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MULTIPHOTON DISSOCIATION, PREDISSOCIATION, AND AUTOIONIZATION OF THE HYDROGEN MOLECULE

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We report here observations of dissociation and ionization of the hydrogen molecule by the second harmonic of a neodynium laser. We show that an important role can be played in these processes by multiphoton transitions into highly-excited H_2^* Rydberg states. Owing to the strong interaction of the nuclear motion with the electron motion, the excitation of these states is accompanied by a fast nonradiative transition into the continuous spectrum of the electronic wave function (auto-ionization) or the nuclear wave function (predissociation) of the molecule.

Our experiment enables us to compare the probabilities of direct multiphoton ionization of H_2 and auto-ionization of optically excited Rydberg states. The latter channel is more probable. Multiphoton ionization of H_2 can proceed via predissociation in oscillations during the oscillations, as well as by direct transition of the excited terms into the continuous spectrum of the nuclear wave function, with formation of hydrogen atoms in the ground state H (n = 1) and the excited state H* (n = 2).

Multiphoton dissociation of molecules in a field of optical frequency is usually associated, in the main, not with electronic transitions but with excitation of nuclear oscillations. The vibrational transitions can be noticeable
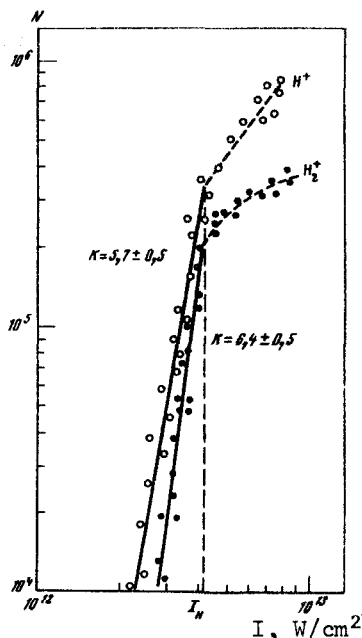

Fig. 1. Number of ions produced as a result of dissociation (N_{H^+}) and ionization ($N_{H_2^+}$) of H_2 molecules vs. the intensity I. The breaks on the curves at $I_H = 4 \times 10^{12}$ W/cm^2 corresponds to saturation of the ion signals, i.e., to dissociation (with subsequent ionization of the atoms) or ionization of all $n_0 V = 4 \times 10^5$ molecules in the focal region ($n_0 = 4 \times 10^{12}$ is the density of H_2 in the focal region, $V = (1 \pm 0.4) \times 10^{-7}$ cm^3 is the effective volume of interaction [5] for six-photon processes.

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for polar molecules having a con-
stant dipole moment and IR absorp-
tion spectra [1]. Such a buildup
of oscillations is possible in the
hydrogen molecule, in principle,
only as a result of an induced di-
pole moment [2]. The interaction
of H_2 with the radiation of ruby
and neodymium lasers was previously
investigated in [3] and [4], respec-
tively. What was mainly observed
were H_2^+ ions. The dependence of
the number of observed H_2^+ ions on
the intensity was determined.

The second harmonic of a Q-
switched neodymium laser was focused
inside a vacuum chamber. The energy
in a pulse centered at $\lambda = 5293$ Å
and half-width $\hbar\Gamma \simeq 25$ cm^{-1} amounted
to 3 J at a duration $\tau_0 = 27$ nsec.
The space-time distribution of the
intensity in the focal region was
determined by the method described
in [5].

The beam of H_2 molecules enter-
ed the vacuum chamber through a
capillary in a direction perpendicu-
lar both to the laser beam and to
the direction in which the ions
were registered. The ions were
drawn out of the focal region by a
transverse constant electric field
(1500 V/cm), were shaped by an ion-
optical system, mass-separated in a
magnetic spectrograph, and detected
with an electron multiplier. The
number of ions N had a power-law de-
pendence on the intensity, $N_{H^+} \sim$
$I^{5.7\pm0.5}$ and $N_{H_2^+} \sim I^{6.4\pm0.5}$ (Fig. 1).

