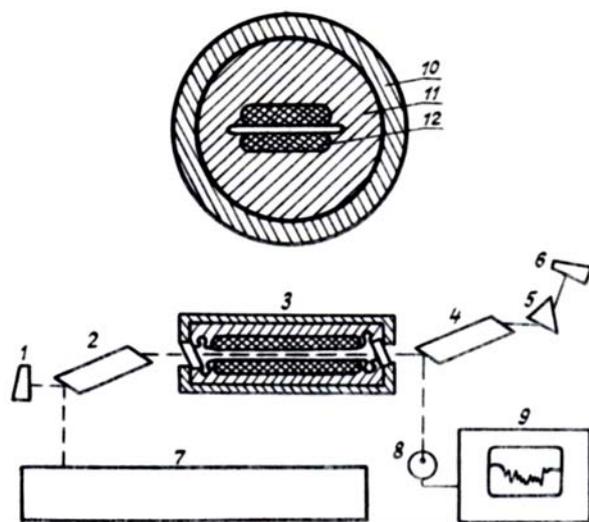

FIG. 1. Flow-chart of the experimental set-up: resonator cavity mirrors (1, 6), active elements (2. 4), high-pressure cell with capacitor plates 12 (3), prism (5), spectrograph (7). photodetector (8), oscillograph (9), steel case (10), isolator (11).

To obtain prolonged quasicontinuous generation at the luminescence edge at frequencies below 9100 cm^{-1} the laser cavity contains two lasers 2 and 4 with Brewster Nd elements, each 160 mm long, pumped at 4000 J each. By varying the element-to-element triggering pause, a 200-μs maximum duration of laser generation was achieved.

It corresponds to an IC spectrometer threshold sensitivity of $4 \cdot 10^{-7}$ cm^{-1} when its temporally integrated IC spectrum is recorded. The shape of the generated pulse was monitored by the photodetector 8 and oscillograph 9. The laser radiation spectrum was recorded by the monochromator 7 with a spectral resolution of 0.08 cm^{-1}, and an error of 0.05 cm^{-11} 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 to class 10. Plate edges and corners, as well as every other metal edge within the cell, were rounded to prevent electric breakdown, and the surfaces were covered with chromium. The plates were inserted into a special plexiglas holder 11, of a specially designed shape, and the whole construction was tightly secured within the metal case of the cell 10, 1 cm thick. The breakdown voltage on the surface of the isolating materials separating the plates under the condition of a high-pressure gas atmosphere was lower than the same voltage in the case of no isolation. Therefore the holder had contoured cavities cut into it to increase the pathway along the dielectric surface up to 3 cm. The actual distance between the plates remained at 4 mm. Cell windows, each 15 mm thick, were positioned at the Brewster angle to the optical axis to exclude parasitic selectivity.

An important factor for obtaining high electric field intensity is careful cleaning of the surfaces. After cleaning and assembly of the cell its internal surfaces were washed additionally by ethanol. Electrodes were artificially "aged" by raising the voltage to above-breakdown level, so as to produce such a breakdown for a short time, after which the electrodes were recleaned and washed. This procedure significantly increased breakdown voltage, and hence, the attainable electric field intensity. Such breakdowns burn away minor inhomogeneities and high points from the electrode surfaces. The cell design provides the ability to turn the electrodes by 90° to produce electric fields both parallel and perpendicular to the polarization plane of the laser radiation. Such a cell can operate at gas pressures up to 20 atm and capacitor voltages up to 50 kV, thus providing electric field intensities as high as 125000 V/cm.

RESULTS

The $S_2(4)$ and $S_2(5)$ hydrogen lines in laser radiation, polarized parallel to the applied external electric field at $E = 125.000$ V/cm, were recorded using the above-described spectrometer. The positions of the line centers were determined with relation to water vapor lines from the spectrum of atmospheric air present in the laser cavity between the hydrogen-containing cell and the resonator mirrors. The measured line frequencies were $S_2(4) = 9092.26$ cm^{-1} and $S_2 = 9215.23$ cm^{-1} at $P = 20$ atm. The low intensity of the recorded lines, (their absorption coefficients only slightly exceeded the spectrometer threshold sensitivity) precluded studying their dependence on either the electric field 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} (Ref. 8).

Using the rotational level energies for the lower vibrational state of the transition, we determined the upper level energies for the transition of $V = 2$: $E_2(6) = 10261.14$ 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, plus energies for lower rotational levels of the $V = 2$ state from Ref. 8 (see Table I).

