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The EF, GK, $H^1\Sigma_g^+$, $I^1\Pi_g$, and $J^1\Delta_g$ States of HD: Term Values and Fluorescence Lifetimes†

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Vacuum ultraviolet−visible double resonance excitation has been employed to populate rovibronic levels of the EF, GK, $H^1\Sigma_g^+$, $I^1\Pi_g$, and $J^1\Delta_g$ states of HD in the range between 113000 and 118600 cm^{-1} above the ground-state $X^1\Sigma_g^+$. Tunable coherent vacuum ultraviolet light, generated by a four-wave mixing process in Xe, prepares HD in the intermediate $B^1\Sigma_u^+$ ($v = 6$, 7, and 10) state. Subsequent absorption of visible laser radiation brings HD to the higher gerade states. Term values of 42 rovibronic levels are determined for the first time. The single rovibronic fluorescence lifetimes are measured under collision-free conditions. The observed lifetimes for the $H^1\Sigma_g^+$ state are generally longer than the theoretical values, whereas those of the EF and $GK^1\Sigma_g^+$ states are considerably shorter than the calculations. The rotational variation of the $EF^1\Sigma_g^+$ state lifetimes can be well understood in terms of the nonadiabatic coupling among the upper gerade manifolds. The rotational dependence of the lifetimes for the $GK^1\Sigma_g^+$ state exhibits a good correspondence to the coupling with the nearby $B^1\Sigma_u^+$ rovibronic levels.

Introduction

The spectroscopy of molecular hydrogen and its isotopomers has attracted much attention since the early days of quantum mechanics. In recent years, a large number of experimental investigations have been reported concerning the vibronic structure of the electronically excited states with gerade symmetry. The gerade states cannot be reached by a single dipole-allowed transition from the ground state. This difficulty has been overcome by the double resonant excitation method: the frequency up-conversion technique using tunable laser radiation has enabled us to populate ungerade levels located in the vacuum ultraviolet (VUV) region under a pulsed regime. Through a subsequent excitation combined with detection of ions[1−4] or photons,[5] the upper gerade manifolds are sensitively probed in a state-selective manner. On the other hand, ab initio treatments of gerade excited states have been developed by Dressler, Wolniewicz, and coworkers over the last quarter century (see ref 6 and references therein). A different approach through multichannel quantum defect theory (MQDT) has been developed by Jungen and Ross to reproduce observations of states having u symmetry and g symmetry.[7,8] Quadrelli, Dressler, and Wolniewicz have performed ab initio calculations based on the nonadiabatic coupling among gerade manifolds, evaluating several important quantities such as energy eigenvalues and radiative lifetimes.[6] These calculations have served as the criteria for the identification of new laser excitation lines. Thus far, concerning H_2 and D_2, the spectroscopic assignment has been largely accomplished for the gerade levels below the second dissociation limit. The perturbations in the excited states are reflected not only in the vibronic structure but in the radiative lifetimes. Collision free lifetimes of single rovibronic levels of the gerade levels have been determined by our group for H_2 and D_2 since 1992.[9−11] On the whole, the measured lifetimes are in reasonable agreement with ab initio calculations, verifying the excellent performance of the theoretical treatments.

A spectroscopic study of HD provides information not only on the reduced mass effect but also on quantum mechanical issues related to the symmetry of the electronic wave function. Within the framework of the Born−Oppenheimer approximation, HD is considered as a homonuclear molecule obeying g, u symmetry rules. This is not the case, however, in rotating HD, where there is no symmetry (+, −) property to help in preserving the g−u property of electronic states. Such g−u mixing in the electronically excited states has been recognized as an appearance of the weak $EF^1\Sigma_g^+-X^1\Sigma_g^+$ transitions in the VUV region.[12,13] The ab initio calculation including a g−u coupling Hamiltonian has been recently carried out for the double-minimum $H\bar{H}^1\Sigma_g^+$ and $B''\bar{B}^1\Sigma_u^+$ states.[14] Concerning the fluorescence lifetimes, only a few experimental values have been published: Chandler and Thorne prepared HD in the $EF^1\Sigma_g^+$ ($v =$ 0, 3, and 6) states by two-photon absorption.[15] The lifetimes, obtained by changing the delay between excitation and ionization lasers, agree fairly well with ab initio values. However, because the nonadiabatic coupling of the other gerade states is negligible in these lower vibrational states, i.e., these states are nearly isolated, no detailed discussion on the vibrational and rotational dependence of lifetimes was realized.

In the current experiment, we conducted a systematic survey of energy terms and fluorescence lifetimes of HD molecules in the EF, GK, $H^1\Sigma_g^+$, $I^1\Pi_g$, and $J^1\Delta_g$ states in the range between 113000 and 118600 cm^{-1}, where severe nonadiabatic mixing is expected to cause a perturbed rovibronic structure and a wide variation of fluorescence lifetimes. With the aid of ab initio calculations, term values of 42 rovibronic levels have been determined. Collision-free fluorescence lifetimes of these levels are compared with the recent theoretical works. The effect of g−u mixing is also to be discussed.

Experiment

The experimental procedure is similar to that published in our previous paper,[5] and is thus described only briefly here. The VUV radiation for the excitation of $B^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ (v, 0) is generated by resonant four-wave sum-frequency mixing in

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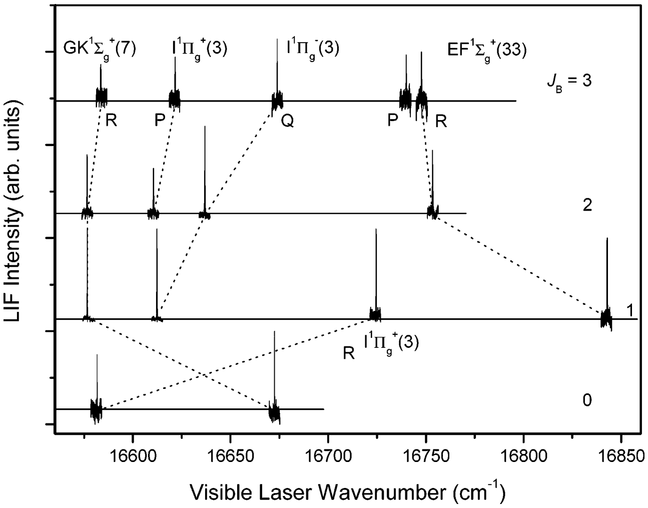

Figure 1. Double resonant excitation spectra in the energy region relevant to the GK$^1\Sigma_g^+$ (v = 7) and EF$^1\Sigma_g^+$ (v = 33) ← B$^1\Sigma_u^+$ (v = 10, J_B) transitions. Dotted lines connect the P, Q, and R branches, showing a perturbed rovibronic structure.

