Autoionization of H_2 Induced by a Doubly Excited Triplet State

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A fast beam of H_2 molecules in the metastable $c\,^3\Pi_u^-$ state is photoionized with visible laser light in the region 540–670 nm. Very strong photoionization from high vibrational levels is observed with a conversion of up to ten vibrational quanta into electronic energy. This extreme non-Franck-Condon behavior is attributed to avoided crossings between the doubly excited $2p\sigma_u 2p\pi_u Q_1\,^3\Pi_g$ state and the singly excited $1snd\,^3\Pi_g$ Rydberg states with $n \geq 3$.

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The photoionization of molecular hydrogen has been extensively studied in recent years. For the singlet states, a variety of schemes for multiphoton excitation from the ground state has been developed.[1-4] The spectroscopy of the triplet states usually starts from the metastable $c\,^3\Pi_u^-$ state, which can be populated in electron impact excitation of a slow molecular beam[5,6] or by resonant charge exchange in alkali vapor of a fast beam of H_2^+.[7] The latter technique is used in the present work.

All the bound triplet states observed so far are singly excited Rydberg states in the sense that their configuration is well described as an H_2^+ core in the electronic ground state with a loosely bound outer electron. When photoionization proceeds via such a Rydberg state, it usually follows rather strict propensity rules in the vibrational quantum number: Vibrational autoionization of pure Rydberg states becomes less and less efficient with increasing Δv.[8,9] Therefore it is quite remarkable that we in the present experiment observe strong one-photon ionization with a change of as much as ten vibrational quanta.

Recently, a non-Franck-Condon behavior was observed in multiphoton ionization via the $C\,^1\Pi_u$ state.[10,11] This was explained by Chupka[12] and by Hickman[13] as resulting from excitation of a repulsive doubly excited state which on its way towards dissociation has a number of avoided crossings with the potential curves of H_2^+ and the high-n Rydberg states. This results in competition between dissociation and autoionization with a change of several vibrational quanta. The extreme non-Franck-Condon photoionization observed in the present work results from excitation directly into a system of avoided crossings between the doubly excited $2p\sigma_u 2p\pi_u Q_1\,^3\Pi_g$ state and the singly excited $1snd\,^3\Pi_g$ states.

The present experiments were carried out on a fast neutral-beam apparatus at SRI International[7] and on a similar apparatus at the University of Aarhus. There was excellent agreement between the results obtained in the two laboratories. An H_2^+ beam of 1.4-2 keV undergoes resonant charge transfer in Cs vapor producing a fast neutral beam of H_2 in the metastable $c\,^3\Pi_u^-$ state. The beam is excited in a collinear geometry with about 500 mW of visible light from a cw dye laser with a bandwidth of 1 cm^{-1}. The ions formed in the 0.8-m laser/beam interaction region are deflected onto a Channeltron detector. The laser beam is modulated with a mechanical chopper and the modulated ion signal from the Channeltron is recorded on a computer. The strong lines in the spectrum represent more than 10 times as many ions as the spontaneous and electric-field- and collision-induced ionization of the metastable molecules. Even the modest cw laser power saturates the strong optical transitions, indicating that they are vibrationally and electronically allowed.

Figure 1 shows a portion of the spectrum. The full spectrum consists of three groups (like the one shown), separated by regions with only few and weak lines. The three groups fall near 640, 600, and 560 nm. A fourth group of lines appears to begin at 670 nm at the very red end of our laser range. Most of the spectrum is not yet assigned, but a few lines have been identified in terms of an unambiguous assignment of the lower-state vibrational and rotational quantum numbers. The lines represent transitions from $v''=9$–12 in the $c\,^3\Pi_u^-$ state; the three groups contain transitions to the same upper levels from different lower-state vibrational levels.

