New Experimental Insight into the Ground State Potential Surface of Triatomic Hydrogen

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Continuous UV spectra emitted by the triatomic hydrogen molecules H_3, D_3, H_2D, and D_2H have been measured between 200 and 400 nm and exhibit two pronounced maxima. The two maxima in the spectra are interpreted as arising from the decay to both sheets of the ground state potential surface which form a conical intersection at the point of equilateral symmetry. This is confirmed by a detailed computer simulation. The fact that the H_3 ground state potential surface has two sheets is, to our knowledge, observed here experimentally for the first time.

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Even though the existence of H_3, the simplest neutral, polyatomic molecule, was predicted already early in this century, e.g., [1], it was observed spectroscopically only in 1979 [2]. Since Herzberg first investigated the spectra of H_3 and D_3 using the visible and infrared light emitted by a hollow cathode discharge, e.g., [3], this fundamental molecule has attracted great interest among spectroscopists and astrophysicists. Some of the important results inferred from these spectra were the dissociative character of the ground state and the Rydberg character of the bound excited states. Deeper insight into the structure of H_3 and in particular of the ground state of this molecule is desirable for a better understanding of the most elementary chemical reaction between H and H_2, since the exchange of hydrogen atoms proceeds via the ground state potential surface of triatomic hydrogen [4]. Not long ago, Collings *et al.* made an effort to investigate the transition state (HD_2^{++}) of this prototypal reaction by excitation of the scattering system ($H+D_2$) using UV light [5]. Recently, Nieh and Valentini [6] seem to have observed vibrations of the linear H_3 reaction complex, referred to as Feshbach resonances.

Mass selected, fast molecular beams made it possible to explore the spectra of the isotopically mixed molecules H_2D and D_2H [7] as well as to measure lifetimes of all isotopomers [8]. In further beam experiments, Rydberg states close to the ionization limit were studied by laser excitation of the only metastable state, $2p\,^2A_2''N=K=0$ [9,10]. In 1985, Leventhal and co-workers [11] reported the observation of an UV continuum of D_3 ranging from 190 to 280 nm. In the present contribution we report UV spectra of all four isotopomers containing H and D, which, for the case of D_3, deviate appreciably from Leventhal's observation. This deviation is interpreted as arising from the structure of the ground state potential surface of triatomic hydrogen which, according to theory, consists of two sheets forming a conical intersection [12]. Other polyatomic Jahn-Teller systems, e.g., Na_3 or Li_3, should also possess such a double-sheeted ground state, and, to our knowledge, this is the first time the upper sheet of the ground state surface of a triatomic Jahn-Teller system has been experimentally identified.

A detailed description of our experimental setup has been given elsewhere [13]. To summarize, the ions corresponding to the investigated molecule, e.g., H_3^+, were generated in a duoplasmatron from which an ion beam of about 50 μA was extracted and accelerated to 15 keV, then mass selected in a sector magnetic field and neutralized while crossing a cesium atomic beam. In the present experiment continuous spectra were observed in the region from 200 to 400 nm with a resolution of about 1.0 nm. The radiation emitted by the neutral molecular beam was focused onto the entrace slit of a monochromator and detected by a photomultiplier. The spectra are given in Fig. 1; all the sharp peaks are lines from residual cesium. The intensities have been corrected for the detection sensitivity of the apparatus using the known intensity distributions of the spectra of a deuterium lamp and a tungsten band lamp. In addition the cesium lines were removed by a numerical method and the spectra were smoothed, resulting in an effective resolution of 10 nm. The smoothed spectra are represented in Fig. 1 as thick solid lines.

Each of the graphs in Fig. 1 additionally displays lifetimes measured at different wavelengths. The lifetimes were obtained by setting the monochromator to the wavelength given on the abscissa and moving the cesium oven step by step along the molecular beam, away from the point where the luminescence was collected while measuring the decay of the light intensity. The lifetimes were obtained by dividing the decay length of the count rate by the speed of the molecules. As shown in Fig. 1, the variation of the lifetime with wavelength for a certain isotopomer is small and therefore one mean value can be reported (Table I). This mean value decreases from 9.9 ns for D_3 to 3.9 ns for H_3 in this isotopomer series. Similar lifetimes have been measured in the visible spectra and were explained by increasing predissociation of the $n=3$ levels in the series from D_3 to H_3 [8,9].