Xe. Two dye lasers (Continnum ND6000, 0.08 cm^{-1} spectral width) are pumped simultaneously by frequency doubled and tripled outputs of a Q-switched Nd:YAG laser (Continuum Surelite II). The output of the dye laser I is converted into ultraviolet by a BBO crystal whose frequency is a fixed resonance to the two-photon transition of 6p[1/2, 0] ← $^1S_0$ of Xe (E = 80119.474 cm^{-1}). The output of dye laser II is collinearly coupled with the UV beam through a dichroic mirror. Both beams are then focused by a lens into a mixing chamber where Xe gas is provided from a pulsed valve synchronized with laser pulses. The resulting VUV beam is introduced to a differentially evacuated main chamber through a hole (d = 5 mm). Visible light from a dye laser (Continuum ND6000, 0.08 cm^{-1} spectral width, ∼ 4 ns pulse duaration) pumped by a Nd:YAG laser (Continuum Surelite I) is employed for subsequent excitation from the intermediate levels to the upper gerade manifolds. The laser beam is collimated properly and introduced into the main chamber from the opposite direction to the VUV radiation. The wavenumber is calibrated by simultaneous recording of the I_2 excitation spectrum.

The VUV coherent radiation is tuned to the single rovibronic transition of the Lyman band system (B ← X) by monitoring the VUV fluorescence with a solar blind photomultiplier (Hamamatsu R1459). The intermediate levels used in the current experiment are B(v = 6, 7, and 10, J_B = 1 ∼ 4). The transitions to the upper gerade states are then interrogated by observing the visible/near-IR fluorescence with another photomultiplier (Hamamatsu R666) through suitable color filters (R-60 etc.) For the lifetime measurements, the output from the photomultiplier is fed into a digital oscilloscope (Tektronix TDS620B) and processed by a microcomputer. The whole system operates at 10 Hz. The delay between two Nd:YAG laser pulses is controlled by a digital delay generator (Stanford Reserach DG535). Both laser pulses are set to overlap because of the short lifetime of the B$^1\Sigma_u^+$ state. HD gas (96% purity) is purchased from Isotec Inc. and used as received.

Results and Discussion

Spectral Assignments. In general, spectral assignment is rather straightforward by simply referring to the theoretical term values reported by Wolniewicz et al.[6,14] Figure 1 illustrates typical double resonant excitation spectra. The spectral region corresponds to the GK7 ← B10 transition where a heavy mixing of EF$^1\Sigma_g^+$ and I$^1\Pi_g^+$ adiabatic states is predicted. The notation GK7 represents GK$^1\Sigma_g^+$(v = 7), where v numbers the vibrational levels in the full double potential energy wells. The analyses of these spectral traces result in the plots of term values against $J(J + 1)$ as shown in Figure 2. To determine total energies, measured transition wavenumbers are added to the rovibronic energies of the B state.[12] In the present experiment, the final J = 0 levels which are accessible only by the P branch from B(v, J_B = 1) are not detectable.

Quadrelli, Dressler, and Wolniewicz[6] calculated term values and the corresponding nonadiabatic wave functions Ψ for the upper gerade manifolds. For three J = 1 levels between 117300 and 117600 cm^{-1}, the energies and the three largest coefficients in the expansion in adiabatic vibronic functions, ψ, are given as follows:

$$\begin{aligned} E_{\text{calc}} = 117563.91\ \text{cm}^{-1}\ \Psi(\text{EF33}) &= 0.876\psi(\text{EF33}) - 0.441\psi(\text{GK7}) - 0.114\psi(\text{I3}) \\ 117396.90\ \text{cm}^{-1}\ \Psi(\text{GK7}) &= 0.621\psi(\text{I3}) - 0.583\psi(\text{GK7}) - 0.390\psi(\text{EF33}) \\ 117312.92\ \text{cm}^{-1}\ \Psi(\text{I3}) &= 0.769\psi(\text{I3}) + 0.525\psi(\text{GK7}) + 0.265\psi(\text{EF32}) \end{aligned}$$

In principle, states whose wave functions are dominated by a leading contribution are given the associated electronic labeling. The level at the lowest energy is thus labeled as I3. Accordingly, the next lowest level is nominally designated as GK7. The nonadiabatic wave functions for J = 2 are

$$\begin{aligned} E_{\text{calc}} = 117595.48\ \text{cm}^{-1}\ \Psi(\text{EF33}) &= 0.798\psi(\text{EF33}) - 0.509\psi(\text{GK7}) + 0.266\psi(\text{I3}) \\ 117467.14\ \text{cm}^{-1}\ \Psi(\text{I3}) &= 0.677\psi(\text{I3}) - 0.523\psi(\text{EF33}) - 0.414\psi(\text{GK7}) \\ 117333.32\ \text{cm}^{-1}\ \Psi(\text{GK7}) &= 0.657\psi(\text{I3}) + 0.622\psi(\text{GK7}) + 0.289\psi(\text{EF32}) \end{aligned}$$

For the lowest two levels, the contribution of ψ(I3) is comparable and, in such strongly mixed states, the labeling is rather arbitrary. We adopt the notation as GK7 for the lowest energy level because the second largest contribution is ψ(GK7). The above designations apparently result in crossing of I$^1\Pi_g^+$(v = 3) with GK$^1\Sigma_g^+$(v = 7) as depicted in Figure 2.

