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COMMUNICATIONS

Optical–optical double-resonance spectroscopy of autoionizing states of water

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Double resonance excitation of vibrationally autoionizing states of the water molecule has been performed for the first time. Tunable, coherent vacuum ultraviolet light was used to excite selected rotational levels of the $\tilde{\mathbf{C}}\ ^1\mathbf{B}_1$ state with one quantum of symmetric stretch vibrational energy (100), from which (100) Rydberg states were excited with a second dye laser. The Rydberg character of the $\tilde{\mathbf{C}}\ ^1\mathbf{B}_1$ state leads to strong vibrational selectivity for the (100) states in the second transition; therefore, the resonances due to these states are greatly enhanced compared to the case of direct excitation from the ground state, and spectrally simplified due to the well-defined angular momentum of the intermediate state level. The spectra show unexpected peaks which might be attributable to significant 1-mixing in the $\tilde{\mathbf{C}}\ ^1\mathbf{B}_1$ state as well as the presence of interloping linear states. © *1997 American Institute of Physics.* [S0021-9606(97)02539-7]

Optical–optical double resonance with rotational state resolution has been applied to the study of the spectroscopy and dynamics of the highly excited states of a number of diatomic systems.[1] The use of intermediate resonance leads to significant spectral simplification, a feature which is of crucial importance in regions of high state density such as that near the ionization threshold. Such studies have led to a greatly enhanced understanding of the mechanisms underlying the spectra and decay dynamics of highly excited states of diatomic molecules. Another approach which can limit the complexity of molecular spectra is cooling the sample in a supersonic expansion. While this approach can yield beneficial results with large molecules for which rotational resolution is difficult or impossible, even for species with large rotational energy spacings it is generally impossible to restrict the population of the initial state to essentially one rotational level. This can make unambiguous identification of the excited states' angular momentum properties difficult. Spectra of highly excited states obtained by direct excitation from the ground state are also generally complicated by the simultaneous excitation of a number of vibrational modes, due to the fact that the molecular geometry typically changes significantly between the ground states of the neutral and the molecular ion.

While a variety of optical multiple resonances techniques such as ion dip spectroscopy have been applied to the study of low-lying states of polyatomic molecules,[2] the extension of double resonance techniques to the study of their highly excited states has been slow in coming. Autoionizing states of NO_2 have been studied with vibrational mode resolution,[3] autoionizing structures in other molecules such as aniline[4] and diazobicyclooctane have been observed without rotational resolution using two-color schemes,[5] and a very recent study has reported the excitation of high ($n \sim 100$) Rydberg states of benzene from single rotational levels of the first excited singlet state.[6] However, the general extension of these techniques to fully quantum state-resolved studies of interesting polyatomic molecules has been hampered by the fact that potential intermediate states which do not predissociate rapidly are rare in polyatomic molecules, when compared to diatomics. Lifetime broadening due to dissociative decay can make rotational resolution impossible; additionally, even if the ground–intermediate state transition can be rotationally resolved, any further excitation from the intermediate state must compete with this rapid depopulation process. Consequently, far less is known about the spectroscopy and dynamics of the highly excited states of even small polyatomic molecules than is the case for diatomic systems.

In this Communication we report on the first application of double-resonance excitation, using vacuum–ultraviolet (vuv) light to drive the first step from the ground state to an intermediate state, to the rotationally resolved excitation of autoionizing states of a polyatomic molecule. The system studied, water, serves a prototypical asymmetric top molecule and is well suited for this work due to its relatively large rotational energy spacing and the fact that is has several transitions to electronically excited states whose rotational structure has been resolved and analyzed. Intermediate resonance with selected rotational levels of the $\tilde{\mathbf{C}}\ ^1\mathbf{B}_1(100)$ Rydberg state results in the production of a fully angular momentum selected excited state population for further excitation to the highly excited states of interest, as well as a significant degree of vibrational selectivity of the final highly excited state. This approach allows high-quality, relatively simple spectra of vibrationally autoionizing states of water to be acquired under collision-free conditions, thereby providing detailed experimental information for comparison to quantum defect theory calculations.

Rydberg states of water with one quantum of symmetric stretch excitation (100) which lie above the ionization limit of the molecule can autoionize vibrationally. These states have been studied several times through direct, single-photon excitation from the ground state in samples cooled through supersonic expansion,[7] and the experimental results have been analyzed in the framework of quantum defect theory.[8] In such a situation, several of the lowest rotational states of the ground state have significant populations and transitions from any of these initial states may be observed, a feature which increases the difficulty of state identification. Another aspect of single-photon excitation from the ground state which determines the resultant spectra is the fact that the ground state geometry of the molecule differs significantly from that of the ion; as a result, the Franck–Condon factors for excitation to a variety of different symmetric stretch and bending mode final Rydberg states are significant. Because of this, transitions to the autoionizing states from the ground state have rather low intensity and ride on a large background of direct photoionization; consequently, they cannot be observed to high principal quantum number without becoming lost in noise. Stepwise excitation through the $\tilde{\mathbf{C}}\ {}^1\mathbf{B}_1(100)$ state, used in the work we report on here, allows transitions to the (100) autoionizing states to be observed with both rotational and vibrational selectivity.

