INVESTIGATION OF ABSORPTION SPECTRUM FOR THE ”2-0” TRANSITION INDUCED BY ELECTRIC FIELD II. DETERMINATION OF THE MATRIX ELEMENTS OF THE POLARIZABILITY TENSOR

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*Using an intracavity laser spectrometer the ”2—0” transition absorption spectrum of molecular hydrogen, induced by an electric field, was measured in the 1-*μm *spectral range. The integral absorption coefficient measured for the lines* $Q_2(0)$, $Q_2(1)$, *and* $Q_2(2)$ *have made it possible for the first time to determine the matrix element of the mean polarizability* α_{20} *for the ”2—0” transition of the* H_2 *molecule. The value of* α_{20} *averages* 0.0176 $Å^3$ *over three measurements.*

Symmetrical distribution of electric charge in the hydrogen molecule results in its zero electrical dipole moment. That is why hydrogen is not radiatively active in the IR electromagnetic domain. However, the H_2 molecule is polarizable, which opens up a possibility to overcome this difficulty. An external electric field destroys the symmetry of its electron shell and induces a dipole moment in the molecule, so that formerly prohibited dipole transitions become allowed. Therefore, one needs to know the H_2 molecular polarizability, i.e., one of the fundamental quantitative characteristics of the molecule, in order to describe various processes in which the molecule can take part.

So far only the ground vibrational transition ”1—0” matrix elements of the polarizability tensor for the H_2 molecule has been determined from its absorption spectra. induced by an external electric field. [1,2,3] Intracavity measurements of the H_2 absorption spectra around 1 μm, induced by an external electric field,[4] would make it possible to determine its polarizability for the ”2—0” transitions, and this constitute the aim of the present study.

THE ELECTRIC FIELD-INDUCED H_2 ABSORPTION

The dipole moment induced by an external electric field is a tensor; usually, however, the average polarizability $\alpha = \frac{1}{3}(2\alpha_\perp + \alpha_\parallel)$ and polarization anisotropy $\gamma = \alpha_\parallel = \alpha_\perp$ are considered, expressed in terms of polarizabilities along and across the internuclear axis, $\alpha_\parallel$, and α.

The integral absorption coefficient for a vibrational-rotational line, induced by an external electric field parallel to the electric vector of the linearly polarized optical radiation, is equal to

$$A_z = \frac{8\pi^3 \nu N l}{hc} E^2 \Big[\langle V'|\alpha|V\rangle^2 \delta_{J'J} + \langle V'|\gamma|V\rangle^2 \times$$

$$\times \frac{4}{45}(2J'+1)(2J+1)\begin{pmatrix} J' & 2 & J \\ 0 & 0 & 0 \end{pmatrix}^2 \Big]. \quad (1)$$

(see Ref. 5).

If the electric field is directed perpendicularly to the optical radiation polarization plane, the respective coefficient for the spectral line is

$$A_x = \frac{8\pi^3 \nu N l}{hc} E^2 \langle V'|\gamma|V\rangle^2 \times$$

$$\times \frac{1}{15}(2J'+1)(2J+1)\begin{pmatrix} J' & 2 & J \\ 0 & 0 & 0 \end{pmatrix}^2 \Big]. \quad (2)$$

where $\langle V'|\alpha|V\rangle = \alpha v'v$ is the matrix element of the average polarizability for the molecular transition $V'–V$; $\langle V'|\gamma|V\rangle = \gamma v'v$ is the anisotropy matrix element for polarization of that transition; $\begin{pmatrix} J' & 2 & J \\ 0 & 0 & 0 \end{pmatrix}$ are the Wiener symbols; E is the electric field intensity; ν is transition frequency; N is the number of molecules in the initial state per unit volume of the medium; l is the path length; h is Planck’s constant; c is the speed of light. Selection rules for the absorption spectrum induced by such an electric field are: $\Delta J = 0$ (Q-branch); $\Delta J = 2$ (S-branch); $\Delta J = -2$ (O-branch).

As seen from the expression for the integral absorption coefficient, the contribution of the average polarizability and its anisotropy depends both on the particular branch of the vibrational- rotational band, and on the angle between the applied electric field and the polarization plane of the optical radiation. Relationships (1) and (2) demonstrate that one can

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determine the matrix elements of the average polarizability from the measured absorption coefficient for the Q-branch; meanwhile those for the S-branch would only yield the anisotropy matrix element for the transition polarizability. Strictly speaking, the intensities of two Q-branch lines could yield matrix elements of both the average polarizability and the transition polarization anisotropy. However, according to actual calculations, to estimate the polarization anisotropy matrix element credibly the error in determining line integral absorption coefficient of the lines should be less that 0.2%, and such an accuracy level is hard to attain at the present state of experimental art.

EXPERIMENT

The external electric field-induced absorption spectrum of the hydrogen molecule was obtained using the experimental installation described in Ref. 4. For the intracavity laser spectrometer we used an instrument build around a LiF crystal dye-center laser, described in ample detail in Ref. 6. The spectral resolution of the spectrometer was 0.05 cm^{-1}, and its absorption threshold sensitivity was $4 \cdot 10^{-7}$ cm^{-1}.

