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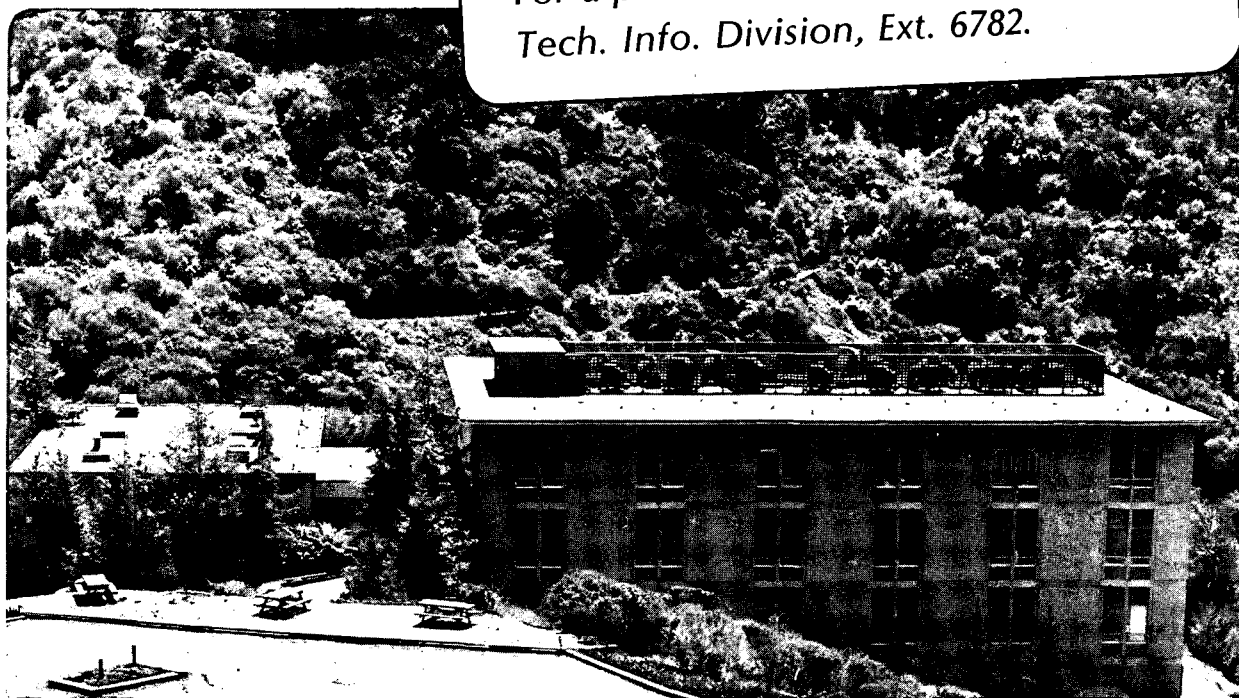
INFRARED INTENSITIES OF H_3O^+ , H_2DO^+ , HD_2O^+ AND D_3O^+

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INFRARED INTENSITIES OF H_3O^+ , H_2DO^+ , HD_2O^+ , and D_3O^+

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Saykally and co-workers have recently observed the infrared spectra^{1,2} of HCO^+ and HN_2^+ , and their spectroscopic technique shows promise for the detection of a large number of other polyatomic molecular ions. An immediate target is H_3O^+ , for which the subtleties of the rotation-inversion problem³ may make assignments difficult. In this respect, the availability of theoretical predictions for the infrared intensities may be of some help in unraveling the observed vibrational spectra. Moreover, since the deuterated molecules H_2DO^+ and HD_2O^+ remove the problems³ associated with C_{3v} symmetry, the identification of these species may in fact be simpler. Therefore, in this note we report infrared intensities for all four isotopic molecules H_3O^+ , H_2DO^+ , HD_2O^+ , and D_3O^+ .

