

Multiphoton ionization vibrational state selection of H_2O^+ , D_2O^+ and HDO^+

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Abstract

We present a study of single color (2 + 1) resonance-enhanced multiphoton ionization (REMPI) of H_2O , D_2O , and HDO via several Rydberg states lying in the energy range from 80 000 to 86 000 cm^{-1} . Photoelectron spectra (PES) show that the corresponding cations can be vibrationally state-selected for most vibrational states. The exception is the bend of H_2O^+ and HDO^+ , where mixing in the REMPI intermediate level results in weak ion intensity and only $\sim 50\%$ state purity.

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1. Introduction

The water cation is important in a number of environments, including the upper atmosphere [1–3] and comet tails [4–9]. For this reason, and also because H_2O^+ is a simple cation with high frequency and dynamically distinct vibrational modes, we are interested in applying the technique of mode-selective differential reactive scattering to water cation chemistry [10,11]. For this purpose, it is necessary to generate pulsed, narrow kinetic energy H_2O^+ beams with controllable excitation, ideally in all three vibrational modes.

Tonkyn and White demonstrated rotational and vibrational selection of H_2O^+ using vacuum ultraviolet-pulsed field ionization [12], however, this technique is relatively complicated, and the work of Glab, Pratt, and co-workers suggests that single-color resonance-enhanced multiphoton ionization (REMPI) might be suitable [13]. Their results for REMPI through the origin of the $\text{C } ^1\text{B}_1$ state indicated that the ionization was highly diagonal, i.e., ions were gen-

erated in the same vibrational state that was pumped in the C state.

Band assignments for water in the 80 000–86 000 cm^{-1} range have been reported in several previous REMPI studies [14–18]. Water has a $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2$ configuration resulting in a $^1\text{A}_1$ ground electronic state. In the states probed in our studies, one electron is promoted out of the non-bonding $1b_1$ (out-of-plane O p_x) orbital. In the cation, this non-bonding electron is ionized, and the resulting changes in bond length and angle are small (see Table 1). In the $\text{C } ^1\text{B}_1$ state, the configuration is $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)(3p_{a_1})$ where the $3p_{a_1}$ orbital is a $3p_z$ Rydberg orbital, so that the resulting geometry is also quite similar to that of the cation. In absence of perturbations or other interactions that might tend to complicate the story, it is expected that the Frank–Condon factors for ionization of the C state should be quite diagonal, as was reported by Glab, Pratt and coworkers for the C origin band [19]. On the other hand, the C state is strongly predissociated [16,20], and there are several nearby electronic states that can potentially mix with the C state. It is not clear, therefore, that state selection is feasible when pumping through vibrationally excited levels of the C state. The study reported here extends the previous REMPI work to include HDO , and also includes photoelectron spectra for

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Table 1
Theoretical and measured vibrational energies for $\text{H}_2\text{O}^{(+)}$, $\text{D}_2\text{O}^{(+)}$ and $\text{HDO}^{(+)}$

		ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	Bond length (\AA)	X–O–X angle (degr)
$\text{H}_2\text{O}^{\text{a}}$	X $^1\text{A}_1$	3656.7	1594.6	3755.8	0.96 ^d	105.2 ^d
	C $^1\text{B}_1$	3180	1402	–	1.02 ^d	106.9 ^d
$\text{H}_2\text{O}^{+\text{b}}$	X $^2\text{B}_1$	3182.7	1401.7	3219.5	0.99 ^c	109.0 ^c
$\text{D}_2\text{O}^{\text{a}}$	X $^1\text{A}_1$	2761.5	1178.3	2788.1	0.96 ^d	104.8 ^d
	C $^1\text{B}_1$	2338	1038	–	1.01 ^d	107.6 ^d
$\text{D}_2\text{O}^{+\text{b}}$	X $^2\text{B}_1$	2326.7	1040.5	2392.7	–	–
HDO^{c}	X $^1\text{A}_1$	2727	1402	3707	–	–
$\text{HDO}^{+\text{b}}$	X $^2\text{B}_1$	2365.6	1236.1	3199.4	–	–

^a Vibrational energies for H_2O and D_2O from Ref. [16].

^b Vibrational energies for cations from Ref. [25].

^c Vibrational energies for HDO from Ref. [32].