The matrix element of the average polarizability for the 2–0 hydrogen molecular transition was estimated for the first time in our study from the measured integral absorption coefficients in the $Q_2(0)$, $Q_2(1)$ and $Q_2(2)$ lines. To reduce their measurement error such measurements were made with respect to the known integral absorption coefficients of carbon dioxide lines with known intensity.[7] The intracavity spectrometer simultaneously recorded both hydrogen and carbon dioxide lines, the latter agent being introduced into the laser cavity in an auxiliary cell. The spectral distance between the measured H_2 and CO_2 lines did not exceed 100 cm^{-1} for these lines (the latter being approximately 400 cm^{-1} wide), so that generation conditions in the neighboring lines could be considered identical. Measurements were conducted at $T = 293$ K. For field intensities up to 80.000 V/cm the dependence of the integral absorption coefficient on E^2 remains linear. To reduce the measurement error for the transition polarizability matrix elements the electric field was held at a level to maintain close values for the hydrogen and the reference CO_2 integral absorption coefficients. The error in measuring the integral absorption coefficients comprises the errors in determining the electric field intensity, the gas pressure, and in determining the absorption coefficients by the intracavity laser spectroscopy technique. The resulting measurement error did not exceed 20%.

MEASUREMENT RESULTS

The integral absorption coefficient for carbon dioxide is equal to

$$A_1 = S_1 \mu_1 \cdot L_{eff} \cdot N_1 \, , \tag{3}$$

where S_1 is the CO_2 line intensity; L_{eff} is the effective length of absorption layer in the laser cavity for the given generation duration; μ_1 is the coefficient of cavity loading by the CO_2-containing cell; N_1 is the concentration of CO_2 molecules.

By measuring experimentally the ratio of the areas of the H_2 absorption lines dips to those of CO_2, one can obtain the integral coefficient A_2 for hydrogen. On the other hand, one can write for A_2 (for the Q-branch lines) from the relationships (1) and (2);

$$A_2(J) = \frac{8\pi^3 \nu N_J l}{hc} M_{20}^2(J) = \frac{8\pi^3 \nu N_J l}{hc} E^2 \times$$

$$\times \left[\alpha_{20}^2 + \gamma_{20}^2 \frac{4}{45} (2J' + 1)(2J + 1) \begin{pmatrix} J' & 2 & J \\ 0 & 0 & 0 \end{pmatrix}^2 \right] . \tag{4}$$

With the Boltzmann factor taken into account the occupancy of the lower level of the transition is

$$N_J = N_v \cdot \frac{1}{Q_R} (2J + 1) g_J \cdot \exp\left[- \frac{E_J}{k_B T} \right] \tag{5}$$

here N_v is the occupancy of the lower vibrational state; Q_R is the rotational statistical sum; E_J is the energy of the lower level; $g_J = 1$ for levels with even values, and $g_J = 3$ for levels with odd values of J.

Specific expressions for the squares of the matrix elements of the induced dipole moment of the measured lines $Q_2(0)$, $Q_2(1)$, $Q_2(2)$ can now be written in the following form:

$$M_{20}^2(0) = E^2 \alpha_{20}^2 \tag{6}$$

$$M_{20}^2(1) = E^2 \left[\alpha_{20}^2 + \frac{8}{225} \gamma_{20}^2 \right] \tag{7}$$

$$M_{20}^2(2) = E^2 \left[\alpha_{20}^2 + \frac{8}{315} \gamma_{20}^2 \right] \tag{8}$$

Since *ab initio* calculations yield $\gamma_{20} \simeq \frac{1}{10} \alpha \hbar_{20}$ for the vibrational transition "2–0", one can evaluate the matrix element a from the expressions (6)-(8). Results of determining α from three measured lines are given in Table I; experimental conditions are also described there. The average value obtained from three measurements is $\alpha = 0.0176$ Å^3. Deviations of separate a values from their average remain within the measurement error margin.

A relative estimate of the polarizability anisotropy matrix element can be obtained from the integral absorption line coefficient measured from the S-branch of the "2–0" band. Employing expressions (6)–(8) one can then refine the numerical value of α_{20}. It can be further used to forecast the intensities and absorption coefficients of the "2–0" band lines, not directly measured in the experiment, and theoretically estimate matrix elements of the dipole moment.

TABLE I.

Values of matrix element of polarizability tensor of 2–0 transition of H_2 molecule.

$Q_2(J)$	ν_J, cm^{-1}	P, atm	$A_2 \cdot 10^4$, cm^{-1}	l, cm	$E^2 \cdot 10^{-8}$, V^2/cm^2	α_{20}, Å^3
$Q_2(0)$	8087	17	7.58	30	135	0.0172
$Q_2(1)$	8075	14	9.12	30	38	0.0174
$Q_3(2)$	8052	17	7.57	30	135	0.0183

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