The spectra in Figs. 1(a), 1(b), and 1(d) clearly show two distinct maxima about $\Delta E=9600$ cm^{-1} apart. An energy splitting of this magnitude between excited states cannot be found in published energy level schemes of H_3, and we have to turn to the ground state in order to ex-

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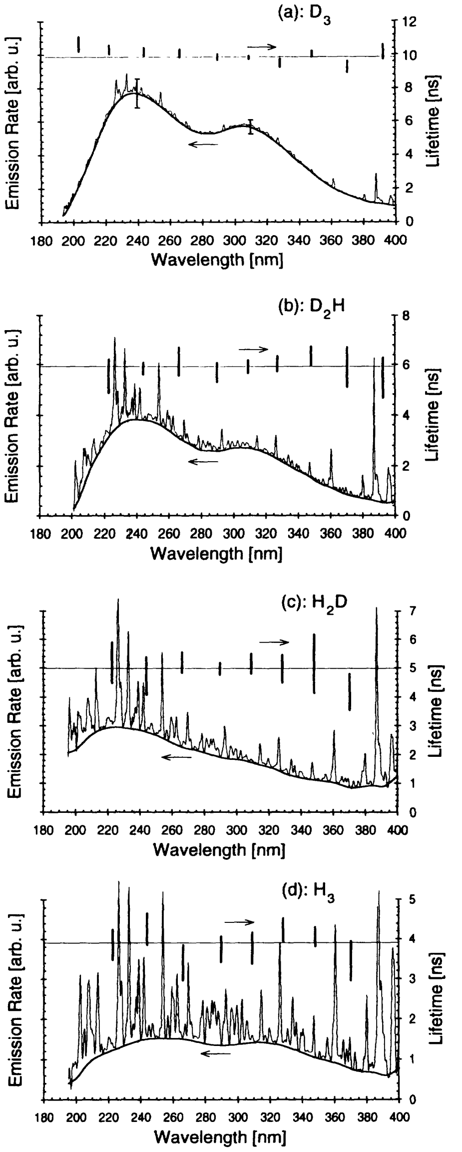

FIG. 1. The UV spectra of the different isotopomers of triatomic hydrogen, corrected for the sensitivity of the detection system (left ordinate). The narrow peaks are cesium lines. The thick solid lines depict the spectra after removal of the cesium lines. The spectra of H_3, D_3, and D_2H show a characteristic minimum (not present in the spectrum of H_2D, since D_2 is in this case also transmitted by the mass selector and so the spectra of both molecules are superimposed). The error bars on the spectrum in (a) indicate the total uncertainty originating from correction for the detection sensitivity, count number statistics, repeatability, and the removal of the cesium background. In the upper part, the figures show lifetimes (right ordinate) measured at different wavelengths including error bars.

TABLE I. Mean lifetimes for the different isotopomers. Given are weighted mean values of lifetimes measured at different wavelengths as shown in Fig. 1.

D_3	D_2H	H_2D	H_3
9.9(4) ns	5.9(4) ns	5.0(5) ns	3.9(5) ns

plain the appearance of these two maxima. A closer look at the ground state hypersurface reveals two sheets forming a conical intersection in the q_1, q_2 subspace. The orthogonal coordinates q_0, q_1, and q_2 for the normal vibrations are introduced here following Porter, Stevens, and Karplus [14]. The symmetrical stretch of the H_3 molecule is described by q_0, while q_1 and q_2 describe the unsymmetrical vibrational motions, which are energetically degenerate. The point of intersection corresponds to the equilateral D_{3h} symmetry. The lower sheet represents a dissociating potential while the upper sheet gives rise to the existence of quasibound vibrational states whose short lifetime is due to their coupling to the lower, dissociating sheet. H_3 in the upper $n=3$ levels, where the molecule is close to D_{3h} geometry, can decay to vibrational states supported by the upper and lower sheets. A rough estimate of the energy splitting in the spectrum that follows from this ground state surface model leads to a result close to the observed splitting. For a more detailed interpretation of the measured D_3 spectrum, computer simulations were performed using few parameters, principally the cone slope of the conical intersection and the energy separation between the $n=3$ levels and the $2p\,^2E'$ state. The simulated spectrum was then fitted to the experimental spectrum. The parameters determined in this way are compared with values derived from *ab initio* calculations of different authors. In the following the calculations are outlined, and a more detailed description will be given elsewhere. Because of the degeneracy of the normal modes associated with q_1 and q_2 a transformation to coordinates q_0, q, and φ is performed,

$$q_0=q_0,\quad q_1\equiv q\sin\varphi,\quad q_2\equiv q\cos\varphi\,; \tag{1}$$

q describes the deviation from the equilateral D_{3h} symmetry, and φ the angle in the q_1, q_2 subspace as illustrated in Fig. 2. Following King and Morokuma [15] the potential surface can be expanded near D_{3h} symmetry:

$$V_{\pm}(q_0,q,\varphi)=D_1(q_0)\pm D_4(q_0)q+[D_2(q_0)\pm D_5(q_0)\cos 3\varphi]q^2+\cdots\,. \tag{2}$$

The states correlating to the degenerate E states of D_{3h} symmetry, e.g., the ground state, exhibit a conical intersection: For $q\neq 0$ the degeneracy is lifted, and the "+" sign describes the upper and the "−" sign the lower sheet of the potential surface, both shaped as cones to first order in q.

