Direct Measurement of a Pure Rotation Transition in H_2^+

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The $N = 1 \leftarrow 0$ pure rotation transition in the $\nu = 19$ level of the ground electronic state of H_2^+ was observed at $14\,961.7 \pm 1.1$ MHz. Recent theory predicts significant electric dipole intensity in forbidden rotation and rotation-vibration transitions involving levels near the dissociation limit; the relevant levels are bound by only 0.74 and 0.22 cm^{-1}. The transition was predicted to have a transition moment of 0.42 D; our measurement is consistent with this value.

Among the most strongly forbidden transitions in molecular spectroscopy are those between adjacent rotational levels of a homonuclear diatomic molecule; they gain intensity only as a result of the g/u mixing of electronic states by the nuclear hyperfine Hamiltonian [1]. Transitions between *ortho* and *para* states by radiative or nonreactive collisional processes are therefore forbidden. So familiar is this (usually excellent) selection rule that it is often incorrectly believed that conversion of *ortho* to *para* species by means of radiative or nonreactive collisional processes is strictly forbidden [2]. However, nuclear spins are not completely decoupled from the rest of the molecule but interact through the nuclear hyperfine Hamiltonian. The g/u mixing induced by the hyperfine Hamiltonian close to a dissociation limit was discussed by Broyer *et al.* [3]; because the hyperfine constants are small *ortho-para* transition probabilities are small, but their probability scales with the magnitude of the hyperfine couplings and with the proximity of *ortho* and *para* states to one another, which can be small at a degenerate dissociation limit. For systems where *ortho* and *para* states are widely separated, the transition probabilities are minute; e.g., the rate of the $J = 0 \leftarrow J = 1$ *ortho-para* electric dipole transition in the ground vibrational and electronic state of molecular hydrogen is calculated to be about 2×10^{-13} per year [4].

Collisions of atoms at ultracold temperatures are important in cooling and trapping atoms and molecules and in photoassociation spectroscopy [5]. Ultracold neutral plasmas have recently been created [6], and ultracold atom-ion collisions have been investigated theoretically [7]. Spin polarized hydrogen atoms have been photoassociated [8] at 0.15 K, and it is possible that proton-hydrogen atom $(H^+$-$H)$ collisions could now be investigated at low collision energies where *ortho-para* interactions are significant (at such energies only the spin exchange can formally be identified but it is related to charge exchange) [9]. Calculations of proton-hydrogen atom collisions have previously assumed no coupling between the $1s\sigma_g$ and $2p\sigma_u$ states [9,10], but at collision energies lower than ≈ 0.1 eV the effect of coupling between *ortho* and *para* partial waves becomes important and increases as the collision energy is lowered.

Few observations of *ortho-para* mixing have been made. Ozier [11] *et al.* observed *ortho-para* transitions in methane by magnetically tuning *ortho* and *para* levels through degeneracy (see also Fig. 1 of [12]). Bordé *et al.* [13] measured crossover resonances in infrared saturation spectra due to the mixing of vibration-rotation states of $^{32}SF_6$ by nuclear hyperfine interactions (see also Fig. 2 of [12]). Electronic g/u symmetry breaking was observed in $^{127}I_2$ at the $^2P_{3/2}$-$^2P_{1/2}$ dissociation limit [14] and in Cs_2 at the first dissociation limit [15]. *Ortho-para* conversion in polyatomic molecules (particularly $^{12,13}CH_3F$) by collisions has been investigated using light-induced drift [16].

