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ISOTOPIC EFFECTS IN XPS SPECTRA OF H₂O AND D₂O

D. NORDFORS, S. SVENSSON and U. GELIUS

Department of Physics, Uppsala University, PO Box 530, S-751 21 Uppsala, Sweden

XPS results on the valence electron spectra of H₂O and D₂O show small but clearly detectable isotope effects. For the outermost ²B₁, ²A₁, and ²B₂ states the effects are comparable with the earlier UPS-results. For the inner valence levels the isotope effects are demonstrated for the first time.

Isotope effects in UPS (Ultraviolet Photoelectron Spectroscopy) of H₂O and D₂O have been studied for almost twenty years. The optimum resolution that can be obtained in UPS is ≤ 10 meV and therefore the vibrational structure of the outermost ²B₁, ²A₁ and ²B₂ levels in the H₂O⁺ and D₂O⁺ ions is easily resolved and has been studied in great detail /1,2,15/.

For the innermost valence orbital ionization, 2a₁⁻¹, no isotope effects in the H₂O and D₂O molecules have been reported. The inner valence region of H₂O has been studied using XPS (X-ray photoelectron spectroscopy) /3/, synchrotron radiation excited electron spectroscopy /4/ and (e,2e) spectroscopy /5,6/. The interest has however been focussed to the correlation effects and the structures that appear in this energy region. Due to the resolution obtainable with XPS, (e-2e) and synchrotron radiation excited photoelectron spectroscopy in this energy range no study of the individual vibrational levels has been made. However, using high resolution XPS, isotope effects can be detected by studying the XPS line shapes, i.e. the vibration progression envelopes.

The experiment was carried out on our ESCA instrument for gas phase studies equipped with a monochromatized Al Kα X-radiation source (1487 eV) /7/. Calibration was done using the UPS ionization potential of 12.62 eV for H₂O and 12.63 eV for D₂O for the 1b₂ lone pair electrons.

The experimental spectra of the valence region of H₂O and D₂O are displayed in figs. 1a and 1b.

Figures 1a and 1b show two regions of the XPS spectra for H₂O and D₂O. The D₂O spectrum is shadowed.
Since $1b_2^{-1}$ is a vacancy in a non-bonding orbital the line shape is described by a Poisson distribution with a small fwhm. The remaining orbitals are bonding and ionization from these excite strong vibrations in the final state according to the Franck-Condon rule.

Due to electron correlation and relaxation effects the inner valence region shows a broad structure consisting of at least three peaks and a long shake-off continuum towards higher binding energies as well as a weak satellite at 27eV. Cambi et al. [3] conclude from their binary (e, 2e) experiments that the features above 25 eV are dominantly of "s-type" and can therefore be attributed from the $2a_1$ orbital.

The CI states included in the inner valence region are according to calculations /3,8,9,10,11,12/ expected to lack electrons in bonding orbitals or have excited electrons to antibonding orbitals. Most calculations predict between two and four states of considerable intensity. In attempt to achieve a physically relevant quantitative analysis we have fitted the inner valence structure (27 eV satellite excluded) with three gaussian peaks and a long and smooth continuum tail, this being the composition suggested by the eye as well as being a feasible one (with exception for the continuum) regarding previous calculations .

D$_2$O was fitted first, and the positions of the peaks were locked to the D$_2$O values while fitting H$_2$O since the ionization energies should be the same for both molecules apart from a 15 meV isotope shift which is compensated for.

It should be pointed out that the inner-valence structure may very well contain more than three states (27 eV satellite excluded) and that the lineshapes of these might vary. Due to the fitting procedures used the results from the experimental data are more uncertain for peak widths and intensities than for the peak positions.

A simple model for vibrational broadening in XPS spectra was proposed by L.J.Saethre et al./13/:

$$f = k_s \left( \frac{dE_f}{dx} \right)_{eq} \Delta X_G$$

where $f$ is the fwhm, $\Delta X_G$ the ground state vibrational amplitude, $(dE_f/dx)_{eq}$ the slope of the final state potential curve at the ground state equilibrium position, and $k_s$ a parameter which depends on the lineshape and approximations involved. In other words, the FWHM of a vibrationally broadened line is described by the ground state probability density projected on to the energy axis by the slope of the final state potential function (See fig.2).

For the multi-dimensional case the system will be confined within an ellipsoid spanned by ground state vibrational energies along the corresponding initial state normal coordinate vectors. The ground state vibrational amplitude in the one-dimensional case is for several dimensions replaced by a diameter of the ground state ellipsoid. Changing the mass of the nuclei will not effect the potential but will effect the fundamental vibrational frequencies, and thus move the confines of the ellipsoid. In this experiment the normal coordinate vectors of the substituted molecule are parallel with those of the initial one. Considering this, Saethre's model, and using the fact that the harmonic oscillator approximation applies well to the potential confining the ground state ellipsoid and assuming that $k_s$ is the same for both molecules the following crude model for the relation between the fwhm's $f$ and $f'$ for the two molecules can be deduced:

$$\left[ \sqrt{v'_j/v_j} \right]_{min} \leq f/f' \leq \left[ \sqrt{v'_j/v_j} \right]_{max}$$

where $v_j'$ and $v_j$ are corresponding fundamental frequencies of the neutral molecules.