The following features are worth comment. (1) In 1990, Quadrelli, Dressler, and Wolniewicz calculated the rovibronic structures of H_2, HD, and D_2 by including the nonadiabatic coupling among upper gerade manifolds.[6] In 1999, Reinhold et al. took a symmetry-breaking Hamiltonian into consideration, which is responsible for the g−u coupling in HD.[14] They concentrated on the strong interaction between nearby B″$\bar{\text{B}}$ and H$\bar{\text{H}}$ vibrational levels and obtained the term values of these four states. Their old (ab initio II) as well as new (ab initio I) term energies for the H$^1\Sigma_g^+$ state are listed in Table 1 together with the difference Δ between their and our values. In the old version, Δ drastically increases as the vibrational quantum number, from ∼7 cm^{-1} for H0 to ∼55 cm^{-1} for H2. In the new version, the agreement is substantially improved for H1 and H2 as well. For v = 0, however, inclusion of the g−u mixing term makes the agreement worse. (2) One of the unidentified VUV absorption bands near 116000 cm^{-1} reported by Dabrowski and Herzberg[12] is assignable to GK6. The appearance of the GK ← X transition in VUV indicates the coupling between GK and the ungerade manifold. (3) We identified two levels near 118500

TABLE 1: Term Values (cm^{-1}) and Fluorescence Lifetimes (ns) of EF, GK, H$^1\Sigma_g^+$, I$^1\Pi_g$, and J$^1\Delta_g$ States of HD

v	J	this work	ab initio I[a]	Δ[b]	ab initio II[c]	Δ[d]	experiment[e]	Δ[f]	lifetime
H$^1\Sigma_g^+$									
0	1	113144.97	113155.88	10.91	113152.59	7.62			108.2 ± 4.8
	2	113228.82	113245.74	16.92	113236.51	7.69			95.9 ± 0.8
1	1	115114.10	115109.92	−4.18	115130.08	15.98			132.5 ± 5.5
	2	115197.10	115195.64	−1.46	115213.62	16.52			121.2 ± 0.8
	3	115321.18	115323.58	2.40	115338.80	17.62			123.4 ± 3.7
2	1	116946.86	116969.34	22.48	117001.13	54.27			84.3 ± 1.7
	2	117023.57	117050.95	27.38	117080.56	56.99			88.9 ± 1.2
GK$^1\Sigma_g^+$									
6	1	116538.18			116578.44	40.26	116538.20	0.00	31.8 ± 1.1
	2	116573.35			116612.03	38.68	116573.21	0.16	15.6 ± 0.1
	3	116633.26			116664.05	30.79	116633.41	−0.14	17.5 ± 0.1
	4	116719.33			116740.39	21.06	116719.57	−0.25	15.0 ± 0.3
7	1	117383.61			117396.90	13.29	117383.64	−0.03	23.2 ± 0.3
	2	117308.57			117333.32	24.75			32.4 ± 0.1
	3	117349.63			117376.19	26.56			32.9 ± 0.3
	4	117418.16			117443.74	25.58			23.2 ± 0.4
8	1	117981.30			118018.40	37.10			49.2 ± 0.9
	2	118016.79			118049.78	32.99	118016.72	0.07	29.8 ± 1.4
	3	118072.24			118097.42	25.18			30.6 ± 0.8
	4	118142.45			118159.55	17.10			61.6 ± 1.6
9	1	-			118516.10		118461.17		
	2	118500.37			118539.77	39.40			25.4 ± 0.6
	3	118544.26			118574.71	30.45			45.9 ± 1.5
EF$^1\Sigma_g^+$									
31	3	116841.02			116863.48	22.46			103.4 ± 1.4
33	1	-			117563.91		117540.00		
	2	117574.66			117595.48	20.82	117574.32	0.34	66.6 ± 5.9
	3	117526.55			117540.43	13.88			49.6 ± 1.7
	4	117582.30			117600.69	18.39			73.0 ± 1.8
35	1	118160.72			118185.40	24.68			121.7 ± 6.5
	2	118177.13			118201.85	24.72			113.9 ± 3.3
	3	118201.88			118226.98	25.10			98.9 ± 0.4
36	1	118404.27			118420.27	16.00			150.4 ± 7.4
	2	118417.39			118433.66	16.27			146.4 ± 2.5
	3	118436.18			118453.01	16.83			144.3 ± 4.8
37	1	118582.75			118610.54	27.79			79.6 ± 13.6
I$^1\Pi_g^+$									
3	1	117292.73			117312.92	20.19			29.6 ± 2.5
	2	117456.37			117467.14	10.77	117456.35	0.02	31.7 ± 0.7
5	3	118611.88			118625.07	13.19			57.8 ± 1.9
I$^1\Pi_g^-$									
3	1	117344.34			117347.35	3.01			20.7 ± 0.1
	2	117409.91			117412.72	2.81	117409.96	−0.05	20.0 ± 0.1
	3	117508.42			117511.28	2.86	117508.65	−0.23	19.6 ± 0.6
J$^1\Delta_g^+$									
3	2	118109.00			118116.95	7.95			23.6 ± 0.1
	3	118230.25			118238.59	8.34			25.4 ± 0.5
	4	118388.39			118397.10	8.71			23.8 ± 1.1
J$^1\Delta_g^-$									
3	2	118108.73							25.2 ± 0.2

[a] Reference 14. [b] Ab initio I(including g−u symmetry breaking) minus this work. [c] Reference 6. [d] Ab initio II(not including g−u symmetry breaking) minus this work. [e] Reference 6. Assignments by Quadrelli, Dressler, and Wolniewicz with the aid of ab initio calculations. [f] This work minus values in exp column.

