F and from the ^{14}N line $\bar{a}=[+(3.4^{+2.0}_{-2.9})+i(3.3^{+6.7}_{-2.6})]$ F. The very large uncertainties in the scattering lengths for ^{14}N compared to ^{16}O reflect the fact that the 3*d* atomic state is less sensitive to the strong $\bar{p}$-nucleus interaction in nitrogen than in oxygen. A more precise measurement of the shifts and widths would be useful in constraining $\bar{a}$ for oxygen, but less useful for nitrogen because of the lower sensitivity. Statistically the value of $\bar{a}$ which best fits all four pieces of data is $\bar{a}=[(2.9^{+1.4}_{-1.0})+i(1.5^{+1.2}_{-0.6})]$ F. Even though these parameters have large errors, the real part seems considerably different from the value obtained by properly averaging the zero-energy *S*-wave $\bar{p}$-nucleon scattering lengths given by Bryan and Phillips,[3] namely, $\bar{a}=(-0.88+i0.81)$ F. Similar behavior has been noted in kaonic-atom data.[4] However, one might not expect agreement since our treatment is rather a simple one and also, with the $\bar{p}$-nucleus system, we are concerned with energies below threshold.

It is of interest to investigate the sensitivity of the calculations to the nuclear-shape parameters. If we assume a strong-interaction potential of the (Fermi) form given above with our central value for $\bar{a}=(2.9+i1.5)$ F and with the values of $\bar{c}$ given earlier, we find that the linewidth measurement restricts the value of *z* to the range 0.43 to 0.55 F for ^{16}O and to the range 0.40 to 0.47 F for ^{14}N.

We also wish to report here the observation of the x ray from the $3d\rightarrow 2p$ transition in the $\bar{p}$-He atom. Although the data obtained so far are not sufficiently precise to enable us to obtain a significant value for the width or energy of the line, nevertheless, the observation shows that Stark-effect mixing is not strong enough to cause the nuclear absorption of the antiprotons before they reach the 2*p* state.

Further analysis of all these data is proceeding and will be fully reported later.

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[1] A. Bamberger, U. Lynen, H. Piekarz, J. Piekarz, B. Povh, H. G. Ritter, G. Backenstoss, T. Bunaciu, J. Egger, W. D. Hamilton, and H. Koch, Phys. Lett. 33B, 233 (1970).

[2] T. E. O. Ericson and F. Scheck, Nucl. Phys. B19, 450 (1970).

[3] R. A. Bryan and R. J. N. Phillips, Nucl. Phys. B5, 201 (1968).

[4] J. H. Koch and M. M. Sternheim, Phys. Rev. Lett. 28, 1061 (1972).

Multiphoton Ionization and Dissociation of Molecular Hydrogen at 1.06 μm

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This paper reports the experimental investigation of the multiphoton dissociation and ionization of the hydrogen molecule under the influence of Nd-glass laser radiation at 1.06 μm. The higher electronic states of the potential-energy curves of H_2 are found to play the dominant role. An eleven-photon process is the initial step in the formation of H^+ and a twelve-photon process is the initial step in the formation of H_2^+.

Very little work has been carried out on multiphoton ionization and dissociation of molecules under the influence of laser radiation.[1,2] This Letter presents the results of an experimental investigation of multiphoton ionization and dissociation of hydrogen molecules with Nd-glass laser radiation at 10 590 Å.