The hydrogen molecule ion, H_2^+, is the simplest molecule [17], its electronic Hamiltonian is exactly soluble within the Born-Oppenheimer approximation [18], and its vibration-rotation energies are the most accurately calculated of any molecule [17]. We usually express the total molecular wave function as the product $|\text{elec, vib, rot}\rangle |\text{nuc. spin}\rangle$, where the first ket may be called the coordinate function [1]. For the ground electronic state $(1s\sigma_g \equiv X^2\Sigma_g^+)$ of H_2^+, where the nuclei have spin $\frac{1}{2}$, we combine symmetric coordinate functions (that have even rotational quantum number N) with *para* nuclear spin functions $(I = 0)$, and antisymmetric coordinate functions (odd N) with *ortho* nuclear spin functions $(I = 1)$. The expectation value of the electric dipole operator for either a g or a u symmetrized function is identically zero, and so electric dipole transitions between adjacent rotational levels are forbidden. Similarly, nonreactive collisions of homonuclear diatomics (with spin) obey the selection rule $\Delta N =$ even. Electronic symmetry breakdown in HD^+ has been demonstrated experimentally by both spectroscopy [19] and collisions [20]. Previously, microwave transitions in H_2^+ [19] were observed between near-dissociation levels of the ground electronic state $(1s\sigma_g \equiv X^2\Sigma_g^+)$ and the first excited electronic state $(2p\sigma_u \equiv A^2\Sigma_u^+)$. A surprisingly large (6.0 MHz) hyperfine splitting was observed [21] in one transition of H_2^+. The observed hyperfine splitting was explained quantitatively by Moss [22] as arising from an electronic g/u symmetry breaking interaction that led to *ortho-para* mixing.

For an account of electronic g/u symmetry breaking in H_2^+, the reader is referred to the papers by Moss [22] and Bunker and Moss [23]. In brief, the nuclear hyperfine Hamiltonian causes mixing between *ortho* and *para* levels of different electronic states. In the case of H_2^+, only the Fermi contact term is important in the hyperfine Hamiltonian which becomes $H_{\text{hyperfine}} = K(\delta_1 \mathbf{i}_1 \cdot \mathbf{s} + \delta_2 \mathbf{i}_2 \cdot \mathbf{s})$, where $K\delta_i$ returns the electron density at nucleon i, $\mathbf{i}_i$ is the spin of nucleon i, and $\mathbf{s}$ is the electron spin. We can

determine the extent of *ortho-para* mixing by perturbation theory; as the unperturbed states we use hyperfine split vibration rotation levels of each electronic state. The appropriate basis functions can be written $|\psi_e\rangle |v, N\rangle |\mathbf{s I G}\rangle$; the first ket is an electronic wave function ($1s\sigma_g$ or $2p\sigma_u$), the second is a vibration rotation wave function, and the third is a spin function. The spin coupling scheme appropriate to H_2^+ is $\mathbf{i}_1 + \mathbf{i}_2 = \mathbf{I}$ ($I = 0; 1$), $\mathbf{I} + \mathbf{s} = \mathbf{G}$ ($G = \frac{1}{2}; \frac{1}{2}, \frac{3}{2}$). For the usual g/u symmetrized basis, the following combinations of functions are allowed:

$$|\psi_e\rangle = 1s\sigma_g \quad N \text{ even} \Rightarrow I = 0 \ (para) \quad \text{and} \quad G = \frac{1}{2}$$
$$N \text{ odd} \Rightarrow I = 1 \ (ortho) \quad \text{and} \quad G = \frac{1}{2} \text{ or } \frac{3}{2}$$
$$|\psi_e\rangle = 2p\sigma_u \quad N \text{ even} \Rightarrow I = 1 \ (ortho) \quad \text{and} \quad G = \frac{1}{2} \text{ or } \frac{3}{2}$$
$$N \text{ odd} \Rightarrow I = 0 \ (para) \quad \text{and} \quad G = \frac{1}{2}.$$

Ortho ($I = 1$) vibration rotation levels are therefore split into two by the hyperfine interaction as shown in Fig. 1(c). The perturbed states were calculated as follows:

$$|\psi^{\text{mix}}\rangle = |\psi^a\rangle + \mathbf{S}_b \frac{\langle \psi^a | H_{\text{hyp}} | \psi^b \rangle}{E_b - E_a} |\psi^b\rangle, \quad (1)$$

where a and b represent either *ortho* and *para* or *para* and *ortho* wave functions, and $\mathbf{S}$ represents a summation including an integration over the continuous spectrum [25]. The matrix element in the above expression was calculated [24] to be $-(\sqrt{3}/2)\langle v, N | v', N \rangle \frac{1}{2} a$, where a is the free atom Fermi contact parameter (1420 MHz), and selection rules show that $\Delta G = \Delta N = 0$ and mixing occurs only between $G = \frac{1}{2}$ states. The vibrational integrals were evaluated numerically.