cm^{-1} as GK9(J = 2 and 3). The values of Δ, 39.38 and 30.45 cm^{-1} for J = 2 and 3, respectively, which are similar to those of GK8, justify our assignments. Quadrelli, Dressler, and Wolniewicz assigned an unidentified level at 118461.17 cm^{-1} in ref 12 to GK9 (J = 1).[6] The plots of term values vs $J(J + 1)$ for the relevant energy region are illustrated in Figure 3. The term values for the rovibronic levels of the B$^1\Sigma_u^+$ and B′$^1\Sigma_u^+$ states are reproduced from the transition frequencies tabulated in ref 12. Dabrowski and Herzberg pointed out that the B′$^1\Sigma_u^+$ (v = 7) state is heavily perturbed by a nearby $^1\Sigma_g^+$ state.[12] The present experiment confirms that the perturbing state is GK9: in fact, due to an accidental coincidence of GK9 and B′7 near J = 1, GK9 (J = 1) is shifted to the lower energy than extrapolated from J = 2 and 3. (4) Wolniewicz et al. assigned a level at 117540.00 cm^{-1} in ref 12 to EF33 (J = 1). The difference from the ab initio value, 23.91 cm^{-1}, is comparable to those for J = 2 ∼ 4, supporting their assignment. (5) The most likely candidate for the level at 118582.75 cm^{-1} reached from B10 (J_B = 2) is EF37 (J = 1) because (i) EF37 and I5 are the only two nonadiabatic states calculated to be located above 118600 cm^{-1} and (ii) the value of Δ, 27.79 cm^{-1}, is comparable with those of EF33 ∼ EF36.[6] Another level at 118611.88 cm^{-1} also excited from B10 (J_B = 2) is tentatively assigned to I5 (J = 3). The EF37 (J = 3) level is not tabulated in ref 6. The value of Δ, 13.19 cm^{-1}, is somewhat smaller than EF37. A similar tendency was reported in H_2 near the second dissociation limit.[16] Weak emission intensities prevented us from further investigations near the second dissociation limit (H(2s) + D(1s)) at 118664.78 ± 0.07 cm^{-1}.[17]

Absolute accuracy of the term values in the current experiment is largely dependent upon the uncertainty involved in the B$^1\Sigma_u^+$ term energies reported by Dabrowski and Herzberg.[12]

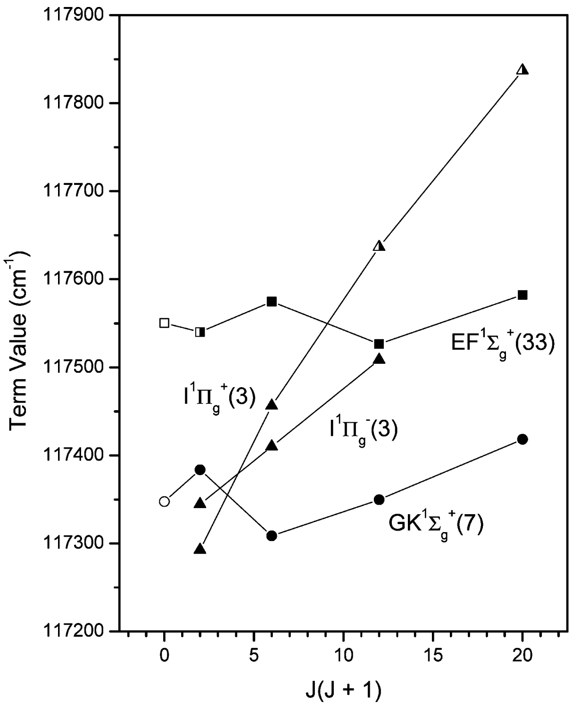

Figure 2. Rovibronic term values vs $J(J + 1)$ for the $EF^1\Sigma_g^+$ ($v = 33$), $GK^1\Sigma_g^+$ ($v = 7$), and $I^1\Pi_g$ ($v = 3$) states. ●, ▲, ■, this work; ○, □, theoretical values from ref 6; ◭, ◨, experimental values listed in ref 6.

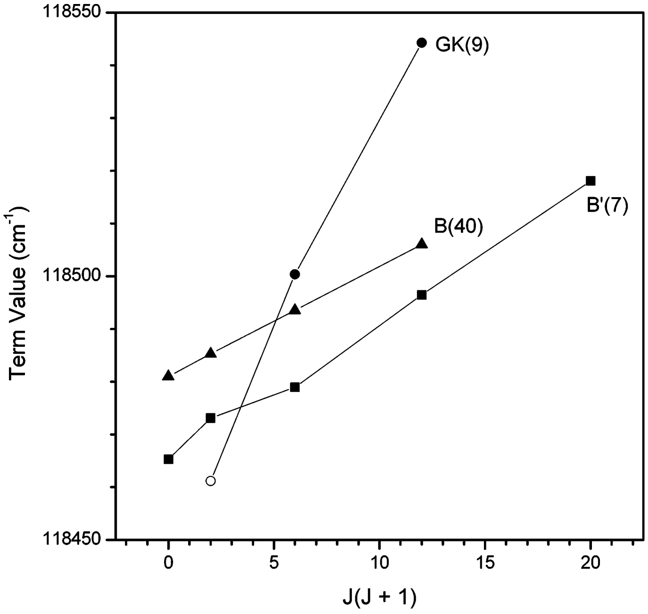

Figure 3. Rovibronic term values vs $J(J + 1)$ for the $GK^1\Sigma_g^+$ ($v = 9$), $B^1\Sigma_u^+$ ($v = 40$), and $B'^1\Sigma_u^+$ ($v = 7$) states. ●, this work; ○, experimental value listed in ref 6; ▲, ■, ref 12. The $GK^1\Sigma_g^+$ ($v = 9$, $J = 0$) level has not been identified experimentally.

