and $F_E^{(1)}$ and $F_E^{(2)}$ first- and second-class induced tensor, or "weak electricity") as

$$\alpha_- = 2(F_M - F_E^{(1)} - F_E^{(2)})/3F_A. \quad (8)$$

Assuming the conserved-vector-current value $F_M/F_A = 3.8/2M$ and $F_E^{(1)}/F_A = 3.7/2M$ as obtained by several independent calculations,[1-10] one obtains from (7) and (8)

$$F_E^{(2)}/F_A = -(0.6 \pm 1.1)/2M. \quad (9)$$

Averaging (9) with the corresponding result of Lebrun *et al.* [Eq. (7) of Ref. 4], one obtains

$$F_E^{(2)}/F_A = +(0.4 \pm 0.6)/2M.$$

This is clearly consistent with the absence of a "large" second-class axial current, e.g., as discussed by Kubodera, Delorme, and Rho.[11]

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Observation of Two-Photon Excitation of the H_2 $E,F\ ^1\Sigma_g^+$ State

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Selective excitation of the $E,F\ ^1\Sigma_g^+$ state of H_2 by two-photon absorption at 193 nm is reported. The excited population is detected by observing fluorescence arising from $E,F\ ^1\Sigma_g^+ \rightarrow B\ ^1\Sigma_u^+$ transitions. Experimental determinations of the radiative lifetime of the E,F level as 100 ± 20 ns and collisional quenching rates for H_2 and He as $(2.1 \pm 0.4) \times 10^{-9}$ and $(0.8 \pm 0.4) \times 10^{-9}$ cm^3/sec, respectively, have been made. These experiments involve the first selective population of an electronically excited *gerade* state of H_2.

Although molecular hydrogen is among the simplest of quantum mechanical systems, occupies a central position in quantum chemistry, and has been extensively studied from a theoretical standpoint, very little experimental data on the collisional properties of the electronically excited states are in existence. Previous work has concerned energy transfer processes involving the HD ($B\ ^1\Sigma_u^+$ state,[1] chemi-ionization[2] arising from Rydberg levels of H_2, and the ob-

servation of laser emission on the Lyman[3] bands of H_2, HD, and D_2 as well as the Werner[4] bands of H_2. These studies have focused exclusively on excited *ungerade* states, and in no instance have the collisional properties of an excited *gerade* level been examined.

The principal limiting factor in the experimental analysis of the collisional behavior of electronically excited states of hydrogen has been the absence of an effective means for selective excitation of the molecular states. Optical pumping techniques,[1] with the exception of the $B\,^1\Sigma_u^+$ state, are made extremely difficult by the lack of a good window material below 1000 Å. Naturally, *gerade* states could not be excited by conventional absorption from the $X\,^1\Sigma_g^+$ level, even without this limitation.

Two-quantum ultraviolet absorption in the reaction

$$\gamma + \gamma + H_2(X\,^1\Sigma_g^+) \rightarrow H_2(E, F\,^1\Sigma_g^+), \qquad (1)$$

however, is not subject to these limitations. Therefore, in the present experiments, we have used the two-photon mechanism in the absorption of intense 193-nm radiation to populate selectively the $E, F\,^1\Sigma_g^+$ state of H_2, as shown in Fig. 1. Through observation of the near-infrared radiation originating from the $E, F\,^1\Sigma_g^+$ level to the $B\,^1\Sigma_u^+$ state, both the detection of the excited E, F state population and the determination of its radiative and collisional deactivation rates are readily accomplished. These experiments clearly demonstrate that this method of excitation will allow the direct evaluation of a wide range of collisional and reactive processes involving electronically excited H_2. Measurements of this type should serve as an excellent basis for comparison with theoretical treatments of scattering and reaction in simple molecular systems.