Figure 2 shows the potential
curves of the H_2 singlet terms [6].
Each intermediate transition in the
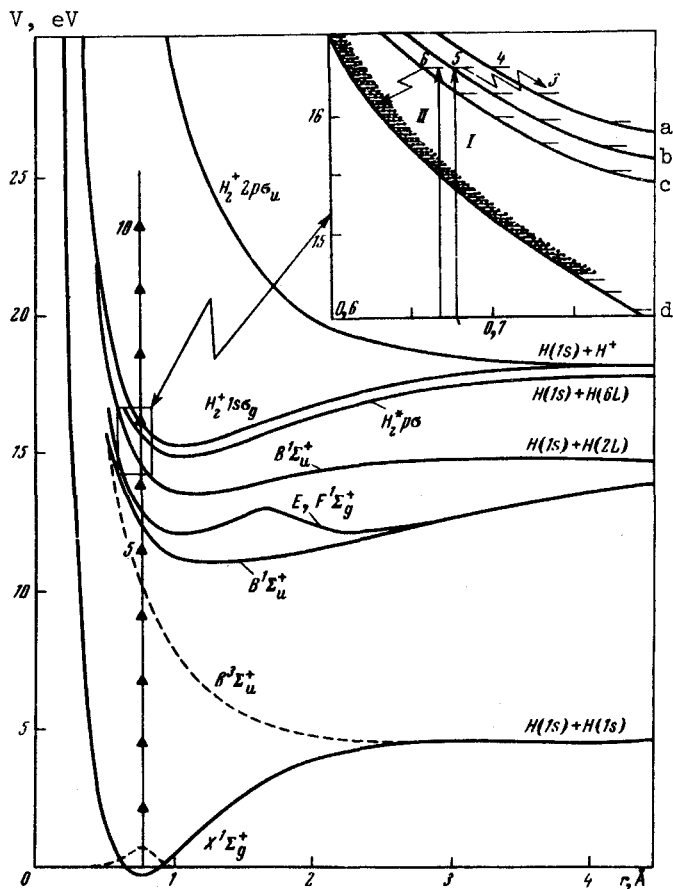composite matrix elements of the
multiphoton transitions in molecules

Fig. 2. Potential curves of singlet
states of H_2 and H_2^+. The dashed curve
marks the lower repulsion term $H_2 b^3\Sigma_u^+$
(triplet). The enlarged-scale insert
shows the potential curves and vibra-
tional levels of the following states:
$H_2^+1s\sigma_g$ (a), $H_2^{*\,1}\Pi_u 8p\pi$ (b), $H_2^{*\,1}\Sigma_u^+(6p\sigma)$
(c), and $B'^1\Sigma_u^+$ (d). The autoionization
of the $8p\pi$ (v = 5) level (I) and the
predissociation of the $6p\sigma$ (v = 6) level
(II) are shown schematically.

[7] occurs between terms of different parity. From the ground X-state of H_2
(even) the transitions of even order go into even states (g), and transitions
in which an odd number of quanta take part go into odd states (u). The energy
of two quanta ($\hbar\omega = 2.345$ eV) is sufficient to dissociate into the continuous
spectrum X-states with odd terms as virtual intermediate states (transitions
to the repulsion $b^3\Sigma_u^+$ term are multiplicity-forbidden). Such transitions, how-
ever, are strongly forbidden by the Franck-Condon principle, owing to the large
change in the momentum of the nuclei.

The observed dissociation of H_2 is connected mainly with transitions into
the continuous spectrum of the B' state. An important role is played by reso-
nances with individual vibrational-rotational levels of the intermediate B, E,
and F states:

$$X + 5\omega \to B^1\Sigma_u^+ \ (v = 3, \ k = 5), \quad X + 6\omega \to E, F^1\Sigma_g^+ \ (v = 21, \ k = 2).$$

In transitions from the most populated level X (v = 0, K = 1), the deviation from these resonances lies within the limits of the laser line width Γ. The vibrational-rotational levels of the B, E, and F states were calculated from the spectroscopic data [8]. The level shifts and broadening were neglected. Taking into account the statistical properties of multimode laser radiation, the conditions of n-photon resonance are of the form $\omega_{io} - n\omega \ll n\Gamma$, where ω_{io} is the transition frequency [9]. For n = 5 and 6 we have $n\Gamma \sim 100$ cm^{-1}, which preliminary estimates show to exceed greatly the level shifts and broadening. Owing to the large rotational constant, the distance between the rotational levels K and K $\pm$ 1 of the B state are relatively large ($\sim$200 cm^{-1}) at K = 5, and five-photon absorption is possible only at one level. The distances between the K and K $\pm$ 1 levels of the E or F (v = 21) state at K = 2 are of the order of 50 cm^{-1}, and simultaneous excitation of two or three levels is possible. In addition, the six-photon X $\to$ E, F transitions entails a smaller change of the rotational energy of the molecule, and therefore competes with the X + 5ω $\to$ B transition.