The experimental method is the same as that employed in multiphoton ionization of atoms.[3] The radiation generated by a *Q*-switched neodymium glass laser is focused with an aspheric lens of 50 mm focal length into a vacuum chamber in order to obtain a laser intensity of up to 10^{13} W/cm^2. Molecular hydrogen is admitted into the

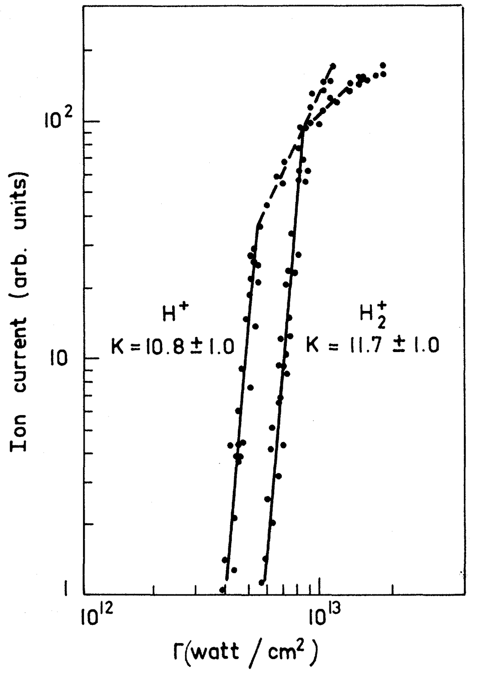

FIG. 1. Log-log plot of the H^+ and $H_2{}^+$ ion signals as functions of laser intensity Γ. These ions result from the interaction of the focused laser pulse with a molecular hydrogen beam.

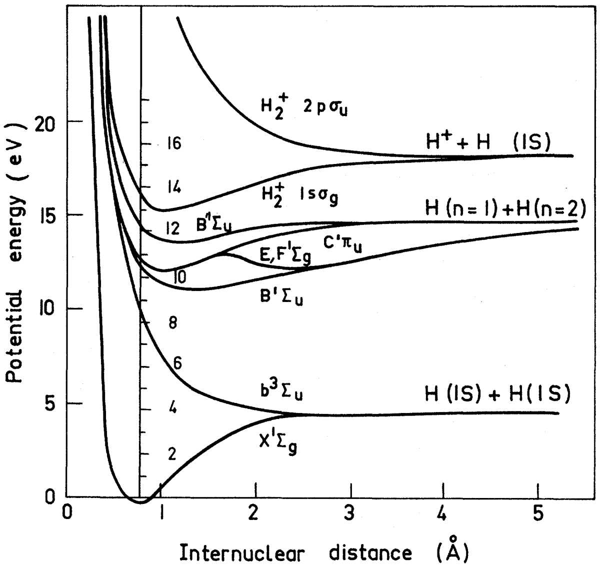

FIG. 2. Potential-energy curves for H_2 and $H_2{}^+$. The vertical dashed line represents the multiphoton transitions from the X, $v = 0$ ground-state level satisfying the Franck-Condon principle.

chamber through a glass tube which terminates with a capillary located 2 cm from the focal point, where the hydrogen density is 4×10^{12} cm^{-3}. The atomic H^+ and molecular $H_2{}^+$ hydrogen ions resulting from the laser interaction with hydrogen molecules at the focal point are analyzed with a magnetic mass spectrometer and detected by an electron multiplier. Figure 1 shows the log-log plot of the number N_i of H^+ and $H_2{}^+$ ions, expressed here as current signals from the electron multiplier as a function of the laser intensity Γ at the focal point. The slope $K = d(\log N_i)/d(\log\Gamma)$ has been found to be $K = 10.8 \pm 1.0$ for H^+ ions and $K = 11.7 \pm 1.0$ for $H_2{}^+$ ions. To understand the origin of the observed atomic hydrogen ions H^+, an examination of the potential-energy curves for H_2 is necessary. The most important electronic states[4] appear in Fig. 2 where the potential energy is expressed both in eV and in number of photons with 1.17-eV energy. It should be pointed out that a 10-photon transition from the ground state of the molecule to the first excited $B^1\Sigma_u{}^+$ state is forbidden by the parity selection rule. The following processes have to be considered to explain the observed slope $K = 10.8 \pm 1.0$ for H^+ ions.

