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Abstract

Full Text

Physical Chemistry

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Induced Infrared Spectrum of Hydrogen in Solution in the Region of the Vibrational Transition $2 \leftarrow 0$

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Symmetric diatomic molecules in the isolated state do not have dipole infrared spectra. Vibrational-rotational transitions forbidden in absorption can be induced by external fields, for example, by intermolecular fields that act on a molecule placed in a condensed phase. The study of induced spectra provides information on intermolecular interactions and the molecular dynamics of liquids and solids.

We recorded the absorption spectrum in the region 7500-9500 cm^{-1} of hydrogen dissolved in carbon tetrachloride. The solutions were prepared directly in an absorption cell consisting of a hollow stainless-steel cylinder 110 cm long with glass windows. The pressure of hydrogen over the solution was 90-130 atm, which corresponds to a maximum solution concentration of about 0.4 mole/l. The need to use a large thickness of absorbing layer imposes increased requirements on the transparency of the solvent.

Fig. 1. Absorption spectrum of a solution of hydrogen in CCl_4. $p = 130$ atm, $d = 110$ cm, $T = 298°$ K

Table 1

Frequencies (cm^{-1}) of components of the vibrational-rotational band 2—0 of hydrogen

	Gas phase*	Gas mixtures**	Solution CCl_4
$Q_2(0)$	8087	8030	(8052)
$Q_2(1)$	8075		8040
$S_2(0)$	8406		8360

	Gas phase*	Gas mixtures**	Solution CCl_4
$S_2(1)$	8604	8630	8570
$S_2(2)$	8785		(8750)

* Calculated from the data of Stoicheff (^{1}).
** According to the data of Ketelaar and Rettschnick (^{2}).

Before use, the carbon tetrachloride was purified by chlorination and fractional distillation.

The spectra were recorded on a spectrometer constructed in our laboratory, with a diffraction grating of 300 lines/mm, a parabolic collimator $F = 500$ mm, and a PbS photoresistor as the radiation detector. The accuracy of determining frequencies was limited by the width of the absorption bands. The spectra were taken at room temperature (298° K).

In the spectral interval studied lies the first overtone of the vibration of the hydrogen molecule. In the spectrum of the solution of H_2 in CCl_4, shown in Fig. 1, several bands are observed that can be identified as components of the Q and S branches. Their frequencies and interpretation are given in Table 1.

The greatest intensity is exhibited by the lowest-frequency band at 8040±5 cm^{-1}, which should be assigned to the purely vibrational transition $2 \leftarrow 0$. This band must consist of a group of components $Q_{\Delta v}(I'')$, with, for normal hydrogen at room temperature, the main part

of the intensity falls on the component $Q_2(1)$ and on a somewhat weaker component $Q_2(0)$. These components merge into a single line, since the separation between them, equal in the gas phase to 12 cm^{-1} (^{1}), is much smaller than their half-width. The next two bands, 8360±10 and 8570±5 cm^{-1}, may be interpreted as the $S_2(0)$ and $S_2(1)$ components (transitions $v' = 2;\ I' = 2 \leftarrow v'' = 0;\ I'' = 0$ and $v' = 2;\ I' = 3 \leftarrow v'' = 0;\ I' = 1$, respectively). The correctness of such an interpretation is confirmed by the fact that, on the wavenumber scale, the separations between the components $Q_2(1)$, $S_2(0)$, and $S_2(1)$ agree, within the error, with the corresponding separations in the spectrum of unperturbed hydrogen molecules.

The weak diffuse maximum at 8800 cm^{-1} probably has a complex nature. First, in this region lies the component $S_2(2)$ ($v' = 2;\ I' = 4 \leftarrow v'' = 0;\ I'' = 2$), presumably located near 8750 cm^{-1} (see below), which in intensity should be comparable with the component $S_2(0)$. Second, the region under consideration may be overlapped by bands of simultaneous transitions with frequencies $\nu_{Q_2}(H_2) + \nu_{CCl}(CCl_4)$: $8040 + 767 = 8807$ cm^{-1} and $8040 + 797 = 8837$ cm^{-1}. Simultaneous transitions of this type were observed earlier in the spectra of gaseous mixtures of hydrogen with CF_4 and SF_6 (^{2}). Analogous combinations on the fundamental tone $\nu_{Q_1}(H_2) + \nu_{CCl}(CCl_4)$ have appreciable intensity (^{3}).