One-photon transitions between the $\tilde{\mathbf{X}}(000)$ and the $\tilde{\mathbf{C}}(100)$ states lie at wavelengths near 120 nm. High intensities of light with the appropriate vacuum ultraviolet wavelengths were produced through two-photon resonant difference-frequency generation in krypton gas.[9] This process was driven using the output of two homebuilt, amplified pulsed dye lasers pumped by a single Nd^{+3}:YAG laser (Continuum NY-61). The first of these two lasers operated at a wavelength tunable around 607 nm and produced 20 mJ pulses with a bandwidth of $\sim$0.03 cm^{-1} and a duration of about 5 ns. This light was frequency tripled using KDP and BBO crystals to give about 1 mJ of tunable 202 nm light, which was focused with a 15 cm focal length lens into a cell containing 10 Torr of krypton. This light was tuned into two-photon resonance with the krypton $4p^6 \rightarrow\rightarrow 5p[1/2]_0$ transition by observing the resulting 2+1 multiphoton ionization signal. Light from the second dye laser, tunable around 660 nm with pulse energies of about 2 mJ and a bandwidth of $\sim$0.2 cm^{-1} was combined with the ultraviolet light using a dichroic mirror and focused with the same lens. Although we have not yet measured the resulting yield of tunable vuv photons, previous work under similar conditions has demonstrated the production of more than 10^{12} photons/pulse with this technique.[10] The vuv light then emerged from the krypton cell through a MgF_2 window and entered the experimental chamber, where it met a simultaneous, counter-propagating beam of light from a third dye laser which was pumped by the third harmonic of the same Nd^{+3}:YAG laser.

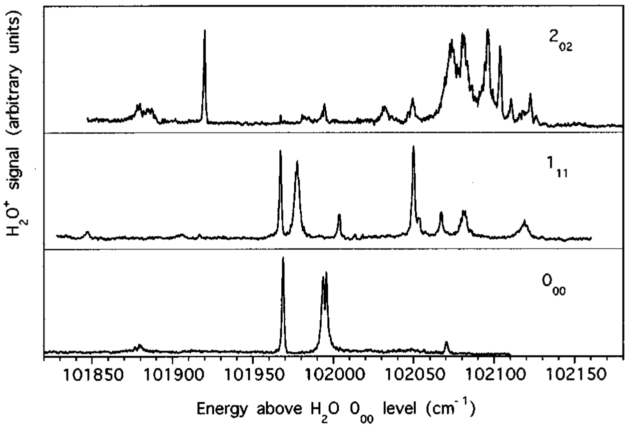

FIG. 1. Spectra of transitions to $n = 6$ autoionizing states from the three lowest rotational levels of ortho-H_2O in the $\tilde{\mathbf{C}}\ {}^1\mathbf{B}_1(100)$ state. the intermediate rotational state is labeled on the left of each spectrum. These spectra are discussed in the text.

This laser, tunable between 555 and 470 nm with a pulse energy of about 5 mJ and bandwidth of 0.03 cm^{-1}, induced transitions from the excited $\tilde{\mathbf{C}}(100)$ state to states lying between the $H_2O^+(000)$ and (100) ionization limits. Both the vuv and visible beams had a beam diameter of roughly 2 mm at the interaction region. The photon energy of the laser driving the second step of the excitation process was calibrated to an accuracy of $\sim$0.5 cm^{-1} using a simultaneously acquired spectrum of neon and uranium lines, observed through the optogalvanic effect in a hollow-cathode lamp. The spectra were converted to total energy above the ground state of the neutral using values for the $\tilde{\mathbf{C}}(100)$ rotational level energies calculated from the constants in Ref. 11, or to energy with respect to the first ionization limit of the molecule by additionally using the value for the ionization energy from Ref. 8 (104 985 cm^{-1}). The overall precision of these converted energy scales is about 2 cm^{-1}.

The laser beams interacted with room-temperature water vapor at a pressure of about 10^{-4} Torr in a differentially pumped time-of-flight mass spectrometer. The water vapor was bled through a hypodermic needle into the high-pressure region, which contained the time-of-flight plates, and pumped out into the flight tube through a 4 mm hole in the lower plate, which was also used to extract ions produced by the laser-molecule interaction. The system was evacuated through the flight tube by a turbomolecular pump. The ions were extracted using a 30 V/cm electric field pulse applied to the plates 50 ns after the laser pulses arrived, and detected with a channeltron after passing through the flight tube.