As the wave functions near dissociation are now described as a mixture of *ortho* and *para* states, pure rotation or pure vibration-rotation transitions borrow intensity as a result of the mixing. The extent of mixing of continuum and bound states increases with proximity to a degenerate dissociation limit for all homonuclear diatomic molecules

with nuclear spin even if the first excited state does not support bound levels. Detailed calculations by Bunker and Moss [23] predicted that pure rotation (and vibration-rotation) transitions between levels within the $1s\sigma_g$ and $2p\sigma_u$ electronic states should have considerable intensity. The pure rotation transition of H_2^+ predicted to be most intense is $N = 1 \leftarrow N = 0$ in the last bound vibrational level ($v = 19$) of the electronic ground state. The transition was calculated to have a transition dipole of 0.42 D [23] and to occur at a frequency of $14\,960 \pm 3$ MHz [24].

Our measurements were made using a modified version of a fast ion beam spectrometer that is described elsewhere [26], and for details of our techniques the reader may consult a recent review [27]. We briefly describe the current experiments. As a preliminary study, we remeasured the $2p\sigma_u(v = 0, N = 2)\text{-}1s\sigma_g(v = 19, N = 1)$ [hereafter $(0, 2)\text{-}(19, 1)$] transition of H_2^+ that shares its upper level [$(19, 1)$] with the transition to be observed. H_2^+ ions were created by electron impact on H_2 and accelerated to 2 or 4 keV (typical beam current $\approx 10^{-7}$ A). H_2^+ was selected by means of a magnetic sector and focused
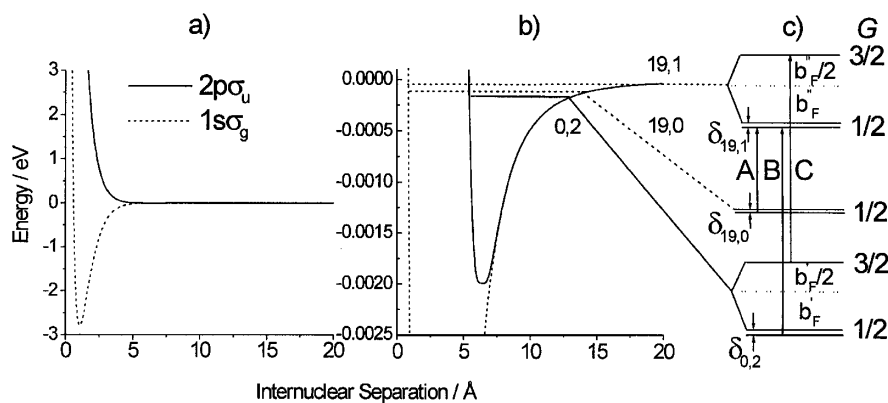

FIG. 1. (a) Potential energy curves (p.e.c.) of H_2^+. (b) P.e.c.'s of H_2^+ near the first dissociation limit showing the shallow well in the $2p\sigma_u$ state and the relevant vibration-rotation energy levels (to scale). (c) Calculated hyperfine levels and observed microwave transitions between them (not to scale). In order to determine the expected frequency of the $(19, 1)\text{-}(19, 0)$ transition (labeled *A* above), we take the difference between the dissociation energies for the $(19, 1)$ and $(19, 0)$ vibration-rotation levels of H_2^+ and correct this center frequency to allow for the hyperfine shifts and electronic g/u symmetry breaking shifts [22] (shown as $\delta_{v,N}$) that affect the $G = \frac{1}{2}$ levels. This yields a predicted frequency for *A* of $14\,960$ MHz [24] (transitions *B* and *C* were previously measured [21]).

into a 40 cm length of rectangular waveguide (WR-62). Microwaves from a synthesizer (Wiltron 6769B) were amplified (HP 8346A) to a maximum output power of 100 mW. The microwave frequency was scanned directly and the microwaves were amplitude modulated (333 Hz, 50% duty cycle) to enable lock-in amplification. The amplified radiation was coupled into the waveguide and passed into the vacuum chamber through a polytetrafluoroethylene window; only the fundamental mode was propagated through the waveguide. After interacting with the microwaves, the H_2^+ beam passed through an electric field of up to 10^4 V cm^{-1}, where selective dissociation of weakly bound ions occurred [19]. When a transition was in resonance, population transfer occurred and we detected the change in population of the $(19, 1)$ level directly. The electric field induced fragments appeared at a well-defined kinetic energy that was set by the position (and, hence, potential) within the electric field at which they fragmented. We selected H^+ fragments at the kinetic energy appropriate to the $(19, 1)$ level using a cylindrical plate electrostatic analyzer and detected the signal against a small background with an off-axis electron multiplier (Thorn EM119). The current from the electron multiplier passed through a transimpedance amplifier (Brookdeal 5002) to a lock-in amplifier (Stanford Research 850).