Most of the experimental material now available on induced absorption of light (see the review (4)) pertains to the gas phase. Data on spectra in the region of the first overtone were obtained by Hare and Welsh (5) for pure gaseous hydrogen at pressures up to 1500 atm, and also by Ketelaar and Röttgerink (2) for mixtures of hydrogen with foreign gases at a pressure of about 150 atm. Welsh and co-workers (6) also described the spectrum of crystalline hydrogen in the region 8000—9500 cm^{-1}. In the spectra of pure hydrogen, both in the gas and in the crystalline phase, the main intensity is due to simultaneous transitions corresponding to simultaneous vibrational (or vibrational and rotational) excitation of two H_2 molecules. This makes comparison difficult with the results of the present work, which pertain to sufficiently strongly diluted solutions of hydrogen. According to the data of (2), in the spectra of mixtures of hydrogen with foreign gases a Q-component and a diffuse structureless S-branch with a maximum near 8630 cm^{-1} are observed.

In a solution of hydrogen in CCl_4, the frequencies of all vibrational-rotational components of the 2—0 band are shifted, in comparison with the frequencies of isolated H_2 molecules, by approximately one and the same amount, namely by 35 cm^{-1}. For the same system, the shift of the components of the fundamental-tone band 1—0 is −25 cm^{-1} (3). This gives, for the relative shifts $(\nu_s - \nu_g)/\nu_g$, values of $-4.3 \cdot 10^{-3}$ and $-6.1 \cdot 10^{-3}$, respectively. The smaller relative shift in absolute value of the vibrational transition $2 \leftarrow 0$ indicates a decrease in the mechanical anharmonicity $x_e\omega_e$, which for hydrogen molecules in solution is 110 cm^{-1} as compared with the anharmonicity in the gas phase ($x_e\omega_e =$ 117.5 cm^{-1}). The phenomenon of a decrease in mechanical anharmonicity under the influence of intermolecular interactions has repeatedly been noted for other objects (7, 8), but has not yet received a clear interpretation. The frequencies of the directly unobserved components $Q_2(0)$ and $S_2(2)$, enclosed in parentheses in Table 1, were obtained by subtracting 35 cm^{-1} from the frequencies of the vibrational-rotational transitions in the spectrum of gaseous hydrogen given in the second column.

The vibrational-rotational components of the first-overtone band of hydrogen in CCl_4 have a noticeably greater width than the corresponding components of the fundamental-tone band. Thus, the half-width of the lines Q_2 and $S_2(1)$ is, respectively, 70 and 90 cm^{-1}, whereas the components Q_1 and $S_1(1)$ have half-widths of about 40 and 60 cm^{-1} (3). Because of the excessively low intensity of the component $S_2(0)$, it is difficult to estimate its half-width.

The difference in the half-widths of the components of the Q and S branches is probably connected with the removal of rotational degeneracy under the action of the intermolecular field of the solvent and with the appearance of differences in the transition frequencies between levels with different values of the magnetic rotational quantum number.

An interesting feature of the band studied is the absence of clearly expressed translational components Q_P and Q_R. They were also not found in the spectra of gaseous compressed hydrogen and gas mixtures (^{2}, ^{5}). These components, which constitute one of the most characteristic features of induced spectra, are generally considered to be due to exchange forces and correspond to vibrational transitions accompanied by changes in the energy of the translational motion of the molecules. In the fundamental tone of the vibration of H_2 in the spectra of solutions (^{3}) and, in particular, in the gas phase (^{5}), the components Q_P and Q_R make the largest contribution to the integral intensity of the band. Hare and Welsh suggested that the sharp decrease in the intensity of the components Q_P and Q_R in the 2—0 band is explained by a mutual compensation of the contributions to the intensity due to electrical and mechanical anharmonicities, similar to what had previously been observed in the spectrum of second-order combination scattering of CCl_4 (^{9}). This suggestion deserves further verification.

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