Figure 1 shows the H_2O^+ ion spectra of transitions from the three lowest rotational levels of ortho-H_2O in the region just above the ionization limit, where transitions to (100) states with $n = 6$ and small quantum defects would be expected to fall. The meaning of the observed peaks will be discussed below. The spectra have been plotted versus total energy above the ground state of the neutral molecule. Most, if not all, of these transitions are probably due to excitation of (100) vibrational states. The small value of the direct background provides evidence of the vibrational selectivity inherent in the double-resonance process, and the signal-to-noise ratio is very good considering that a total of eight pulsed dye laser photons were involved in the excitation process.

The appropriate description of high-lying states of a molecule depends on the principal quantum number involved, since this affects the degree to which the orbital angular momentum of the Rydberg electron is coupled to the molecular framework of the ionic core. For low-lying states, the orbital angular momentum is coupled strongly to the molecular frame; in this limit (Hund's case b), the excited state energy level structure consists of a set of rovibrational states of the molecule for each possible electronic symmetry of the excited electron (i.e., nda_1, nda_2, ndb_1, and ndb_2 for an excited nd electron of an asymmetric top molecule). This corresponds energetically to a situation in which the splittings of the different electronic configurations of the same n greatly exceeds the rotational energy spacing. In the opposite limit, high principal quantum numbers lead to weak coupling with the molecular frame (Hund's case d). In this case, each rotational level of the core serves as the limit of convergence for several Rydberg series with different values of the total angular momentum J (formed by coupling the excited electron's orbital angular momentum with the core rotational angular momentum, now considered to be a good quantum number). The transition between Hund's case b and Hund's case d, or l uncoupling, has been most clearly observed for the np states of molecular hydrogen[12] where the transition occurs for principal quantum numbers of about 10. A similar uncoupling will occur for H_2O , although its analysis will be made more difficult by water's more complicated rotational structure.

The selection rules for electronic excitation of an asymmetric top dictate that excitation can occur from the $\tilde{\mathbf{C}}\ {}^1\mathbf{B}_1(100)$ state, which has a configuration $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)(3pa_1)$, to ${}^1A_1$ states (b_1 orbitals), ${}^1A_2$ states (b_2 orbitals), or ${}^1B_1$ states (a_1 orbitals) in Hund's case b notation. In the absence of l mixing in the $\tilde{\mathbf{C}}$ state and assuming for the moment atomiclike selection rules ($\Delta l = \pm 1$), only s and d final angular momentum states would be expected. Previous work has shown that the s series should have a quantum defect of around 1.5, and should therefore not be observed in this spectral region.[13] Of the d states which can be excited, only the $6d$ members of the Rydberg series which begin with the $3d\tilde{\mathbf{F}}({}^1B_1)$ (da_1 orbital, excitable via type-b selection rules) and the $3d\tilde{\mathbf{F}}({}^1A_1)$ (db_1 orbital, excitable through type-c selection rules) states are expected to have small quantum defects[8] and fall within the energy range of Fig. 1. Other members of the d complex have quantum defects such that they will lie well outside the range of energy displayed in the figure:[8] The higher members of the series beginning with $\tilde{\mathbf{D}}''\ {}^1\mathbf{A}_2\ (3db_2)$ have quantum defects of ~0.33, while the higher members of the series beginning with $\tilde{\mathbf{E}}\ {}^1\mathbf{B}_1(3da_1)$ have quantum defects of ~0.16. The $nda_2\ {}^1\mathbf{B}_2$ states are forbidden in single-photon excitation from the $\tilde{\mathbf{C}}\ {}^1\mathbf{B}_1$ state. So, considering only the $\tilde{\mathbf{F}}$ states, from the 0_{00} ($\mathbf{J_{K_aK_c}}$) level we would expect to excite the 1_{11} rotational level of the $6d\,{}^1B_1$ state and the 1_{10} level of the $6d\ {}^1A_1$ state within this range. The experimental spectrum, however, shows three strong peaks. Considering the 1_{11} intermediate level, we would expect to excite the 0_{00} and 2_{02} levels of the $6d\ {}^1B_1$ state and the 1_{01} and 2_{21} levels of the $6d\ {}^1A_1$ state. Again, the experimental spectrum shows a greater number of pronounced peaks than expected. The spectrum from the 2_{02} state is still more complicated, consisting of transitions to $J = 1,2$, and 3 final states, and also has more peaks that expected from nd states with small quantum defects.