For most of the lines in the spectrum, the width is limited by the 1-cm^{-1} bandwidth of the dye laser. An exception is the $R1$ and $P3$ lines (Fig. 1) which are about 4 cm^{-1} wide, indicating a lifetime of 1.3 ps for the autoionizing upper level. We have also scanned one of the $R7$ lines using a single-frequency dye laser. The homogeneous linewidth corresponds to a lifetime of 70 ps. These lifetimes are much shorter than the fluorescence lifetimes, and so predissociation is the only process that

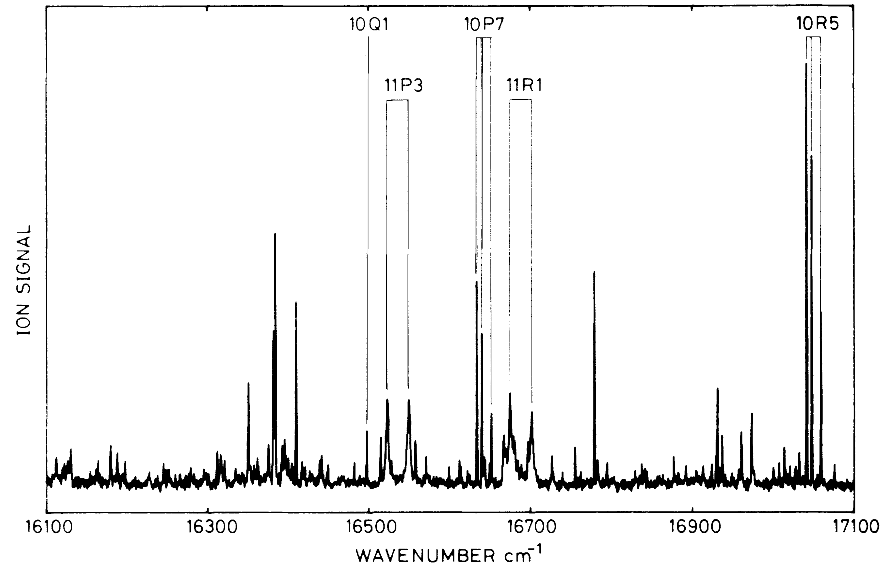

FIG. 1. Portion of the photoionization spectrum of H$_2$ $c\,^3\Pi_u^-$. The transitions are labeled by v'', ΔN, and N''; P, Q, and R denote $\Delta N = -1$, 0, and 1, respectively.

can possibly compete efficiently with autoionization.

The vibrational and rotational splittings observed for the $c\,^3\Pi_u^-$ state agree very well with the *ab initio* calculations of Kolos and Rychlewski[14] as indicated in Table I. We use the theoretical vibrational splittings to define the energy scale relative to $v=1$, $N=1$ in the $c\,^3\Pi_u^-$ state. The ionization potential of this level has been measured accurately[15] and defines the energy levels relative to H_2^+ and the dissociation limits. The assigned transitions and their upper state energy levels are listed in Table II along with the relevant energies of the dissociation limits and of H$_2^+$. Most of the assigned transitons must autoionize into $v^+ \leq 2$ of H$_2^+$. Accordingly, the photoionization from $v''=12$ in the $c\,^3\Pi_u^-$ state has $\Delta v \geq 10$.

Also listed in Table II are energy levels for selected *nd* Rydberg states obtained from a computer simulation based on a model similar to that of Herzberg and Jungen[16] and Eyler and Pipkin.[17] The model neglects all couplings but the rotational coupling between states of the same *n* and *v*. The energy levels of the nonrotating molecule are calculated separately for each *n* with quantum defects derived from the quadrupole moment and polarizability of H$_2^+$. The rotational coupling is then represented in terms of the effective Hamiltonian previously used for the 3*d* states of HD.[18] The simulation indicates that some of the upper-state levels are almost degenerate with Rydberg levels of intermediate *n* and *v*. These near degeneracies explain the appearance of "multiplets" like the $R5$ lines (Fig. 1) with closely spaced upper levels of the same N. The degeneracies may guide the molecule through the higher Rydberg states towards autoionization, but they do not account for the very large Δv observed.