^d Bond lengths and angles were calculated from rotational constants [16].

^e Calculated at QCISD/cc-pVTZ level of theory.

REMPI through all the bands in this energy range with significant intensities. While some levels of the C state are problematic, excellent pathways for generating vibrational mode-selected cations are demonstrated.

2. Experiment

The experiments were performed using a time-of-flight (TOF) mass spectrometer that can be configured to measure either mass spectra, or photoelectron kinetic energy spectra. The experimental setup, and procedures have been discussed previously [21,22]. Briefly, the instrument consists of a differentially pumped, pulsed molecular beam source and an ionization/time-of-flight chamber that contains a 75 cm long magnetically shielded flight tube. Ionization occurs just inside one end of the flight tube at the intersection of the laser and molecular beams. At the other end of the flight tube, there is a micro-channel plate (MCP) detector, appropriately biased to detect either electrons or ions, and shielded from the flight tube region by a high transmission grid. For mass spectrometry, a set of three mesh electrodes is inserted into the ionization end of the flight tube, converting it into a space-focusing geometry [22]. For photoelectron energy analysis, the space focusing electrodes are replaced by a pair of mesh electrodes. The one closer to the MCP is grounded to keep the flight tube field free, and the other electrode can be used to shift the potential of the ionization region slightly. This capability is useful for electron kinetic energy calibration, and to improve collection efficiency for slow electrons. Output signal from the MCP detector is collected and signal averaged

by a digital oscilloscope. This configuration has electron collection efficiency of only $\sim 10^{-4}$, determined by the MCP solid angle. Higher efficiencies could be achieved with guiding or imaging techniques, however, for our purposes (state-selected ion reaction dynamics), only high intensity ionization pathways are useful, and for these, the unguided TOF arrangement is adequate.

H_2O , D_2O , or $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures were seeded in He at a ratio of 1:20 with a backing pressure of one atmosphere. Water was ionized using 2 + 1 REMPI through intermediate levels in the energy range (2ω) between 80 000 and 86 000 cm^{-1} . Because REMPI through the C state is in competition with rapid non-radiative decay of the intermediate, the laser was tightly focused. The bulk of the data presented were taken using pulse energies of 500 μJ –1.5 mJ focused with a ~ 12 cm focal length lens. The focal length was varied down to 40 mm in some experiments, to examine the intensity dependence of REMPI and PES peak ratios.

Photoelectron TOF spectra were converted to energy spectra using the following relation:

$$\text{KE} = \frac{m_e}{2} \left(\frac{L}{t - t_0} \right)^2 + E_0 \quad (1)$$

where KE is the kinetic energy, L is the flight path length, t is the measured TOF, t_0 is a fitted parameter corresponding to the time offset between the laser pulse and oscilloscope sweep initiation, m_e is the mass of the electron, and E_0 is a fitted parameter accounting for potential variations (deliberate or adventitious) along the flight path. In previous studies [22,23], t_0 was found to be small (~ 10 ns). Here, the ion vibrational frequencies are large, distinct, and well known [24,25], thus for the purpose of identifying peaks in the spectra, t_0 can be neglected, and E_0 is simply taken as the potential of the ionization volume, estimated from the position of the laser focus and the voltage applied to the repeller electrode. Spectra taken with different repeller voltages provide a consistency check on the $\text{TOF} \rightarrow \text{KE}$ calibration. In the figures, the photoelectron spectra are plotted as the corresponding ion internal energy (E_{int}) spectra, using $E_{\text{int}} = 3 \cdot h\nu - \text{KE} - \text{IE}$, where $h\nu$ is the photon energy and IE is the ground state ionization energy. The ion vibrational state distributions were obtained by integrating the original TOF peaks, thereby avoiding Jacobian effects. The REMPI laser was normally polarized parallel to the TOF detection axis, however, some experiments were done with polarization rotated by a double Fresnel rhomb, as described below.