It seems likely that the additional peaks in the experimental spectra can be at least partially accounted for by the inclusion of l mixing in the intermediate or the final state. Indeed, since the ionic potential is not centrosymmetric, the orbital angular momentum of the excited electron, l, is not a good quantum number and orbitals, especially those which lie low in energy, should properly be described as being mixtures of different l values. Recent calculations[14] indicate that the $\tilde{\mathbf{C}}$ state, which nominally has a $3pa_1$ excited electron, actually has 14% s character in a single-center expansion about the oxygen atom. Thus excitation of p Rydberg states from the $\tilde{\mathbf{C}}$ state could be quite likely. Also, recent *ab initio* calculations[15] indicate that the quantum defect for the $np\ {}^1A_2$ series should be near 1.0; consequently, transitions to the $7p$ states might fall in the same energy region as the $6d$ states. If such transitions were occurring, it would be natural to expect that $s \rightarrow p$ transitions would show a greater linewidth than $p \rightarrow d$ transitions due to the greater core penetration of the p Rydberg orbital, and consequently larger autoionization rate. We do indeed see a variety of linewidths, ranging from ~1 to ~7 cm^{-1}. It should be noted, however, the linewidths tend to fall at the ends of this range; that is, they are either narrow or broad. The broader of these resonances may well correspond to excitation of $7p$ states. Some degree of increased broadening is also to be expected within a particular nl cluster as the rotational angular momentum quantum numbers of the autoionizing states increase, assuming that the autoionization and/or dissociation rates of these states are due to heterogeneous processes. We should note that the minimum observable linewidth in this experimental approach will be determined by the lifetime broadening of the $\tilde{\mathbf{C}}$ state levels, ~1 cm^{-1} for low rotational states.

Unfortunately, even the inclusion of possible s to p transitions is insufficient to give the observed number of lines in this region of the spectrum. It seems likely that a complete theoretical understanding of these spectra will require the inclusion of interloping linear states. Such states would be expected to be excitable from the $\tilde{\mathbf{C}}$ state because of the large geometry change between the bent neutral and linear ionic states. The importance of such linear-bent state interactions in the Rydberg states of water has been noted before.[7,15]

Figure 2 shows the spectrum of states excited from the 0_{00} rotational level of the $\tilde{\mathbf{C}}\ {}^1\mathbf{B}_1$ state over a broad range of energies up to, and including, the (100) ionization energy. The energy scale of this plot is referred to this ionization energy (104 983 cm^{-1} above the ground state of the neutral molecule[8]). Rydberg states with total angular momentum

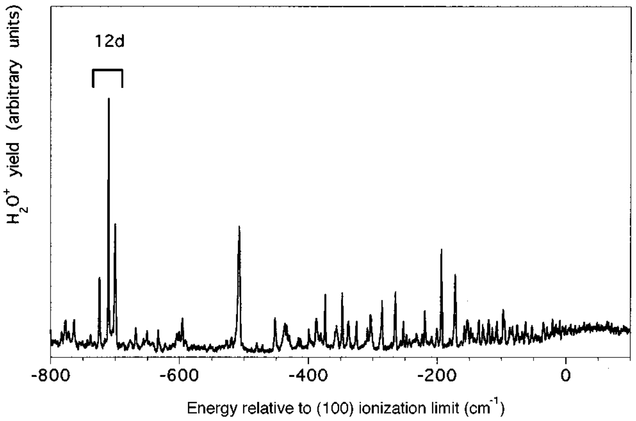

FIG. 2. Spectrum of transitions excited from the 0_{00} rotational level of the $\tilde{\mathbf{C}}\ ^1\mathbf{B}_1(100)$ state, in an energy region containing the (100) ionization limit of the molecule. Autoionizing states with $n = 12$ and greater form strongly interacting series, which converge to limits corresponding to several rotational core states.

quantum number $J = 1$, from $n = 12$ to high values of n, appear as prominent resonances in this spectrum. The different rotational transitions for different values of n begin to overlap at about $n = 15$, signaling the onset of full l uncoupling. Well above this value of n, strongly interacting series of Rydberg states converging to different core rotational levels are observed. This spectrum represents the first observation of Rydberg states of water with such high principal quantum numbers. The detailed understanding of this spectrum, and similar spectra from other rotational levels of the intermediate state, will prove to be a crucial step in the development of multichannel quantum defect theory for asymmetric top molecules.

The work reported here is the beginning of a systematic experimental and theoretical effort to gain an understanding of the spectroscopy and dynamics of the highly excited states of water, at a level of detail which will be much greater than any previous study. The high-quality spectroscopic results made possible by the double-resonance technique described here will be combined with multichannel quantum defect theory (MQDT) analysis by Child to give unambiguous state identifications and a complete picture of the excited state quantum defects and interseries interactions. It will also be possible to study bending mode excited states utilizing intermediate resonance with the $\tilde{\mathbf{C}}(010)$ state. Finally, detection of dissociation fragments and rotationally resolved photoelectron spectroscopic analysis of the autoionization process will complete the picture by giving direct information on the decay dynamics of the highly excited states of this important molecule.

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