TABLE I. Molecular constants for the $c\,^3\Pi_u^-$ state. Experimental values are from this work, and theoretical values are from Ref. 14.

v	ΔG (Expt.)	ΔG (Theor.)	B_v (Expt.)	B_v (Theor.)
9	1300	1298.7	18.26	18.23
10	1175	1175.6	16.83	16.84
11	1046	1046.1	15.36	15.38
12			13.79	13.82

TABLE II. Assigned transitions and energy levels. Transitions are labeled by v'', ΔN, and N''. Energy levels are in inverse centimeters relative to $c\,^3\Pi_u^-$ $v''=1$, $N''=1$.

Transition	$\tilde{\nu}$ (cm^{-1})	E(upper)	Rydberg level (n,v,N)	E
11Q1	15325.4	32309		
10Q1	16497.4			
9Q1	17794.6			
12R5	14910.9	33313		
11P7	15540.4			
11R5	15910.4		(6,4,6)	33299
10P7	16633.6		(9,3,6)	33293
10R5	17041.3		(12,3,6)	33294
9P7	17854.4			
9R5	18298.2			
12P3	15496.1	33658	(8,4,2)	33683
12R1	15632.3			
11P3	16522.7			
11R1	16674.4			
H$_2^+$, $v^+=2$, $N^+=0$		31392		
H$_2^+$, $v^+=3$, $N^+=0$		33334		
H(1s) + H(3s,p,d)		36330		

To account for the strong photoionization, we seek a bound upper state with a potential curve that deviates markedly from that of H_2^+ and the normal Rydberg states. To give a good Franck-Condon factor, the outer turning point in the vibration must be in the region $R = (4.5\text{-}6)a_0$, where the outer turning points for $v'' = 9\text{-}12$ in the $c\,^3\Pi_u^-$ state occur. The upper state must have $^3\Pi_g$ or $^3\Delta_g$ symmetry, since $\Delta N = \pm 1$ transitions, which are observed, are not allowed from the $c\,^3\Pi_u^-$ state to $^3\Sigma_g^+$ states.

By analogy with the recent work on singlet H_2,[10-13] we propose that the photoionization observed here involves a doubly excited state. According to Guberman's calculations,[19] the lowest doubly excited triplet state is the $Q_1\,^3\Pi_g$ state. These calculations were optimized for $R = 1.4a_0$ and seem to have problems in correlation with the correct dissociation limits. Therefore, we choose to describe the $Q_1\,^3\Pi_g$ state in terms of its dominant electronic configuration: a $2p\pi$ electron on an H_2^+ core in the excited state $(2p\sigma)\,^2\Sigma_u^+$. In a diabatic treatment, this doubly excited state correlates with the $n = 2$ limit [i.e., $H(1s)+H(2s,p)$] as illustrated in Fig. 2. Similarly, a diabatic treatment of the singly excited $1snd$ configurations gives rise to a series of $^3\Pi_g$ states, each of which correlates with the dissociation limit of the same principal quantum number. However, in the adiabatic picture, these states undergo avoided crossings with the doubly excited state near $R = 4a_0$. As a result of these crossings the $nd\,^3\Pi_g$ states change character into $(n-1)d\,^3\Pi_g$ over the interval $3a_0 < R < 6a_0$ and they correlate with the $n-1$ dissociation limit. This change of character corresponds to a change of 1 in the quantum defect. The well-known barrier in the $i\,^3\Pi_g$ state[14] results from the crossing of the potential curves of the $3d$ state and the $Q_1\,^3\Pi_g$ state. Beyond the top of the barrier, the $i\,^3\Pi_g$ state assumes the character of the doubly excited state[14] because no d states correlate to the $n = 2$ dissociation limit.

The potential curves in Fig. 2 were derived by our setting up a Hamiltonian in a basis of the $nd\,^3\Pi_g$ states and the $Q_1\,^3\Pi_g$ state. The doubly excited state is coupled to the nd states by a matrix element that varies with n as $n^{-3/2}$.[12] The magnitude of the matrix element is adjusted as a function of R such that the lowest adiabatic state reproduces the potential curve of the $i\,^3\Pi_g$ state.