A quasiresonant eleven-photon transition may occur from the lowest vibrational ($v = 0$) level of the ground electronic state of the molecule, either to the $v = 12$ level of the $B^1\Sigma_u{}^+$ state, or to the $v = 2$ level of the $C^1\Pi_u$ state, that is,

$$H_2 + 11\gamma_E \to H_2(B_1\Sigma_u{}^+,\ v = 12), \tag{1}$$

$$H_2 + 11\gamma_E \to H_2(C^1\Pi_u,\ v = 2). \tag{2}$$

The energy difference between $11E$ (103 911 cm^{-1}) and the $v = 12$ level of the $B^1\Sigma_u{}^+$ state (103 819 cm^{-1})[5] is only 92 cm^{-1}. The corresponding energy difference for the $v = 2$ level of the $C^1\Pi_u$ state is 350 cm^{-1}. These quasiresonant eleven-photon transitions are followed by a two-photon absorption to lead to a dissociation of the molecule, that is,

$$H_2(B^1\Sigma_u{}^+) + 2\gamma_E \to H(n = 1) + H(n = 2), \tag{3}$$

$$H_2(C^1\Pi_u) + 2\gamma_E \to H(n = 1) + H(n = 2). \tag{4}$$

These two-photon dissociation probabilities have not yet been numerically calculated. However, from reference to multiphoton ionization of atoms, these two-photon transition probabilities are so high in the laser intensity used ($\Gamma = 5\times10^{12}$ W/cm^2) that these two-photon transitions can be considered as saturated. Moreover, among these two two-photon transitions leading to dissociation of the molecule, (3) seems to be more probable because it occurs without a significant change in nuclear momentum. The energy gap between the two $B^1\Sigma_u^+$ and $B'^1\Sigma_u^+$ potential-energy curves remains constant and equal to $2E$ within the considered internuclear distance range. The atom of hydrogen with principal quantum number $n=2$ is then ionized through the simultaneous absorption of three photons. From Gontier and Trahin's work,[6] the three-photon ionization probability of hydrogen in the $2s$ state can be calculated to be $W_3=3\times10^{15}$ sec^{-1} with the laser intensity $\Gamma=5\times10^{12}$ W/cm^2. The duration of this three-photon process is thus $10^{-15}\ll10^{-8}$ sec, the effective duration τ_3 of the laser interaction. The total probability of obtaining an H^+ ion is then governed only by the eleven-photon process with the corresponding slope $K=11$.

A twelve-photon transition may occur from the ground state of the molecule to the $v=21$ level of the $E,F^1\Sigma_g^+$ state, that is,

$$H_2+12\gamma_E\rightarrow H_2(E,F^1\Sigma_g^+,\ v=21). \qquad (5)$$

Then an additional one-photon absorption can take place to reach the continuum of the $B'^1\Sigma_u^+$ state, that is,

$$H_2(E,F^1\Sigma_g^+,\ v=21)+1\gamma_E \rightarrow H(n=1)+H(n=2). \qquad (6)$$

The atom of hydrogen with principal quantum number $n=2$ would be ionized through the simultaneous absorption of three photons. The same remark as above applies to the saturation of this three-photon transition in the laser intensity $\Gamma=5\times10^{12}$ W/cm^2, so that the total probability of obtaining H^+ ions would be governed only by the twelve-photon process with the corresponding slope $K=12$. However, this twelve-photon process is most unlikely for two reasons. First, the $v=21$ level of the $E,F^1\Sigma_g^+$ state is proposed as an intermediate in the formation of H^+. The highest reported vibrational level for this state is $v=11$.[4] Undoubtedly, higher vibrational levels of the E,F state do exist, but they have not been observed spectroscopically. Second, the energy gap between the $B'^1\Sigma_u^+$ and the $E,F^1\Sigma_g^+$ curves coincides with E only in a narrow range of internuclear distances. This energy gap E is necessary for transitions without change in nuclear momentum (Franck-Condon principle). In conclusion, the observed H^+ ions probably result from an eleven-photon transition from the ground state of the molecule to the $v=12$ level of the $B^1\Sigma_u^+$ state followed by dissociation of the molecule through an additional two-photon absorption process, and then a three-photon ionization of the atom of hydrogen in the $n=2$ state would take place.