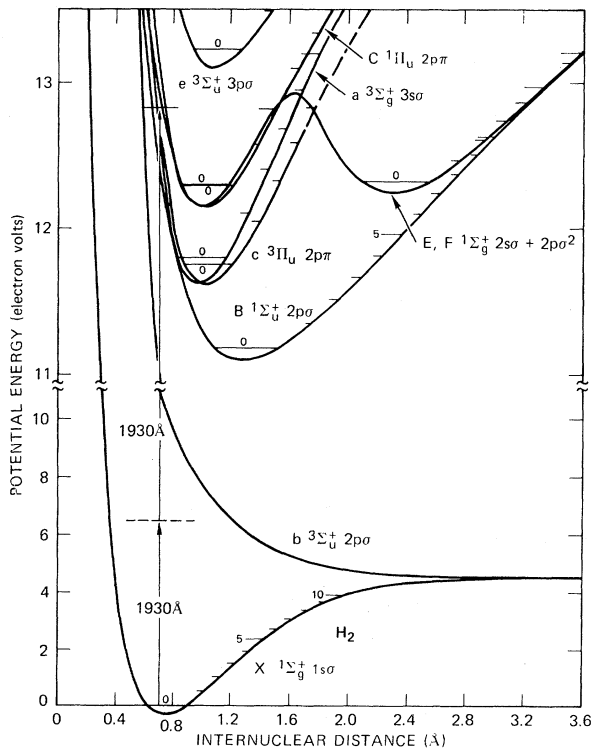

FIG. 1. Energy level diagram of H_2 showing the X, B, and E,F states of interest in this experiment, as well as other states in this energy range, based on graphs in T. E. Sharp, At. Data 2, 119 (1971). Note the change in vertical scale above 10 eV.

The radiation source used in these experiments was a transverse-electric-discharge–excited ArF* excimer laser of the configuration that has been described by Burnham and Djeu.[5] The laser emitted ~15-mJ pulses at 193 nm having a duration of ~15 nsec and a full bandwidth of ~0.5 nm. The spatial profile of the output beam was oblong (10 mm×2 mm) with an overall divergence angle of ~5 mrad. The ultraviolet energy from this source was focused into an experimental cell with a planoconvex Suprasil lens having a focal length of 125 mm. Since the area of the focal spot determined by direct measurement was 1.0×0.3 mm, the peak focused intensity was $\sim 3\times10^8$ W/cm². The fluorescence originating from the irradiated volume was collected and collimated by an $f/1$ Suprasil lens. This fluorescent radiation initially traversed a long-pass filter to eliminate stray reflections of the laser beam and then passed through a selection of 10-nm band-pass filters. Detection was provided by an RCA C31034A photomultiplier tube whose output could either be monitored directly on a Tektronix 7844 oscilloscope or averaged over a consecutive series of pulses with a Tektronix R7912 transient digitizer equipped with a PDP 11/34 computer.

With this apparatus, samples of H_2 were irradiated at gas pressures ranging from 10 mTorr to 300 Torr. Following the 193-nm laser pulse, the H_2 sample exhibited strong fluorescence in the 740–750 and 820–830 nm spectral ranges. The intensity of this fluorescent signal was determined to vary as the square of the incident laser intensity, a fact clearly establishing the characteristic signature of the two-photon absorption.

The near-infrared emission observed in this manner is attributed to radiative decay from the initially excited $v=2$ level of the $E, F\,^1\Sigma_g^+$ state

(inner minimum) at ~12.8 eV to the lower $B\,^1\Sigma_u^+$ vibrational levels.[6] We note that all other states in the vicinity of ~12.8 eV are forbidden for two-quantum excitation from the ground $X\,^1\Sigma_g^+$ state by either parity or spin or both. This point is clearly evident from Fig. 1, which illustrates the molecular levels in the relevant energy range. Since the 193-nm radiation has a linewidth of ~0.5 nm,[5] states in the energy range between ~103 350 and ~103 681 cm^{-1} are populated by the two-photon excitation from the ground level. Therefore, three rotational levels ($j=0$ at 103 552 cm^{-1}, $j=1$ at 103 598 cm^{-1}, and $j=2$ at 103 682 cm^{-1}) of the $E, F\,^1\Sigma_g^+(v=2)$ state are simultaneously excited. We note, however, that a modest reduction in the laser linewidth to ~0.05 nm would be more than sufficient to provide the selective excitation of single rotational levels in this manifold.