Fig.2

The width of the spectral peak is given by the ground state vibrational amplitude projected on to the energy axis by the final state potential curve. In this paper the slope of the final state potential is used. This is shown with thick lines in the figure.
<table>
<thead>
<tr>
<th>State</th>
<th>Molecule</th>
<th>$E_B$ [eV]</th>
<th>$l_m$</th>
<th>$f_{(eV)^2}$</th>
<th>$f_{(eV)^3}$</th>
<th>Asymmetry</th>
<th>$\frac{D_2O/H_2O}{rel.}$</th>
<th>$f_{f^5}$</th>
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</thead>
<tbody>
<tr>
<td>$1b_1$</td>
<td>H$_2$O</td>
<td>12.62</td>
<td>4.01</td>
<td>0.62</td>
<td>-</td>
<td>0.20</td>
<td>1.00</td>
<td>-</td>
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<td></td>
<td>D$_2$O</td>
<td>12.63</td>
<td>4.02</td>
<td>0.61</td>
<td>-</td>
<td>0.17</td>
<td></td>
<td></td>
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<tr>
<td>$3a_1$</td>
<td>H$_2$O</td>
<td>14.87</td>
<td>12.29</td>
<td>1.31</td>
<td>1.16</td>
<td>0.09</td>
<td>1.00</td>
<td>0.85</td>
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<td></td>
<td>D$_2$O</td>
<td>14.90</td>
<td>12.32</td>
<td>1.15</td>
<td>0.99</td>
<td>0.08</td>
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<tr>
<td>$1b_2$</td>
<td>H$_2$O</td>
<td>18.83</td>
<td>3.30</td>
<td>1.97</td>
<td>1.87</td>
<td>0.11</td>
<td>1.01</td>
<td>0.84</td>
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<td></td>
<td>D$_2$O</td>
<td>18.92</td>
<td>3.33</td>
<td>1.69</td>
<td>1.58</td>
<td>0.12</td>
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<td>inner val.</td>
<td>H$_2$O</td>
<td>27.0</td>
<td>1.32</td>
<td>3.53</td>
<td>-</td>
<td>-</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>1</td>
<td>D$_2$O</td>
<td>23.34</td>
<td>1.78</td>
<td>1.68</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
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<tr>
<td>inner val.</td>
<td>H$_2$O</td>
<td>32.1</td>
<td>24.83</td>
<td>1.51</td>
<td>1.38</td>
<td>-</td>
<td>1.1</td>
<td>0.83</td>
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<tr>
<td>2</td>
<td>D$_2$O</td>
<td>28.45</td>
<td>3.49</td>
<td>3.44</td>
<td>-</td>
<td>-</td>
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<td>inner val.</td>
<td>H$_2$O</td>
<td>33.3</td>
<td>25.66</td>
<td>3.07</td>
<td>3.01</td>
<td>-</td>
<td>0.9</td>
<td>0.88</td>
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<tr>
<td>3</td>
<td>D$_2$O</td>
<td>36.5</td>
<td>10.67</td>
<td>4.15</td>
<td>4.11</td>
<td>0.89</td>
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<td>9.54</td>
<td>4.68</td>
<td>4.64</td>
<td>-</td>
<td>1.1</td>
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</tr>
<tr>
<td>4</td>
<td>D$_2$O</td>
<td>36.5</td>
<td>10.67</td>
<td>4.15</td>
<td>4.11</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Percent of valence spectrum intensity
2. $F_{s}$ = observed full width at half maximum
3. $f = (F_{s}^2 - f_s^2)^{1/2}$. The fwhm of the spectrometer function, $f_s$, is approximated to be the same as the width of the lone pair peak: 0.6 eV.
4. Asymmetry parameter [177]
5. $f$ denotes $f$ for D$_2$O
6. UPS value
7. Energy locked to corresponding value of D$_2$O
8. Weak line

The results concerning isotopic broadening of the peaks, the ratio between H$_2$O and D$_2$O peak widths, agree well with what can be expected from the arguments above, see Table 1. Having compensated for the spectrometer broadening, 0.6 eV, the relative fwhms span from 0.83 to 0.89 for the valence states. When compensating, all line shapes were assumed to be gaussian. Using optical data [14] for the fundamental vibrational frequencies $\sqrt{(\nu_{1}/\nu_{1}^{H_2O})}$ are for the different vibrational modes 0.854, 0.860 and 0.861.

Even though UPS has been much used to study isotopic effects in molecules the width of the vibrational progression envelopes have not been used for this purpose. This envelope corresponds to the XPS line profile. Using UPS measurements of H$_2$O and D$_2$O [15] it is found that the relative fwhm of the vibrational progression envelope belonging to the 3a$_{1}^{-1}$ state is 0.845 ± 0.01. The XPS data for the same state gives 0.85.
The region at 37 eV, see fig.3, displays a sudden difference between the spectra of D$_2$O and H$_2$O. A broadening of the D$_2$O peak will not reproduce H$_2$O at this energy. This could be an effect of vibronic coupling, as has been earlier studied in the electron spectrum of C$_2$H$_2$ by A. Flores-Riveros et al. [16]. It would be interesting if this could be investigated in a theoretical calculation.

Acknowledgement

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1. R. Botter and J. Carlier, Jel..Spectr.and rel.phen. 12(1977) 55-66