The next higher $^3\Pi_g$ state, $2\,^3\Pi_g$, has the properties required to account for the photoionization with large Δv. At short internuclear distances, this state is a normal singly excited Rydberg state with $n = 4$. The levels $v = 0\text{-}2$ were observed by Eyler and Pipkin.[17] The avoided crossing with the doubly excited state creates a kink in the $2\,^3\Pi_g$ potential near $R = 4a_0$. The potential goes quickly towards larger R and the electronic wave function changes character from $n = 4$ via a mixture of all n's into $n = 3$. The energies of the upper states observed at consistent with $v' = 7,8$ in the $2\,^3\Pi_g$ state. These levels have their outer turning points in the vibration at the flat portion of the potential so that the maximum of the vibrational wave function occurs just at the avoided crossing with the doubly excited $Q_1\,^3\Pi_g$ state. The photoionization involves a "loss" of several vibrational quanta in the excitation step followed by the conversion of about five vibrational quanta into electronic energy, resulting in H_2^+ with $v^+ = 2\text{-}3$. A more detailed analysis may shift the position of the crossing and consequently change the present assignment of v' in the $2\,^3\Pi_g$ state. We note that the lowest doubly excited Δ state arises from the $n = 3$ limit. As a consequence, the $nd\Delta$ states do not show any anomalous behavior below the $n = 3$ limit, but rather follow a smooth potential energy curve like that of H_2^+. Hence, there is no ambiguity about the assignment of $2\,^3\Pi_g$ as the intermediate state in the observed photoionization.

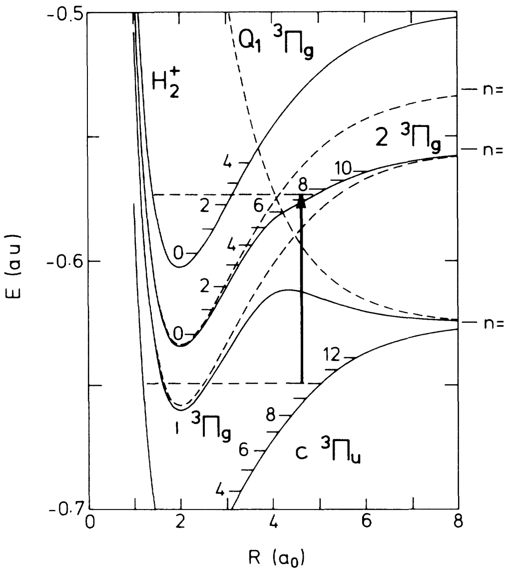

FIG. 2. Potential energy curves for H_2 and H_2^+: dashed line, diabatic states; solid line, adiabatic states. The adiabatic potential curve of the $2\,^3\Pi_g$ state observed in photoionization has the character of the $n = 4$ diabatic state at short R. It develops a kink near the diabatic crossing with the doubly excited state, and assumes the diabatic character of the $n = 3$ state at large R.

The avoided crossings may also lead to dissociation if the coupling to states of lower n dominates. The competition between autoionization and dissociation is probably important in the determination of the relative intensities of the transitions in the ionization spectrum. Using a double resonance technique,[20] we have observed dissociation of the high vibrational levels in both the $3d\ j\,^3\Delta_g$ state and the $2\,^3\Pi_g$ state. This will be the subject of a separate publication.

Quantitative representation of the level energies and the competition between ionization and dissociation can possibly be achieved with use of multichannel quantum-defect theory. This approach was recently applied by Ross and Jungen[21] to calculate accurate level energies in the system of avoided crossings that give rise to the $^1\Sigma_g^+$ double-well states in H_2.

The present experiment illustrates the dramatic effect of a doubly excited state on the dynamics of autoionization and opens new possibilities for the study of the competition between the various decay channels open to a simple molecule in electronically and vibrationally highly excited states.

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