3. Results and discussion

3.1. REMPI of H_2O^+ , HDO^+ and D_2O^+

Fig. 1 summarizes the REMPI spectra obtained by monitoring the parent ion peak in the TOF mass spectrum while the laser wavelength was scanned. The relative intensities of different features in the spectra are arbitrary,

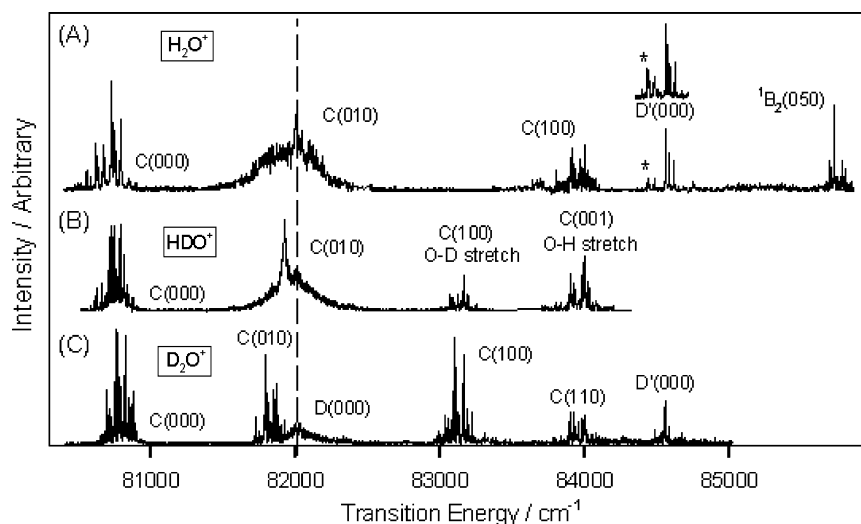


Fig. 1. REMPI scans of (A) H_2O^+ , (B) HDO^+ , (C) D_2O^+ .

because ionization efficiency is found to be strongly power dependent, and laser power varied across the spectral region studied. The strong power dependence and weak REMPI signal levels reflect the fact that the intermediate states undergo rapid non-radiative decay, as discussed in previous studies [14,16–18]. Our spectrum for H_2O is qualitatively similar to those previously measured [14,17,20], the most obvious difference being that the earlier spectra were dominated by the $\text{C}(000)$ band. The more equal band intensities in our spectra simply reflect the fact that our laser power tends to increase as we scan to the blue across this wavelength range.

The assignments in the H_2O and D_2O spectra are based on the REMPI studies of Ashfold and Dixon [14,20] and Dickinson and Softley [17]. For HDO , the assignments are based on the electronic state energies for H_2O , and vibrational frequencies for HDO^+ [26], which are expected to be similar to those for the Rydberg intermediates. Table 1 summarizes the relevant vibrational frequencies.

The $\text{C}(000)$ band is observed for all three isotopologs. For H_2O and D_2O , bands are also observed for the $\text{C}(010)$ and $\text{C}(100)$ transitions, for the D and D' origins, and for a state previously assigned as the (050) level of a linear $^1\text{B}_2$ state of H_2O [17]. For D_2O , we also observe a band around 84000 cm^{-1} , assigned as the $\text{C}(110)$ combination band, based on the expected harmonic vibrational energy expected for such a combination. The intensity of the band was too low to allow photoelectron spectroscopic characterization.

The most spectroscopically interesting feature of the spectra shown in Fig. 1 is the behavior of the $\text{C}(010)$ band as the level of deuteration is changed. For D_2O , the $\text{C}(010)$ band is well separated from the $\text{D}(000)$ band, and has sharp rotational structure, similar to that of the other C state vibrational bands. The $\text{D}(000)$ band is weak and structureless, suggesting that it undergoes rapid non-radiative decay. The D state is a $^1\text{A}_1$ state, and presumably its short lifetime reflects coupling to the lower lying B ($^1\text{A}_1$)

continuum [18,27]. For HDO , the bend frequency increases substantially, such that there starts to be strong overlap between the $\text{C}(010)$ and $\text{D}(000)$ bands. As expected, the $\text{D}(000)$ band is still broad and featureless, but in addition, the $\text{C}(010)$ rotational structure is also substantially broadened. Finally, in H_2O , the $\text{C}(010)$ and $\text{D}(000)$ bands are nearly isoenergetic, and we observe a single broad band, with some residual sharp rotational structure superimposed. This $\text{C}(010)/\text{D}(000)$ band was scanned under different power and molecular beam conditions, always resulting in strongly broadened spectra. This result is consistent with the previous $2 + 1$ REMPI studies of Dickinson and Softley [17]. Previous $3 + 1$ REMPI studies by Ashfold and Dixon [16] using circularly polarized light also show a featureless $\text{D}(000)$ state, with some residual rotational structure. Note that the C state has B_1 electronic symmetry, and the D state is A_1 , and thus electronic mixing is not allowed. Furthermore, the bend mode has A_1 symmetry, thus the $\text{C}(010)$ and $\text{D}(000)$ also are not vibronically coupled. The implication is Coriolis coupling induced by a -axis rotation, and such coupling was inferred in the $3 + 1$ REMPI study reported by Ashfold and Dixon [16]. The photoelectron spectra presented below provide additional insight into the nature of the mixing process.