Ubachs et al. obtained sub-Doppler excitation spectra of HD in the range 92∼98 nm with an estimated error of 0.035 cm^{-1}.[13] The differences of VUV transition frequencies (denoted by Δ_{od} in Table 1 in ref 13) between these two data sets are -0.21 ± 0.19, -0.19 ± 0.19, and -0.17 ± 0.38 cm^{-1} for B−X (14, 0), (13, 0) and (12, 0) bands, respectively; term values by Dabrowski and Herzberg are systematically lower by ∼0.2 cm^{-1} than those by Ubachs et al. The calibration of the vibrational levels ($v = 6$, 7, and 10) employed in the present study is not feasible; it should be kept in mind that the term values listed in Table 1 may involve a similar degree of uncertainty. In fact, our energies for GK6 reveal a maximum disagreement of 0.25 cm^{-1} with those of Dabrowski and Herzberg.

Wavenumbers of the probe transitions observed in this experiment are summarized in Table 2. The differences of term values between P and R branch excitation reach ∼0.14 cm^{-1} on average, which is three times larger than that (≤ 0.05 cm^{-1}) in the case of the EF state of D_2.[5]

Fluorescence Lifetimes. The fluorescence lifetimes could be determined for all the rovibronic levels identified. To obtain smooth decay curves, the time profiles recorded without sample gases were subtracted from those with HD molecules. The net profiles of fluorescence emission exhibit single exponential decays. The dependence of decay rates on the stagnation pressure has been checked at twelve different pressures between 0.2 and 1.5 atm. The standard deviation increases as the stagnation pressure decreases due to a loss of total fluorescence intensities. The mean values are not dependent upon the stagnation pressure within ± 5% error, which verifies that the fluorescence lifetimes have been measured under collision-free conditions. The lifetimes listed in Table 1 are averaged over at least three measurements and the error represents one standard deviation at the stagnation pressure of 1.0 atm. Quadrelli, Dressler, and Wolniewicz[6] reported the radiative lifetimes (hereafter denoted by τ_{calc}) of the nonadiabatically coupled upper gerade levels of HD. Unfortunately, because their calculation is restricted to $J = 0$, direct comparison of our experimental lifetimes (hereafter denoted by τ_{exp}) is not realized. In the following section, we attempt to discuss variations of fluorescence lifetimes in terms of the J-dependent nonadiabatic wave functions.[6]

The $EF^1\Sigma_g^+$ State

EF33. As mentioned in the previous section, EF33 crosses I3 near $J = 3$, resulting in mixture of the adiabatic ψ(I3) function in Ψ(EF33):

$$\Psi(\mathrm{EF33}, J = 0) = 0.898\psi(\mathrm{EF33}) - 0.412\psi(\mathrm{GK7}) + 0.057\psi(\mathrm{I3}) \quad \tau_{calc} = 155 \text{ ns}$$

$$\Psi(\mathrm{EF33}, J = 1) = 0.876\psi(\mathrm{EF33}) - 0.442\psi(\mathrm{GK7}) + 0.114\psi(\mathrm{I3})$$

$$\Psi(\mathrm{EF33}, J = 2) = 0.798\psi(\mathrm{EF33}) - 0.509\psi(\mathrm{GK7}) + 0.266\psi(\mathrm{I3}) \quad \tau_{exp} = 67 \text{ ns}$$

$$\Psi(\mathrm{EF33}, J = 3) = 0.745\psi(\mathrm{EF33}) - 0.582\psi(\mathrm{I3}) + 0.168\psi(\mathrm{GK7}) \quad \tau_{exp} = 50 \text{ ns}$$

$$\Psi(\mathrm{EF33}, J = 4) = 0.867\psi(\mathrm{EF33}) - 0.432\psi(\mathrm{I3}) + 0.115\psi(\mathrm{EF32}) \quad \tau_{exp} = 73 \text{ ns.}$$

For $J = 0$ the ab initio lifetime[6] is given, while for $J > 0$ the current experimental results (rounded to the nearest ns) are given (see Table 1 for actual values with uncertainties). Ψ(I3) involves a fair amount of EF and GK characters accordingly:

$$\Psi(\mathrm{I3}, J = 1) = 0.769\psi(\mathrm{I3}) + 0.525\psi(\mathrm{GK7}) + 0.265\psi(\mathrm{EF32}) \quad \tau_{exp} = 30 \text{ ns}$$

$$\Psi(\mathrm{I3}, J = 2) = 0.677\psi(\mathrm{I3}) - 0.523\psi(\mathrm{EF33}) - 0.414\psi(\mathrm{GK7}) \quad \tau_{exp} = 32 \text{ ns}$$

The fluorescence lifetimes of the $I^1\Pi_g^-$ state, which does not participate in the nonadiabatic coupling, were measured to be ∼20 ns in the current experiment. The inclusion of the short-lived ψ(I3) wave function in Ψ(EF33) reduces the lifetime of