The observed UV radiation cannot originate from the $2s\,^2A_1'$ or the rotating $2p\,^2A_2''$ state, since these states are strongly affected by predissociation. The nonrotating $2p\,^2A_2''$ $N=K=0$ state is metastable and does not contribute to the observed spectra emitted by the fast molecular beam; the radiation therefore has to be emitted from

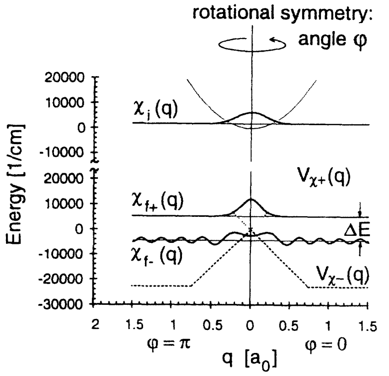

FIG. 2. Section through potential surfaces in the direction of the degenerate vibration q, for $\varphi=0$ and $\varphi=\pi$. In the upper part, the emitting state, i.e., the binding potential and the wave function $\chi_i(q)$ are drawn. The lower part shows the conical intersection corresponding to $2p\,^2E'$, with its binding potential $V_\chi+(q)$ (dotted curve) and repulsive potential $V_\chi-(q)$ (broken line). Corresponding wave functions $\chi_f+(q)$ and $\chi_f-(q)$ are also shown (thick solid lines). Also indicated is the energy gap ΔE, which is responsible for the two maxima in the continuous spectra.

states with $n \geq 3$. For these states, King and Morokuma have estimated various coefficients in Eq. (2) and it is seen that for the initial, emitting states, the D_1 and D_2 terms are dominant, and the other terms may be neglected. The potential surface V_i for the initial states is well approximated by a two-dimensional (the variables being q_0 and q) harmonic potential containing four parameters, namely, the energy of the potential minimum, the equilibrium separation of the nuclei in equilateral symmetry, and the frequencies of the symmetric and degenerate vibrations, respectively. These found parameters have been experimentally determined for the relevant Rydberg states or can be derived from experimental results, e.g., [3,4,9-11].

In view of the wavelength range of the UV emission it is clear that the transitions responsible for the continuous emission must terminate on the dissociative ground state. Therefore we now turn to the potential surface with the conical intersection correlated to $2p\,^2E'$ in D_{3h} geometry as the final state of the transition. The dominant term containing a dependence on q in Eq. (2) is $\pm D_4 q$, giving rise to the conical intersection (Fig. 2). Again, the terms dependent on φ are small, and the dependence of D_4 on q_0 and higher order terms is neglected. This results in a potential V_f for the final state containing one term linearly dependent on q and a second term representing the q_0 dependent part. For the second term, the D_{3h} potential curve was used as given by Petsalakis, Theodorakopoulos, and Wright [16]. Its energy separation from the upper bound states was defined to satisfy $V_u(q_0, q=0) - D_1(q_0) = 2.02$ eV for the upper state $u = 2s\,^2A_1'$ and $q_0 = 1.64a_0$, and a deviation ΔV from 2.02 eV was introduced as a fit parameter.

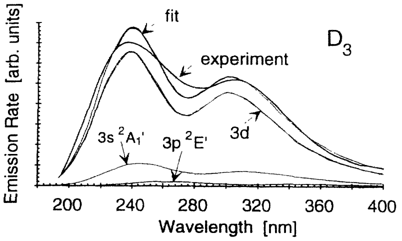

FIG. 3. The simulated UV spectrum of D_3 fitted to the experimental curve and contributions of transitions from the levels indicated to the conical intersection corresponding to $2p\,^2E'$.

In order to obtain the transition moments and to derive the spectra emitted during the transition from the initial to the final states, the vibrational wave functions have to be calculated using the Schrödinger equation. The vibrational wave functions are separable due to the form of the potentials V_i and V_f, the variables being q_0, q, and φ. From the visible spectra it is known that vibrational excitation is small [8,9]; therefore only the vibrational ground state (which is independent of φ) of the initial electronic state is considered. A nonzero overlap integral of the initial wave functions with the vibrational wave functions of the ground state requires the latter to be independent of φ as well. Therefore, vibrational wave functions solely dependent on q_0 and q were used.