A similar mechanism may be suggested to explain the observed slope $K=11.7\pm1.0$ for H_2^+ ions resulting from multiphoton ionization of the hydrogen molecule. It should be pointed out that the transition between the ground state $X^1\Sigma_g^+$ of the molecule and the ground state of the molecular ion is optically connected, and therefore only an odd-order transition is allowed. Transitions with odd order <15 do not have enough energy. However, there is a set of highly excited even Rydberg states which have the ground state of H_2^+ as the limit. The multiphoton ionization of H_2 may result from the twelve-photon excitation of the intermediate state $E,F^1\Sigma_g^+$, that is,

$$H_2+12\gamma_E\rightarrow H_2(E,F^1\Sigma_g^+,\ v=21) \qquad (7)$$

followed by the absorption of two additional photons to give $nd\sigma(^1\Sigma_g^+)$ and $nd\pi(^1\Pi_g)$ Rydberg states. This two-photon process takes place without a significant change in nuclear momentum, satisfying the Franck-Condon principle. Autoionization would then occur in $H_2^+(1s\sigma_g,\ v=3$ or $4)$. Autoionization of H_2 by single-photon absorption is discussed by Chupka and Berkowitz.[7] The law of variation of the number of H^+ ions as a function of the laser intensity shows a limiting value (Fig. 1). This limit would be due to the appearance of the competitive twelve-photon process in the formation of H_2^+ in a laser intensity $\Gamma\geq6\times10^{12}$ W/cm^2. The preceding remark on the $v=21$ level of the $E,F^1\Sigma_g^+$ state applies here. There is probably an adequate density of rotational levels in the excited state of H_2 to permit a nearly exact match of the energy of an integer number of photons to some specific vibrational-rotational level of the excited molecule.

In a second set of experiments, the molecular hydrogen beam was 50% dissociated by radio-frequency radiation before the interaction with the laser radiation. Figure 3 shows the variation of the number of H^+ and H_2^+ ions as a function of the laser intensity Γ. The observed slopes do not change significantly. However, a very significant decrease by a factor of 30 in both the number of atomic and molecular ions is observed with rf dissociation compared to the preceding results. We suggest that this decrease can be essentially explained as follows. The hydrogen molecules are heated to about 10^4 °K when the rf power is turned on. The most populated vibrational level of the hydrogen molecule in the ground state at 300°K (without rf heating) was

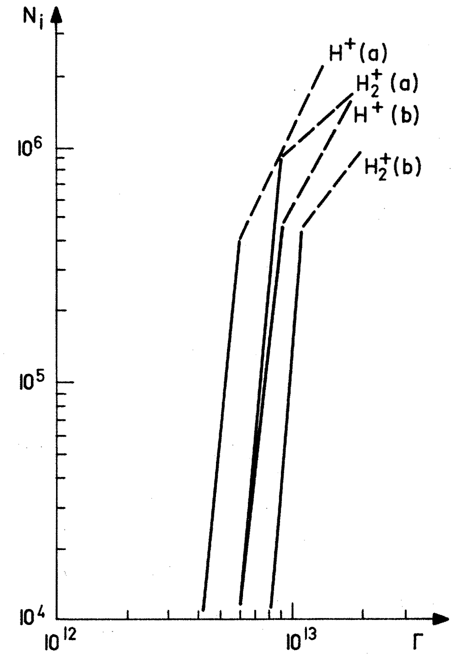

FIG. 3. Variation of the number N_i of H^+ and H_2^+ ions formed as a function of the laser intensity Γ from *a*, molecular hydrogen beam only; *b*, molecular hydrogen beam 50% dissociated by rf power. Experimental points have been deleted in the interest of clarity.