TABLE 2: Wavenumbers (cm^{-1}) of the Probe Transitions

H(0)	←	B(6)		H(1)	←	B(7)		H(2)	←	B(10)	
$J = 1$	←	$J = 0$	16261.03	$J = 1$	←	$J = 0$	17237.44	$J = 1$	←	$J = 0$	16235.63
2	←	1	16321.34	2	←	1	17297.57	2	←	1	16291.54
1	←	2	16190.77	3	←	2	17376.51	1	←	2	16173.82
				1	←	2	17169.38				
GK(6)	←	B(10)		GK(7)	←	B(10)		GK(8)	←	B(10)	
$J = 1$	←	$J = 0$	15826.98	$J = 1$	←	$J = 0$	16672.42	$J = 1$	←	$J = 0$	17270.08
2	←	1	15841.32	2	←	1	16576.54	2	←	1	17284.93
3	←	2	15860.15	3	←	2	16576.52	3	←	2	17299.13
4	←	3	15884.70	4	←	3	16583.53	4	←	3	17307.82
1	←	2	15765.11	1	←	2	16610.53	1	←	2	17208.24
								2	←	3	17181.99
GK(9)	←	B(10)									
$J = 2$	←	$J = 1$	17768.34								
3	←	2	17771.15								
EF(31)	←	B(10)		EF(33)	←	B(10)		EF(35)	←	B(10)	
$J = 3$	←	$J = 2$	16067.91	$J = 2$	←	$J = 1$	16842.73	$J = 1$	←	$J = 0$	17449.50
				3	←	2	16753.44	2	←	1	17445.10
				4	←	3	16747.67	3	←	2	17428.77
				2	←	3	16739.93	1	←	2	17387.66
EF(36)	←	B(10)		EF(37)	←	B(10)					
$J = 2$	←	$J = 1$	17685.36	$J = 1$	←	$J = 2$	17809.64				
3	←	2	17663.07								
1	←	2	17631.16								
$I^1\Pi_g^+(3)$	←	B(10)		$I^1\Pi_g^+(5)$	←	B(10)		$I^1\Pi_g^-(3)$	←	B(10)	
$J = 1$	←	$J = 0$	16581.57	$J = 3$	←	$J = 2$	17838.77	$J = 1$	←	$J = 1$	16612.31
2	←	1	16724.45					2	←	2	16636.80
2	←	3	16621.63					3	←	3	16673.79
$J^1\Delta_g^+(3)$	←	B(10)		$J^1\Delta_g^-(3)$	←	B(10)					
$J = 2$	←	$J = 1$	17376.97	$J = 2$	←	$J = 2$	17335.62				
3	←	2	17457.14								
4	←	3	17553.76								

EF33. In fact, $\Psi(\mathrm{EF33}, J = 3)$, which is contributed to most heavily from $\psi(\mathrm{I3})$, exhibits a lifetime shorter than $J = 2$ and 4. On the other hand, mixing of relatively long-lived adiabatic wave functions such as $\psi(\mathrm{EF32})$ and $\psi(\mathrm{EF33})$ would be partially responsible for the slightly longer lifetimes for $I^1\Pi_g^+(v = 3, J = 1$ and 2) than the $^1\Pi_g^-$ component.

EF35. EF35 crosses J3 near $J = 3$, giving rise to higher probability of finding the adiabatic $\psi(\mathrm{J3})$ wave function in $\Psi(\mathrm{EF35}, J = 3)$:

$$\Psi(\mathrm{EF35}, J = 0) = 0.931\psi(\mathrm{EF35}) + 0.318\psi(\mathrm{GK8}) + 0.102\psi(\mathrm{H3}) \quad \tau_{\mathrm{calc}} = 205 \text{ ns}$$

$$\Psi(\mathrm{EF35}, J = 1) = 0.927\psi(\mathrm{EF35}) + 0.329\psi(\mathrm{GK8}) + 0.100\psi(\mathrm{H3}) \quad \tau_{\mathrm{exp}} = 122 \text{ ns}$$

$$\Psi(\mathrm{EF35}, J = 2) = 0.916\psi(\mathrm{EF35}) + 0.355\psi(\mathrm{GK8}) + 0.098\psi(\mathrm{H3}) \quad \tau_{\mathrm{exp}} = 114 \text{ ns}$$

$$\Psi(\mathrm{EF35}, J = 3) = 0.869\psi(\mathrm{EF35}) + 0.392\psi(\mathrm{GK8}) + 0.243\psi(\mathrm{J3}) \quad \tau_{\mathrm{exp}} = 99 \text{ ns}$$

The radiative lifetime of the $J^1\Delta_g$ state was measured to be ~25 ns. The inclusion of this short-lived electronic state may cause reduction of the lifetime for $J = 3$. τ_{exp} is considerably shorter than τ_{calc} (205 ns) as listed in Table 1.

EF36 and EF37. It is noteworthy that τ_{calc} for EF36 and EF37 are 717 and 241 ns, respectively,[6] which are substantially longer than τ_{exp}. A constant lifetime around 150 ns for EF36 is in accordance with the fact that this state is not heavily perturbed. The overall reduction of fluorescence lifetimes in the $EF^1\Sigma_g^+$ state is presumably attributed to the coupling with the $B^1\Sigma_u^+$ state. The g−u symmetry breaking opens the emission channel from EF down to the ground state, which is strictly forbidden for the homonuclear hydrogen isotopomers. This is consistent with the observation of the EF−X (v, 0) absorption bands over a wide VUV spectral range.[12]

The $GK^1\Sigma_g^+$ State

GK6. According to the nonadiabatic wave function for GK6:

$$\Psi(\mathrm{GK6}, J = 0) = 0.778\psi(\mathrm{GK6}) - 0.430\psi(\mathrm{EF30}) - 0.363\psi(\mathrm{EF31}) \quad \tau_{\mathrm{calc}} = 53.2 \text{ ns}$$

$$\Psi(\mathrm{GK6}, J = 1) = 0.775\psi(\mathrm{GK6}) - 0.418\psi(\mathrm{EF30}) - 0.378\psi(\mathrm{EF31}) \quad \tau_{\mathrm{exp}} = 32 \text{ ns}$$

$$\Psi(\mathrm{GK6}, J = 2) = 0.768\psi(\mathrm{GK6}) - 0.401\psi(\mathrm{EF31}) - 0.394\psi(\mathrm{EF30}) \quad \tau_{\mathrm{exp}} = 16 \text{ ns}$$

$$\Psi(\mathrm{GK6}, J = 3) = 0.745\psi(\mathrm{GK6}) - 0.461\psi(\mathrm{EF31}) - 0.356\psi(\mathrm{EF30}) \quad \tau_{\mathrm{exp}} = 18 \text{ ns}$$

$$\Psi(\mathrm{GK6}, J = 4) = 0.638\psi(\mathrm{GK6}) - 0.525\psi\ (\mathrm{EF31}) - 0.310\psi(\mathrm{J3}) \quad \tau_{\mathrm{exp}} = 15 \text{ ns}$$

No significant variation of lifetimes for $J = 1 \sim 3$ is anticipated; however, a significant difference between the $J = 1$ and the $J = 2$ lifetimes is clearly seen experimentally. This is not explainable within the framework of the nonadiabatic coupling among the gerade states. As plotted in Figure 4, B34 crosses GK6 between $J = 2$ and $J = 3$. We infer that the strong coupling near the crossing region accelerates the radiative decay from GK6 ($J = 2$ and 3) down to the ground state. The shorter lifetime for $J = 4$ may be either due to the mixing of the J3 state or the energy coincidence with the B′4 ($J = 4$) level or a combination of both. Judging from the similar mixing coefficients of $J = 0$ and $J = 1$, the lifetime for $J = 0$ should not be different from that of $J = 1$: τ_{calc} (53.2 ns) overestimates τ_{exp}(31.8 ns at $J = 1$) by 40%.