Reflection from the open ends of the waveguide cell led to microwaves both copropagating and counterpropagating to the ion beam and, hence, each resonance was split into two due to Doppler shifts:

$$\nu_{\text{ion}}^{\overset{\text{CO}}{\text{CT}}} = \nu_{\text{rest}}[(1 \mp v/c)/(1 \pm v/c)]^{1/2} = \nu_{\text{rest}} K^{\overset{\text{CO}}{\text{CT}}},$$

where upper and lower signs refer to radiation copropagating (CO) and counterpropagating (CT) with respect to the ion beam velocity, v. Where we observed both Doppler shifted frequencies, the two observations were used to extract the rest frequency of the transition, ν_{rest}, and the Doppler shift factors $K^{\overset{\text{CO}}{\text{CT}}}$. The remeasurement of the $(19, 1)$-$(0, 2)$ transition enabled us to optimize the collection of fragment protons from $(19, 1)$; we used a source potential of 4000 V, an electric field of 400 V/mm, and a microwave power of 0.126 mW. The spectrum obtained clearly displayed the forward and backward Doppler shifted transition split by the electronic g/u symmetry breaking hyperfine structure. The observation of both forward and backward Doppler shifted peaks enabled the rest frequencies and Doppler shift factors $K^{\overset{\text{CO}}{\text{CT}}}$ of the $(0, 2)$-$(19, 1)$ transitions to be determined. The frequencies were $17\,604 \pm 1$ and $17\,610 \pm 1$ MHz in agreement with the previous measurements and calculations [21], thus verifying the calibration of the synthesizer. Without changing the instrument settings [and therefore continuing to monitor H^+ fragments from the $(19, 1)$ level with the same Doppler shift factors] we then searched, using the full 100 mW microwave power available to us, the frequency range over which the two Doppler shifted components of the $(19, 1)$-$(19, 0)$ transition were expected. After

signal averaging 999 scans, we detected a new transition at a frequency of 14 937 MHz, close to the expected frequency for the counterpropagating Doppler shifted component of the $(19, 1)$-$(19, 0)$ transition, but were unable to detect the copropagating component. To verify our detection of the forbidden transition [$(19, 1)$-$(19, 0)$], we rerecorded both spectra using an ion source voltage of 2000 V. The new line was now observed with a smaller Doppler shift (to higher frequency), and therefore corresponded to a counterpropagating component. We also observed the copropagating component, although it was weak. Both spectra obtained at 2 kV are shown in Fig. 2; using the calculated Doppler shift factors from the allowed (intense) transition, we obtained the rest frequency of the forbidden transition to be $14\,961.7 \pm 1.1$ MHz (95% confidence, five measurements) in excellent agreement with the predicted frequency of $14\,960 \pm 3$ MHz [24]. Our observed linewidths were significantly greater than the instrumental linewidth of 0.07 MHz and were therefore power broadened. We could have lowered the microwave power to overcome this but the scanning times required were prohibitive. As a further proof that we had observed a transition with a level in common with the $(19, 1)$-$(0, 2)$ transition, we obtained the transition in double resonance using a second synthesizer and amplifier. The excellent agreement with the predicted transition frequency and the fact that the transition definitely terminates in the $(19, 1)$ vibration-rotation level shows unambiguously that we have measured the forbidden [$(19, 1)$-$(19, 0)$] pure rotation transition in H_2^+.