TABLE I.

Spectroscopic constants of the vibrational state $V = 2$ of H-molecule, cm^{-1}

Spectro-scopic constants	This paper	Ref. 8	Ref. 7
E_v	8087.000(5)*	8087.005(3)	8087.000(15)
B_v	53.4807(16)	53.482(2)	53.4823(40)
D_v	0.04278(13)	0.0428(2)	0.04272(20)
$H_v \cdot 10^5$	4.94(30)	4.9(6)	3.87
$L_v \cdot 10^8$	-1.34(32)	-	-

* The values of the 68% confidence intervals expressed in the last significant digits are given in parentheses.

Almost all the structural molecular theories are presently based on the Born-Oppenheimer approximation. Within this approximation the nucleus remains fixed, and electrons move in the combined field of nucleus and other electrons.[16] Within the Born-Oppenheimer approximation the effect of the nuclear kinetic energy operator upon the electronic wave functions is ignored. The latter effect can be accounted for in two steps. Initially (the "adiabatic" approximation) first-order perturbation theory is employed and only those corrections are considered which originate from the effect of the nuclear kinetic energy operator within each electronic state. In the second step ("nonadiabatic" approximation), the interaction between various electronic states is taken into account. An important test for correctness of the computations consists of comparing them to the results of experimental energy determinations of levels with high rotational quantum numbers in excited vibrational states.

Figure 2 presents the differences between the experimentally measured energy values for the vibrational-rotational levels of the states $V = 0$ and $V = 2$ and those calculated "ab initio" with[17] and with out[18] nonadiabatic corrections taken into account. Energy levels calculated with the nonadiabatic corrections taken into account for the ground vibrational state correspond to measured ones within an accuracy of less than 0.005 cm^{-1} (Ref. 9). Computation of energy structure without nonadiabatic corrections results in larger errors at high rotational quantum numbers, reaching 0.3 cm^{-1} for $J = 7$.
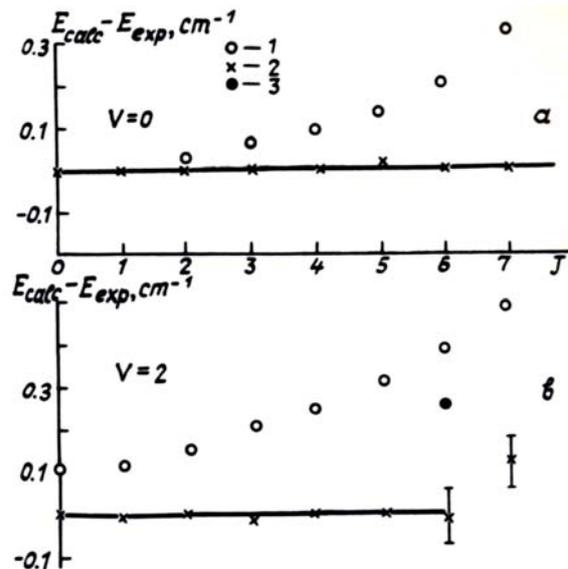

FIG. 2. Experimental data vs. computational results on the H_2 energy structure; nonadiabatic corrections ignored (1) and accounted for (2). a) state $V = 0$ (experimental results taken from Ref. 9); b) state $V = 2$ (experimental taken for $J = 0-5$ taken from Ref. 8, $J = 6-7$ from the present study); computations employing rotational constants from Ref. 8 (3).

For $V = 2$ state the errors in energy structure computed without nonadiabatic corrections amount to 0.5 cm^{-1} for $J = 7$. If, on the other hand, such corrections are accounted for, the errors do not exceed the measurement error for $J \leq 6$, and only for $J = 7$ do they reach 0.12 cm^{-1}, which slightly exceeds the measurement error.

It should be noted that high-precision measurements of the molecular hydrogen energy structure are not of high forecasting value because of the large high-order centrifugal constants of the gas. Indeed, rotational constants for hydrogen yielded by spectral measurements at an error level of approximately 0.001 cm^{-1} would produce an energy error in the next levels $E_2(6)$ and $E_2(7)$ of 0.26 cm^{-1} and 0.77 cm^{-1}, respectively.[8] This result stresses once more the importance of computing "ab initio" the energy structure of the hydrogen molecule and the respective nonadiabatic corrections.

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