GK7. This state is heavily mixed with I3 for $J > 0$. The lifetimes of GK7 are measured to be ~30 ns for $J = 1$~4, which

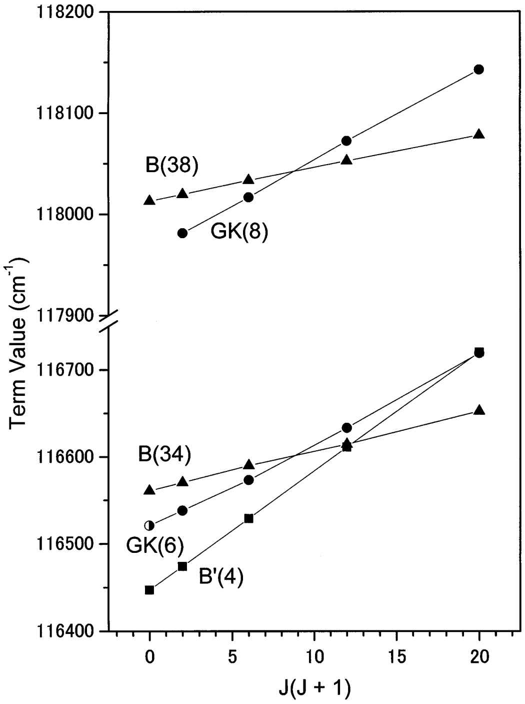

Figure 4. Rovibronic term values vs $J(J + 1)$ in the relevant energy range to the crossing of the $GK^1\Sigma_g^+$ and the $B^1\Sigma_u^+$ states. ●, this work; ◑, experimental value listed in ref 6; ▲, ■, ref 12. The $GK^1\Sigma_g^+$ ($v = 8$, $J = 0$) level has not been identified experimentally.

is substantially shorter than $\tau_{\rm calc}$ (60.5 ns). This would be explainable as the interaction with the short-lived I3.

GK8. This state is mixed mainly with EF 34 and EF35. The mixing coefficients of these two adiabatic states are not sensitively dependent on J. The shorter lifetimes for $J = 2$ and 3 might be ascribed to the perturbation of B38 as plotted in Figure 4.

GK9. There is no large difference in the nonadiabatic wave functions between $J = 2$ and 3. The shorter lifetime for $J = 2$ accords with the accidental coincidence of B40 ($J = 2$) as shown in Figure 3.

The $H^1\Sigma_g^+$ State

H0. With reference to the nonadiabatic wave functions of H0 ($J = 0\sim2$):

$$\Psi(\mathrm{H0}, J = 0) = 0.971\psi(\mathrm{H0}) - 0.197\psi(\mathrm{GK2}) + 0.111\psi(\mathrm{EF23}) \quad \tau_{\rm calc} = 106\ \mathrm{ns}$$

$$\Psi(\mathrm{H0}, J = 1) = 0.960\psi(\mathrm{H0}) - 0.236\psi(\mathrm{GK2}) + 0.117\psi(\mathrm{EF23}) \quad \tau_{\rm exp} = 108\ \mathrm{ns}$$

$$\Psi(\mathrm{H0}, J = 2) = 0.906\psi(\mathrm{H0}) - 0.367\psi(\mathrm{GK2}) + 0.154\psi(\mathrm{EF23}) \quad \tau_{\rm exp} = 96\ \mathrm{ns}$$

the lifetime for $J = 1$ should be close to $\tau_{\rm calc}$. $\tau_{\rm exp}(J = 1)$, 108.2 ns, is comparable with $\tau_{\rm calc}$, showing a perfect agreement between theory and experiment. On the other hand, the contribution of ψ(H0) is considerably reduced in $J = 2$. The somewhat shorter lifetime for $J = 2$, 95.8 ns, is in accordance with the greater contribution from the short-lived GK state.

H1 and H2. The contribution of the adiabatic ψ(H1) wave function is little dependent on J as shown below:

$$\Psi(\mathrm{H1}, J = 0) = 0.969\psi(\mathrm{H1}) - 0.313\psi(\mathrm{GK5}) + 0.171\psi(\mathrm{EF27}) \quad \tau_{\rm calc} = 71.9\ \mathrm{ns}$$

$$\Psi(\mathrm{H1}, J = 1) = 0.973\psi(\mathrm{H1}) - 0.201\psi(\mathrm{GK4}) + 0.064\psi(\mathrm{EF27}) \quad \tau_{\rm exp} = 133\ \mathrm{ns}$$

$$\Psi(\mathrm{H1}, J = 2) = 0.978\psi(\mathrm{H1}) - 0.174\psi(\mathrm{GK4}) + 0.059\psi(\mathrm{GK5}) \quad \tau_{\rm exp} = 121\ \mathrm{ns}$$

$$\Psi(\mathrm{H1}, J = 3) = 0.980\psi(\mathrm{H1}) - 0.145\psi(\mathrm{GK4}) + 0.182\psi(\mathrm{EF28}) \quad \tau_{\rm exp} = 123\ \mathrm{ns}$$

$\tau_{\rm exp}$ ranging from 121 to 133 ns exhibits no strong dependence on J. It should be noted that $\tau_{\rm exp}$ for $J = 1$ and 2 are much longer than $\tau_{\rm calc}$. A similar disagreement is noticed for H2: $\tau_{\rm exp}$ are measured to be 84.3 and 88.9 ns for $J = 1$ and 2, respectively, which are twice as long as $\tau_{\rm calc}$ (41.8 ns) for $J = 0$.