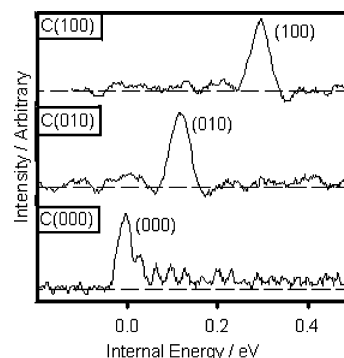
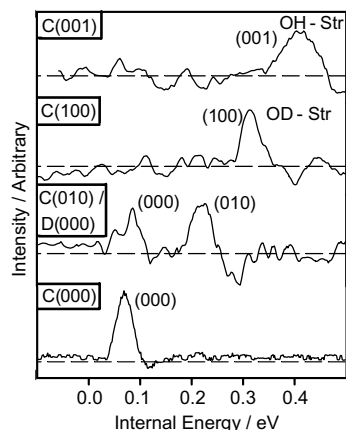
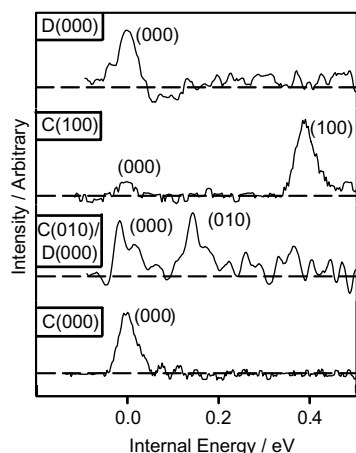


Fig. 2. D_2O^+ photoelectron spectra.

Fig. 3. HDO⁺ photoelectron spectra.Fig. 4. H₂O⁺ photoelectron spectra.

3.2. Photoelectron spectroscopy results

The photoelectron spectra (PES) for D₂O, HDO, and H₂O are presented in Figs. 2–4, respectively, plotted as intensity vs. ion internal energy, as discussed above. The spectroscopic label in a box next to each spectrum indicates the intermediate vibronic level in the REMPI process (e.g. C(000)), and the vibrational state labels (e.g. (000)) indicate the ion vibrational state associated with each PES peak. In each case the PES was taken while pumping the most intense rotational line in the REMPI band. Table 2 lists the energies (two photon) of the transitions pumped for each PES experiment. The more intense spectra (e.g. bottom spectrum in Fig. 2) show oscillatory structure extending to high internal energy (i.e., long time) from the main peaks. This ringing is an artifact of imperfect impedance matching of the detector. In general the spectra are noisy because non-radiative decay of the REMPI intermediate states leads to low signal level, especially for the mixed C(010)/D(000) bands of HDO and H₂O. Nonetheless, when the photoelectron collection efficiency is taken into account, the ion intensity is high enough to allow state-selected ion reaction studies (>100 ions/laser shot).

For D₂O, (Fig. 2) the PES are straightforward to interpret. For each vibronic level of the C state pumped, the resulting PES shows only one significant peak, and the energy of that peak corresponds to generating ions with the same vibrational excitation that was pumped in the REMPI intermediate. For the C(010) PES, there may be a small peak for ground state ions, however, the state selection is at least 90% pure. The only mode we are not able to select is the asymmetric stretch, simply because this mode is not Franck–Condon active in the C ← X transition.

For HDO (Fig. 3) we are able to select essentially pure ground state HDO⁺, and also HDO⁺ with one quantum of the OD stretch (100), or of the OH stretch (001). The situation is more complicated for the band labeled C(010)/D(000), because, as noted above, the HDO bend frequency is such that the C(010) ← X(000) band overlaps the D(000) ← X(000) band. As shown, this overlap results in a bimodal ion internal energy distribution with roughly equal populations of the (000) and (010) levels of HDO⁺.