The dissociation of E, F (v = 21) into the continuous spectrum of the B' state can proceed either directly, E, F(v = 21) + ω $\to$ H + H*, or via predissociation of the H$_2^*$6pσ (v = 6) Rydberg state: E, F(v = 21) + ω $\to$ 6pσ(v = 6) $\to$ H + H*. The first of these processes goes from the external minimum F, and the second from the internal E minimum, where transitions without a change in the nuclear momentum are possible. The intermediate B state dissociates apparently through predissociation. The subsequent ionization of H* (n = 2) and H (n = 1) with absorption of two and six quanta proceeds at I = I_H at the rates $W_2 > 10^{13}$ sec^{-1} (as estimated in accord with the theory of [10]), and $W_6 > 10^9$ sec^{-1} (from the experimentally determined probability). Since the probabilities of transitions from E, F, and B levels (dissociation, predissociation, and ionization of H* and H) become close to unity within a time t $\ll$ τ_p, the slope of the H* curve on Fig. 1 (K = 5.7) is determined by the probabilities of excitation of these states.

The observed H$_2^+$ ions at λ = 0.53 μ are due entirely to auto-ionization of high H$_2^*$ Rydberg states. The energy of the transitions X $\to$ 8pσ (v = 5), 8pπ (v = 5) is close to 7ω, as is the energy of the X $\to$ 6pσ (v = 6) transition [11]. However, whereas the 6pσ (v = 6) level decays via predissociation, the 8pσ (v = 5) and 8pπ (v = 5) levels experience auto-ionization at a rate exceeding 10^{10} sec^{-1}; 8pσ (v = 5) $\to$ H$_2^*$(v = 3) + e [11]. The energy of the direct ionization transition X $\to$ H$_2^+$(v = 4) + e is also close to 7ω [6]. Whereas the subsequent decay H$_2^+$1sσ_g(v = 3) + ω $\to$ H + H$^+$ is strongly forbidden by the Franck-Condon principle, the final level for direct ionization H$_2^+$1sσ_g (v = 4) should dissociate rapidly at I = I_H. The cross sections of the processes H$_2^+$ (v = 3, 4) + ω $\to$ H + H$^+$, calculated by the method of [7], are equal to 7.9×10^{-27} and 4.3×10^{-23} cm^2. At I = I_H the times of photodissociation of these levels are $\tau_3 = 10^{-5}$ sec $\gg$ τ_p and τ_4 = 2 nsec $\ll$ τ_p. The observation of H$_2^+$ ions at I = I_H indicates that the auto-ionization channel predominates in the experiment performed at λ = 0.53 μ.

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FERMI RESONANCE IN RAMAN SCATTERING OF LIGHT BY POLARITONS IN AN α-HIO₃ CRYSTAL

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Polariton Fermi resonance occurs when the frequency ν' of the dipole-active vibration of the crystal lattice (in the general case, of any order) is close to the frequency $\nu_p(\theta)$ of a polariton of the same symmetry.

This communication is devoted to the first observation of polariton Fermi resonance in Raman scattering of light by polaritons in the biaxial crystal α-HIO₃, which belongs to the point symmetry 222. This phenomenon occurs when the polariton branch $\nu_p(\theta)$ connected with the dipole active phonon B_1 ($\nu_p(\theta=90°)$ = 736 cm^{-1} [3]) crosses the branch of two bound photons of symmetry B_2 and B_3, which form upon binding a state with symmetry $B_2 \times B_3 \times A = B_1$ and with frequency $\nu' \simeq 650$ cm^{-1} (a weak vibration of symmetry B_1 at frequency ∿650 cm^{-1} was observed in absorption [3]). The crossing of the branches of the bound state of two phonons and a polariton was attained by suitable choice of the directions of polarization and propagation of the exciting radiation in the crystal, with allowance for the polariton character of the optical-phonon dispersion. The scattering of light by polaritons was observed with the aid of a photographic technique wherein the spectrograph slit was placed in the focal plane of a lens located behind the investigated sample.

The figure shows the frequency vs. angle spectra of the Raman scattering of light in an α-HIO₃ crystal when the exciting radiation of an argon laser ($\lambda_0 = 5145$ Å) propagates in the principal plane YZ of the crystal at an angle $\theta = 32°$ (a) and 39° (b) to the crystallographic axis Z (the designation of the crystallographic axes corresponds to the condition $N_X \gtrsim N_Y > N_Z$, where N_i are the principal values of the refractive indices of the crystal), where θ is the angle between the directions of the wave vectors $\vec{k}_0$ and $\vec{k}_s$ of the exciting and scattered radiation, and ν is the frequency shift of the scattered Stokes radiation. The exciting radiation was polarized perpendicular and the spectrograph slit was parallel to the crystallographic X axis.

The three intense horizontal lines in the figure, with frequencies 633, 715, and 782 cm^{-1}, correspond to the Raman scattering of light by the nonpolar lattice vibrations of symmetry A [3], whose scattering frequency does not depend on the scattering angle θ.