The $E, F\,^1\Sigma_g^+(v=2)$ state radiatively decays to the $B\,^1\Sigma_u^+(v=1)$ and $B\,^1\Sigma_u^+(v=0)$ states with emission in P and R branches in the 824–837- and 743–754-nm spectral regions, respectively. On account of the 10-nm bandwidth of the interference filters used in this experiment, we were unable to resolve the rotational structure of this emission in these initial studies. As further confirmation concerning the origin of these fluorescent signals, the ratio of observed emission intensity in the 830-nm band to that in the 750-nm band was found to be 1.4 ± 0.2. This result agrees well with theoretical calculations of the Einstein A coefficients[7] which give $A_{2,1}/A_{2,0}=1.51$.

Although strong near-infrared emission signals were observed in H_2, irradiation of D_2 under identical conditions produced no detectable fluorescence. On account of the substantial isotopic shifts of the vibrational and rotational energies, the D_2 $E, F\,^1\Sigma_g^+(v=2)$ state lies at ~102 740 cm^{-1}, so that there are no transitions from the ground $X\,^1\Sigma_g^+(v=0)$ level that fall within the appropriate energy band.[8] Similarly, the HD $E, F\,^1\Sigma_g^+(v=2)$ level[9] at ~103 220 cm^{-1} also falls in such a position that no appreciable excitation is expected.

In order to determine the relaxation rate of the E, F state, the photomultiplier output was averaged over twenty consecutive pulses with the transient digitizer. At H_2 pressures above approximately 0.5 Torr, the infrared fluorescence adiabatically follows the excitation pulse, a fact indicating that the relaxation time of the excited states was less than ~20 ns. Measurements of fluorescence decay rate below ~0.5 Torr are shown in Fig. 2. These data indicate that the

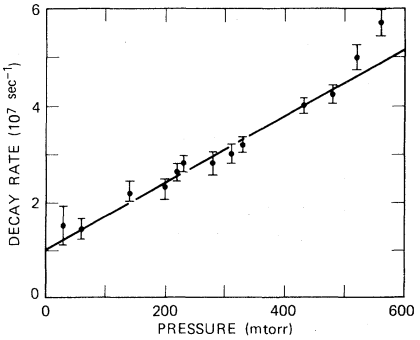

FIG. 2. Fluorescence decay rate as a function of H_2 pressure in pure H_2 from 0 to 500 mTorr.

radiative lifetime of the excited *gerade* state is 100 ± 20 ns and that the total collisional quenching rate by H_2 is $(2.1\pm0.4)\times10^{-9}$ cm^3 sec^{-1}. This radiative lifetime is in excellent agreement with the theoretical value of 90 ns derived from the theoretical studies of Wolniewicz[7] and the Franck-Condon factors of Spindler.[10] Similar measurements in He/H_2 mixtures give the quenching rate by He of $(0.8\pm0.4)\times10^{-9}$ cm^3 sec^{-1}.

On the basis of the large He quenching rate, the dominant inelastic collisional processes are expected to be rotational relaxation and population of the $C\,^1\Pi_u$ state in the reaction

$$H_2(E, F\,^1\Sigma_g^+) + H_2(X\,^1\Sigma_g^+) \rightarrow H_2(C\,^1\Pi_u) + H_2(X\,^1\Sigma_g^+) \qquad (2)$$

which then radiates rapidly to $X\,^1\Sigma_g^+$ emitting Werner-band radiation. As noted from Fig. 1, the $E, F\,^1\Sigma_g^+$ and $C\,^1\Pi_u$ states are very nearly degenerate in the region of the inner minimum. Furthermore, these two states are connected by a large electric dipole transition moment enabling a relatively long-range collisional electric field to generate appreciable mixing. We note that on account of the near degeneracy of the potential wells of the initial and final states, the nuclear motions need only be very weakly coupled in the collisional amplitude. In this sense, the dynamics quite closely resemble the quenching of $H(2s)$ to $H(2p)$ by collisions.[11]