Finally, for H₂O (Fig. 4) we can produce pure ground state ions by pumping the origin bands of either the C or D' states, consistent with the C(000) results of Glab et al. [19]. When pumping the C(100) ← X(000) transition, H₂O⁺ is produced predominantly in the (100) state, however, there appears to be a small admixture of ground state ions as well. As noted above, the H₂O C(010) and D(000) bands are strongly mixed, and as a result, the H₂O⁺ generated when pumping this band is roughly half in the ground state, and half with one quantum of bend excitation. This, and the corresponding band in HDO, are unique in generating two ion states with substantial populations. Furthermore, because the two ion states reflect the two components of the Coriolis-mixed intermediate state, we might expect different angular distributions for the two photoelectron peaks. If so, the intensity ratios do not accurately reflect the ion state branching ratios. We measured the intensity ratios of the (000) and (010) photoelectron peaks for laser polarizations parallel and perpendicular to the flight tube axis, for two different wavelengths within the broad C(010)/D(000) REMPI band. Within experimental uncertainty ($\sim \pm 20\%$) there is no polarization dependence of the intensity ratio. We also looked at the polarization dependence for the C(000) REMPI transition, and in this case where there is only one significant photoelectron peak, it is not surprising that there is no change in ion state distribution (i.e., no new peaks grow in).

Table 2 summarizes the ion vibrational state populations found for REMPI through the various intermediate levels. From the perspective of state-selected ion reaction studies, REMPI through the C state is quite promising. We are able to cleanly produce ground state ions for all three isotopologs, select both the bend and symmetric stretch for D₂O⁺, the OD and OH stretches for HDO⁺, and the symmetric stretch for H₂O⁺. The fact that for H₂O⁺ and HDO⁺ we can only produce bend-excited ions in a $\sim 50:50$ mixture with ground state ions is not a serious limitation, because we can measure reaction cross sections

Table 2
Pumping wavelengths and resulting H_2O^+ , D_2O^+ and HDO^+ state purities

2W (cm^{-1})	Intermediate C/D state	Specie vibrational distribution	Mode description
H_2O^+			
80547	000	(000) 100%	Ground state
81946	C(010)	(000) 48% (010) 52%	Bend
82289	C(010)	(000) 91% (010) 9%	Bend
81917	C(010)	(000) 67% (010) 33%	Bend
83898	C(100)	(000) 10% (100) 90%	Symmetric stretch
84561	D(000)	(000) 100%	Ground state
D_2O^+			
80779	C(000)	(000) 100%	Ground state
81798	C(010)	(010) 100%	Bend
83098	C(100)	(100) 100%	Symmetric stretch
HDO^+			
80792	C(000)	(000) 100%	Ground state
81926	C(010)	(010) 56% (000) 44%	Bend
83170	C(100)	(100) 100%	O–D Stretch
83908	C(001)	(001) 100%	O–H Stretch

Spectra were assigned by Softley [33].

for ground state ions separately, and obtain the bend-excited cross sections by subtraction [28–30]. The fact that the Franck–Condon factors for ionization of the water C state are quite diagonal, also suggests that it should be possible to produce asymmetric stretch-excited H_2O^+ and D_2O^+ by pumping the IR-active (001) mode of the neutral precursor with an IR laser, then doing 2 + 1 REMPI through the C(001) intermediate. Similar, it should be possible to generate overtone-excited ions by IR-pumping the neutral precursor, then ionizing with REMPI through the C state, although it may be that predissociation limits the level of accessible vibrational energy.

The goal in using reactant state selection to probe reaction dynamics is to be able to select a number of different modes that involve different types of motions, with high vibrational frequencies so that the resulting effects are large. Furthermore, we have shown that quasiclassical trajectories can be very helpful in deducing the mechanistic origins of the vibrational effects, which are often quite counterintuitive. We have found other state-selection systems (e.g. OCS^+ [31], H_2CO^+ [22], NO_2^+ [21]) where more vibrational modes can be selected, however, water provides an excellent combination of selectable high frequency modes, and amenability to use of high level electronic structure methods for calculating forces and gradients in trajectory calculations.

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