We could not directly measure the intensity of the $(19, 1)$-$(19, 0)$ transition, but we made a comparison with the intensity of the $(19, 1)$-$(0, 2)$ transition. In principle,
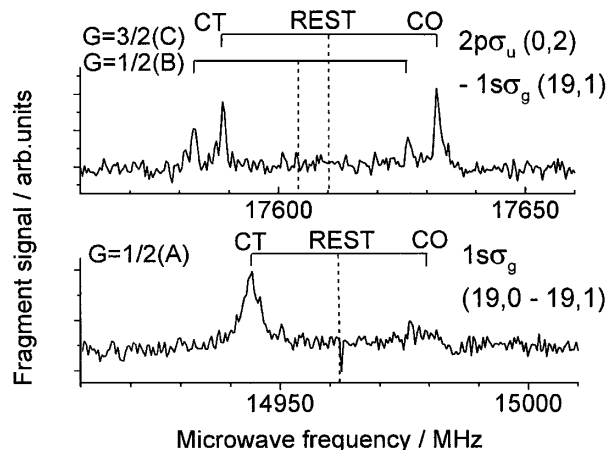

FIG. 2. A comparison of the dipole allowed $2p\sigma_u(0, 2)$-$1s\sigma_g(19, 1)$ spectrum (one scan, microwave power = 0.126 mW) and the pure rotation $1s\sigma_g(19, 1)$-$1s\sigma_g(19, 0)$ spectrum (999 scans, microwave power = 100 mW) obtained at a beam potential of 2 kV. CO and CT refer to the copropagating and counterpropagating Doppler-shifted components ν^{CO} and ν^{CT} of the transitions; the rest frequencies, $\sqrt{(\nu^{\text{CO}}\nu^{\text{CT}})}$, are indicated by dotted lines; A, B, and C refer to Fig. 1.

the relative transition probability could have been measured using the radiative broadening, but the more intense transition was saturated at higher microwave powers due to the minute number of ions available in the ion beam. We therefore used the following analysis: Our observed intensity can be written as $I \propto CFP(N_u - N_l)|\langle u|\mu|l\rangle|^2$, where C is the collection efficiency for fragment protons, F is the fragmentation rate from the level monitored, P is the microwave power, $(N_u - N_l)$ is the population difference, and $\langle u|\mu|l\rangle$ is the transition dipole. As we monitored transitions from one level [(19,1)] in both measurements, using identical instrument settings, the only factors that differed between the two transitions were the microwave powers (known), the transition dipoles (to be compared), and the population differences between the states. Unfortunately, we had no way of measuring or calculating the population differences; earlier work [19] showed that Franck-Condon factors for ionization are not predictive of populations for upper levels of D_2^+. We therefore arbitrarily assumed that the population differences were the same for the two transitions. Accepting this approximation, we expected to observe the transitions in the ratio of the square of the theoretically predicted transition dipoles [23], that is, in the ratio $I\big((19,1)\text{-}(0,2)\big)/I\big((19,1)\text{-}(19,0)\big) = (23\ \text{D})^2/(0.42\ \text{D})^2 \approx 3000$. In order to measure the relative intensities of the transitions, we assumed that the noise level was constant and defined the intensities by $I = S\Gamma/NP\sqrt{\omega}$, where $S = $ signal, $\Gamma = $ linewidth, $N = $ noise, $P = $ microwave power, and $\omega = $ measurement bandwidth. We ignored the power broadening of the transitions. Within these approximations, we found the ratio of intensities to be 8000, in reasonable agreement with the predicted value of ≈ 3000.

We measured a pure rotation transition in H_2^+ between levels close to dissociation where significant electric dipole intensity results from *ortho-para* mixing caused by the hyperfine Hamiltonian; the frequency of the transition is in excellent agreement with the value predicted by Moss [24], and the intensity is consistent with the theoretical value [23]. There are many other forbidden rotation and vibration-rotation transitions in H_2^+ and D_2^+ [24] that could be detected with suitable frequency sources. We are searching for these forbidden transitions and will present a full account in due course. Obvious candidates for similar observations with our apparatus are $^3\text{He}_2^+$, $^{6,7}\text{Li}_2^+$, and $^{21}\text{Ne}_2^+$.

Bunker and Moss predict that all homonuclear diatomic ions with nonzero nuclear spins should also have a forbidden pure rotation (or rotation-vibration) spectrum involving states near dissociation, including molecules where the first excited state is purely repulsive. This result will hold good for many transitions in homonuclear molecules with nuclear spin and nonzero hyperfine interactions (subject to some selection rules) as has been demonstrated for molecular iodine [14]. Such *ortho-para* mixing may have consequences for observations and calculations of ultralow energy homonuclear atom/atom and atom/atomic-ion collisions.

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