Finally, to calculate the spectra, the dipole transition rate R was calculated. Since no detailed information is available on the electronic dipole moment, it was expanded into a product of two first order factors in q_0 and q, which resulted in two additional fit parameters. This approach neglected effects of the geometric phase [17].

For each electronic transition starting from the different upper electronic states, the spectral contribution was obtained by summing R over transitions to all vibrational states of both sheets of the conical intersection. The discrete vibrational states of the upper sheet decay very rapidly due to the nonadiabatic coupling to the lower sheet; i.e., they are quasibound. For all those states, a common lifetime τ was assumed, short enough to cause an emission continuum rather than a discrete spectrum. Finally, spectral contributions from the $3d$, $3s\,^2A_1'$, and $3p\,^2E'$ levels were combined. The transitions from $3p\,^2A_2''$ are forbidden in D_{3h} symmetry and levels with $n \geq 4$ are weakly populated as is known from observation of the visible spectra [8,9]. This choice of emitting levels is also supported by the good agreement of the lifetimes measured for the UV emitting states and the lifetimes for these states previously measured in the visible spectra [8,9]. To reduce the number of fit parameters, the emission intensity ratios were computed using estimated charge transfer cross sections [18] and electronic transition matrix elements [16]. The simulated spectrum was fitted to the experimental spectrum with fit parameters ΔV, D_4, τ, and two more parameters to account for the variation of the electric dipole moment with q_0 and q, re-

TABLE II. Parameters as they result from the fit of the simulated to the experimental D_3 spectrum.

D_4	ΔV	τ
$30\,346 \pm 710\ \mathrm{cm}^{-1}/a_0$	$-80 \pm 80\ \mathrm{cm}^{-1}$	2 fs

spectively. The fact that the experimental spectrum did not show any vibrational structure was taken into account in the simulation of the UV continuum by choosing τ to be only 2 fs. The fit of the D_3 spectrum is shown in Fig. 3, and the resulting fit parameters are given in Table II. Figure 4 shows our result for the slope D_4 as a function of the equilibrium distance q_0 in the D_3 triangle. It is in good agreement with theoretically obtained values taken from the work of different authors: Porter, Stevens, and Karplus [14], King and Morokuma [15], Petsalakis, Theodorakopoulos, and Wright [16], and Varandas [19].

Multiplying the width $0.3a_0$ of the initial vibrational wave function $\chi_i(q)$ (Fig. 2) by the cone slope D_4 of Table II gives a rough estimate of the separation of the emission maxima for D_3 which agrees well with $\Delta E = 9600\ \mathrm{cm}^{-1}$ as found in the experimental spectrum. Also, our value for ΔV (i.e., the deviation from the value obtained from *ab initio* calculations of the energy separation between excited states and the ground state) proves to be very small. To conclude, a first simulation of the D_3 spectrum, containing various approximations, fits the experimental spectrum well and yields fit parameters in good agreement with theoretical values published previously. The good agreement supports our interpretation that the two maxima of the experimental UV spectrum are due to the decay of the bound $n=3$ levels to the upper and lower sheet of the conical intersection of the potential surface correlated to $2p^2E'$. In the case of D_3 and H_3, the strong Jahn-Teller interaction reduces the symmetry of the molecule from D_{3h} to C_{2v}, and thus is responsible for the appearance of the two maxima in the UV spectra. D_2H already possesses C_{2v} symmetry and, with the potential surfaces of the molecule being (in good approximation) independent of the substitution of isotopes, the identical spectral pattern for D_3 and D_2H is comprehensible. The region close to the intersection of the two sheets of the ground state is reflected in the UV spectrum as the local minimum in intensity [(Figs. 1(a), 1(b), and 1(d)]. The existence of this intersection gives rise to the appearance of the geometric phase in the reaction between H and H_2, as was pointed out by Wu and Kuppermann [17].

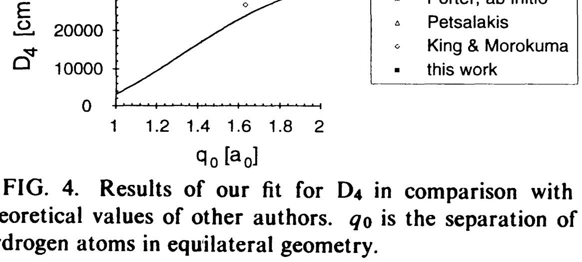

FIG. 4. Results of our fit for D_4 in comparison with the theoretical values of other authors. q_0 is the separation of the hydrogen atoms in equilateral geometry.

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