These data allow us to appraise the excited-state density generated in our experiment, and, therefore, provide a means for the evaluation of the two-photon absorption cross section for Reaction (1). At large densities of H_2, production and collisional quenching of the E, F state are much faster than the radiative decay rate. Hence, we

may write in the steady-state approximation an expression for the excited-state density n^* as

$$n^* = \alpha I^2/\hbar\omega k_q , \quad (3)$$

in which $\alpha = \sigma/I$ is the ratio of the two-photon absorption cross section σ the laser intensity I. In addition, ω denotes the laser frequency and $k_q = 2\times10^{-9}$ cm^3 sec^{-1} is the collisional quenching rate. At H_2 densities above $\sim 2\times10^{18}$ cm^{-3}, with a laser energy ~ 10 mJ, signals of $\sim 4\times10^{12}$ photoelectrons per second were observed in the 820–830-nm range. Since our light collection system has a 0.15% detection efficiency, these data correspond to photon flux, $\Phi = 4.5\times10^{15}$ sec^{-1}. If we assume that the length of the focal region is ~ 6 mm, giving a focal volume $V \cong 1.8\times10^{-3}$ cm^3, we conclude that $n^* \cong \Phi\tau/V \cong 2.5\times10^{11}$ cm^3, upon substitution of the value for $\tau = 100$ ns, the radiative lifetime of the $E, F\,^1\Sigma_g^+$ state determined above. These results, in conjunction with expression (3), yield a value of $\alpha \cong 10^{-32}$ cm^4/W.

This value may be compared with independent estimates of the two-photon cross section derived from standard perturbation theory.[12] The result for the cross section σ in this framework is

$$\sigma = [(2\pi)^2/\hbar c^2] I\omega |M_{fg}|^2 g(\omega) . \quad (4)$$

Appearing in expression (4) are the line-shape factor $g(\omega)$, which contains the appropriate linewidth, and the two-quantum matrix element M_{fg}. The latter may be conveniently written in the form

$$M_{fg}(\omega) = 2\sum_k \frac{\langle f|\hat{\epsilon}_1\cdot\vec{\mu}_{op}|k\rangle\langle k|\hat{\epsilon}_2\cdot\vec{\mu}_{op}|g\rangle}{E_{kg}-\hbar\omega} . \quad (5)$$

In this expression $\hat{\epsilon}_1$ and $\hat{\epsilon}_2$ denote the polarization vectors of the optical waves; $\vec{\mu}_{op}$ represents the electric dipole operator; $E_{kg} - \hbar\omega = \Delta\omega_{kg}$ is the energy denominator; and g, k, and f denote the ground, intermediate, and final states, respectively. If we assume that the dominant intermediate state is the $B\,^1\Sigma_u^+$ level, we can then take $\Delta\omega_{kg} \cong 45\times10^3$ cm^{-1}, $\mu_{fk}^2 \cong \mu_{kg}^2 \cong (1\text{ D})^2$ as characteristic hydrogenic values, and 2×10^7 MHz (effective laser linewidth) as the proper linewidth factor. These considerations provide the result $\alpha = \sigma/I \cong 9\times10^{-33}$ cm^4/W, a value which agrees to within 10% of the magnitude for α established from the experimental results. In view of the approximations and estimates that have been made, this agreement is remarkable.

In conclusion, we have observed selective excitation of the H_2 $E, F\,^1\Sigma_g^+$ state by two-photon absorption of ultraviolet laser radiation. Excited-state densities $\sim 2\times10^{11}$ have been achieved, a value which may be increased greatly by modest experimental improvements. This excitation technique has been used to measure the collisional and radiative decay rates of the E, F state. The experimentally determined values for the cross section for two-photon excitation and the radiative lifetime of the $E, F\,^1\Sigma_g^+$ state are found to compare very favorably with theoretical estimates. We note here that other collisional processes, such as rotational and vibrational relaxation, electronic energy transfer, para-ortho conversion, and formation of HD by four-center reaction may also be studied by this technique.