the $v=0$ level. It may be suggested that, because of rf heating, the population of the vibrational levels is governed by the Boltzmann distribution corresponding to vibrational temperature of about 10^4 °K, and in that case the population of the $v=0$ level is approximately an order of magnitude less than without rf heating. Therefore a small fraction of molecules can be found in the same conditions as above for eleven- or twelve-photon transitions from the $v=0$ level of the ground state to $B^1\Sigma_u^+$, $v=12$ or $E,F^1\Sigma_g^+$, $v=21$ intermediate excited states. Figure 4 illustrates the change in transition conditions from excited vibrational levels of the ground state. The most probable transitions from each excited vibrational level of the ground $X^1\Sigma_g^+$ state are those which begin in the vicinity of the right-hand reversal point. For example, a transition which occurs near the right-hand reversal point of the $X^1\Sigma_g^+$, $v=3$ vibrational level terminates at the $v=28$ vibrational level of the $B^1\Sigma_u^+$ state. This vertical transition which occurs without change in the relative positions of the nuclei of the molecules requires a very significant change in the relative velocities, and consequently such a transition is unlikely (Franck-Condon principle).[8] As in the work of Busch *et al*,[9] the determination of the kinetic energy of the H^+ fragments could aid in the interpretation of the mechanism of formation of the observed H^+ ions.

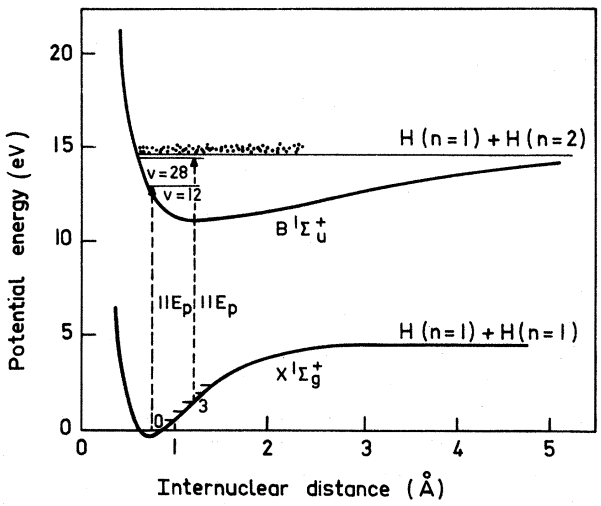

FIG. 4. Schematic representation of the eleven-photon transitions from $v=0$ and $v=3$ vibrational levels of the ground state. The $(X^1\Sigma_g^+, v=0)\rightarrow(B^1\Sigma_u^+, v=12)$ transition occurs without change in nuclear momentum The second $(X^1\Sigma_g^+, v=3)\rightarrow(B^1\Sigma_u^+, v=28)$ transition (which begins in the vicinity of the right-hand reversal point) requires, on the contrary, a significant change in nuclear momentum, and hence does not satisfy the Franck-Condon principle.

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[1] S. L. Chin, Phys. Rev. A 4, 992 (1971).

[2] N. K. Berejetskaya, G. S. Voronov, G. A. Delone, N. B. Delone, and G. K. Piskova, Zh. Eksp. Teor. Fiz. 58, 753 (1970) [Sov. Phys. JETP 31, 403 (1970)].

[3] P. Agostini, G. Barjot, G. Mainfray, C. Manus, and J. Thebault, IEEE J. Quantum Electron. 6, 782 (1970).

[4] T. E. Sharp, At. Data 2, 119 (1971).

[5] *Tables of Constants, Vol. 17: Spectroscopic Data Relative to Diatomic Molecules*, edited by S. Bourcier and B. Rosen (Pergamon, New York, 1971).

[6] Y. Gontier and M. Trahin, Phys. Rev. A 4, 1896 (1971).

[7] W. A. Chupka and J. Berkowitz, J. Chem. Phys. 51, 4244 (1969).

[8] G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, Princeton, N. J., 1950).

[9] G. E. Busch, R. T. Mahoney, R. I. Morse, and K. R. Wilson, J. Chem. Phys. 51, 837 (1969).