The longer $\tau_{\rm exp}$ than $\tau_{\rm calc}$ for the H state is an opposite tendency to the GK and EF states. No sign of enhancement of the radiative decay rate implies the weak coupling between H and the ungerade manifolds. The accidental crossing of B31 with H1 between $J = 2$ and 3 as illustrated in Figure 5 gives no noticeable influence on $\tau_{\rm exp}$, showing the negligible coupling between H and B. As pointed out in the previous section, an inclusion of the interaction of H with B″ makes the agreement of term values between calculation and experiment even worse for H0.[14] The better agreement for $v = 1$ and 2 suggests the influence of g−u coupling, although the interaction is not strong enough to be reflected on the lifetimes. This is in sharp contrast to the case of $\bar{\mathrm{B}}$ and $\bar{\mathrm{H}}$ outer-well states in which a complete breakdown of g−u symmetry over a wide range of v and J quantum numbers causes substantial reduction of lifetimes compared with H_2 and D_2.[18,19] The complete mixing between $\bar{\mathrm{B}}$ and $\bar{\mathrm{H}}$ states originates from the nearby coincident shapes of their potential energy functions. The adiabatic potentials of H and B″ are of similar appearance but the H state has a much lower minimum than B″: the B″0 ($J = 0$) level is calculated to be located at 117029.82 cm^{-1}, which is close to H2 and ~3900 cm^{-1} higher than H0.[14] This large energy gap may weaken the coupling between H and B″.

The $I^1\Pi_g$, and $J^1\Delta_g$ States. There are no theoretical lifetimes available for the I and J states of HD. The lifetimes of I3 and J3 are comparable with those of I0 and J0 of H_2, ~20 and ~25 ns, respectively.[9] No appreciable lifetime shortening by the g−u mixing was found, although several vibronic levels belonging to the I state were observed in the VUV absorption spectra.[12]

In summary, we report the results of a systematic survey on the term values and fluorescence lifetimes of the EF, GK, $H^1\Sigma_g^+$, $I^1\Pi_g$, and $J^1\Delta_g$ states of HD molecules for the first time. Term energies of 42 rovibronic levels have been determined and identified unambiguously with the aid of ab initio calculations. The theoretical term values[14] for the $H^1\Sigma_g^+$($v = 1$ and 2) states are in better agreement with the experimental ones when the symmetry breaking term between the $\mathrm{H}\bar{\mathrm{H}}^1\Sigma_g^+$ and $\mathrm{B}''\bar{\mathrm{B}}^1\Sigma_u^+$ states is accounted for. In contrast to this, the agreement becomes worse for the $H^1\Sigma_g^+$($v = 0$) state. Further ab initio work needs to be done to clarify this issue. The fluorescence lifetimes have been measured under collision-free conditions for all the identified levels. The experimental lifetimes of the $H^1\Sigma_g^+$($v = 0$) state are in good agreement with theory, whereas those of $H^1\Sigma_g^+$($v = 1$ and 2) are double the calculated one. On the other hand, the measured lifetimes for the EF and $GK^1\Sigma_g^+$ states were significantly shorter than calculations. The overall

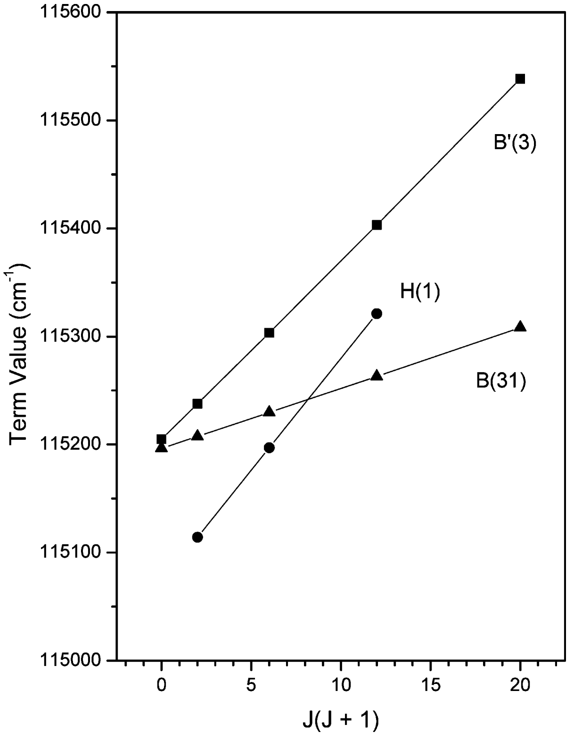

Figure 5. Rovibronic term values vs $J(J + 1)$ for the $H^1\Sigma_g^+$ ($v = 1$), $B^1\Sigma_u^+$ ($v = 31$), and $B'^1\Sigma_u^+$ ($v = 3$) states. ●, this work; ▲, ■, ref 12. The $H^1\Sigma_g^+$ ($v = 1$, $J = 0$) level has not been identified experimentally.

reduction of fluorescence lifetimes in the $EF^1\Sigma_g^+$ state accords with appearance of the $EF^1\Sigma_g^+-X^1\Sigma_g^+$ (v, 0) bands induced mainly by the $EF^1\Sigma_g^+-B^1\Sigma_u^+$ mixing. The rotational dependence of lifetimes for the $EF^1\Sigma_g^+$ state, where no apparent perturbation from the nearby ungerade vibronic states is present, is well interpreted in terms of the nonadiabatic coupling among gerade states. The lifetime shortening in the $GK^1\Sigma_g^+$ state occurs at the specific rovibronic levels near the crossing region with the $B^1\Sigma_u^+$ state, revealing the local coupling between $GK^1\Sigma_g^+$ and $B^1\Sigma_u^+$ manifolds. Our data provide a test ground for future theoretical calculations.

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