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Evidence for a Resonance in e^+-H S-Wave Scattering

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Using the coordinate rotation method with Pekeris trial functions, we find evidence that a resonance occurs in e^+-H S-wave scattering at a complex energy ($-0.257\,374 - i\,0.000\,067$) Ry. No lower resonance is found in the calculation.

Since the prediction by Mittleman[1] of an infinite sequence of resonances in positron-hydrogen scattering below the excitation thresholds, there have been some attempts (described by Wakid[2]) to locate the lowest such resonance, and some associated controversy.[3] Apparently these previous calculations either had a basis set which was too restricted to locate the resonance accurately or else used procedures which could generate nonphysical resonances. We present here a general method which couples sparse-matrix techniques for large basis sets with a stable, numerically convergent procedure to obtain an estimate for the lowest resonance location which appears to be accurate to six significant figures.

We shall describe the e^+-H system by means of the Hamiltonian

$$H(\vec{\mathbf{r}}) = -\nabla_1^2 - \nabla_2^2 - \frac{2}{r_1} + \frac{2}{r^2} - \frac{2}{|\vec{\mathbf{r}}_1 - \vec{\mathbf{r}}_2|},$$

where $\vec{\mathbf{r}}_1$ and $\vec{\mathbf{r}}_2$ are the coordinates of electron and positron, and the proton is fixed at the origin. Define $H_\alpha(\vec{\mathbf{r}})$ by

$$H_\alpha(\vec{\mathbf{r}}) = H(\vec{\mathbf{r}}e^{i\alpha}),$$

where each component of the coordinate vector is multiplied by a factor $e^{i\alpha}$, $\alpha > 0$. It has been shown rigorously[4] that the spectrum of H_α consists of a series of rays, making an angle -2α with the positive real axis, that start from each of the thresholds in the problem. These thresholds are those associated with the hydrogen atom at $-n^{-2}$, $n = 1, 2, \ldots$, and those connected with positronium at $-0.5m^{-2}$, $m = 1, 2, \ldots$. In addition, there may be discrete points in that part of the complex plane swept out by the rays as α is increased to its chosen value from zero, and also points on the real axis below $E = -1$ corresponding to three-body bound states.

It is very likely that the complex discrete points are associated with resonances, as would be the case for short-range potentials,[5] and this correspondence certainly occurs in the case of e^--H scattering.[6] We assume it to be true in the present case.

If E_r, $\mathrm{Im}E_r < 0$, is a discrete point in the spectrum of H_α, then there is a normalizable function ψ such that

$$H_\alpha\psi = E_r\psi.$$

A variational estimate of E_r may be found by approximating ψ by a linear combination of normalizable basis functions $\varphi_i(r)$, so that

$$\psi \approx \psi_t = \sum_{i=1}^{N} c_i \varphi_i,$$

and finding a stationary value of $[E_r]$, where

$$[E_r] = \frac{\int d^3r_1 d^3r_2 \psi_t H_\alpha \psi_t}{\int d^3r_1 d^3r_2 \psi_t \psi_t}.$$

If the coefficients c_i are varied, the problem reduces to the calculation of the eigenvalues $\lambda(k)$, $k = 1, \ldots, N$, given by

$$\sum_{j=1}^{N} H_{ij} x_j^{(k)} = \lambda^{(k)} \sum_{j=1}^{N} N_{ij} x_j^{(k)}, \quad i = 1, \ldots, N, \qquad (1)$$

where

$$H_{ij} = \int d^3r_1 d^3r_2 \, \varphi_i H_\alpha \varphi_j, \quad N_{ij} = \int d^3r_1 d^3r_2 \, \varphi_i \varphi_j.$$

With the use of Hylleraas trial functions, this approach has located several resonances in e^--H scattering.[6,7] After the main results of this Let-