Self-consistent field (SCF) analytical gradient techniques were used to determine equilibrium geometries and harmonic vibrational frequencies in this research. All theoretical predictions were made with the HONDO system of programs using double zeta plus polarization (DZ+P) and extended (Ext) basis sets. Earlier studies⁴ of H_3O^+ have shown that polarization functions may be required in order to converge to the accepted pyramidal geometry. The DZ+P basis for oxygen is the standard Huzinaga-Dunning⁵ (9s 5p/4s 2p) with a set of d-functions on oxygen ($\alpha = 0.8$). For each hydrogen atom, the analogous (4s 1p/2s 1p) set was used, with a scale factor of 1.2 for the s functions and polarization function orbital exponent $\alpha_p(\text{H}) = 1.0$. The larger extended basis for oxygen is the Huzinaga-Dunning⁶ (10s 6p 1d/6s 4p 1d) set with $\alpha = 0.8$, and for hydrogen van Duijneveldt's⁷ (6s 1p/4s 1p) with $\alpha = 1.0$. Infrared intensities were determined via finite differences of predicted dipole moments.

In keeping with earlier work,^{8,9} the double zeta plus polarization basis yielded a slightly pyramidal geometry (HOH = 114.4°) and a bond length somewhat longer than that of water (0.963 Å as opposed to 0.944 Å for DZ+P SCF water.) The extended basis set gave a slightly more pyramidal geometry (HOH = 114.1°) and a virtually unchanged bond length (0.962 Å). These results as well as those for the optimized D_{3h} geometry, the expected inversion transition state, are summarized in Table I.

Table II gives the double zeta plus polarization vibrational frequencies for H₃O⁺ and the various deuterated species. The complete set of harmonic vibrational frequencies shows the pyramidal structure to be a true minimum on the potential energy surface. We expect these frequencies to be about 12% too large, due to neglect of correlation effects and anharmonicities. One may obtain a more accurate estimate of the difference between the theoretical predictions and the exact (unknown) fundamentals by comparing ν_1 and ν_3 with the corresponding OH stretching frequencies in water. Previous theoretical work on water by Yamaguchi and Schaefer¹⁰ showed a difference of 12.28% between the known experimental frequencies and the DZP SCF results. Applying this correction to the harmonic frequencies in Table II, one may estimate the OH stretching fundamentals to be 3512(e) and 3393(a) [H₃O⁺], 3512(a'') and 3438(a') [H₂DO⁺], and 3476(a') [HD₂O⁺].

Infrared intensities for these vibrations, given in units of (debye)²/(Å²-amu), are also seen in Table II. The magnitude of the intensities for the various deuterated species are readily interpreted in terms of the normal modes of vibration (analogous to those defined by Herzberg¹¹ for ammonia). The addition of one deuterium splits the

degeneracy of the ν_3 mode into an a' and an a'' vibration. The a'' vibration involves little motion of the deuterium and hence we expect no significant difference between the intensity of this band and the H_3O^+ ν_3 band. On the other hand, the a' mode depends largely on the motion of the deuterium and the intensity shows a change of more than a factor of two. Similarly, for the ν_4 degenerate vibration, the substitution of a single deuterium yields an a'' band with similar intensity and an a' band with a much weaker intensity. The addition of a second deuterium makes direct analysis of the intensity magnitudes more difficult due to the increasing influence of the D-O stretch. The trideuterated species has degenerate frequencies directly analogous to those of H_3O^+ , with intensities a factor of two smaller.

The same qualitative trends are seen in the intensities and frequencies calculated using the extended basis set (Table II). The close agreement in the results for the two basis sets indicates little need to go beyond the DZP basis when predicting SCF harmonic frequencies and intensities. In particular, when the appropriate correction factor¹⁰ is applied to the extended basis results, the OH stretching fundamentals are estimated to be 3500(e) and 3396(a_1) [H_3O^+], 3500(a'') and 3435(a') [H_2DO^+], and 3469(a') [HD_2O^+].

In conclusion, it is hoped that the infrared intensities for H_3O^+ and the deuterated molecules will facilitate vibrational analysis. The stretching frequencies and intensities are expected to be fairly reliable, but it should be noted that there are obvious difficulties associated with predictions of the bending frequencies.^{3,12} We predict a barrier to inversion of 1.08 kcal/mole from the extended basis set calculation, and a barrier this small will necessitate nontrivial

corrections to the harmonic bending frequencies.

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Table I. Predicted stationary point geometries for the H_3O^+ molecular ion.

Symmetry Method	C_{3v}		D_{3h}
	DZ+P SCF	Ext SCF	Ext SCF
$r_e(\text{O-H}), \text{\AA}$	0.963	0.962	0.958
$\theta_e(\text{HOH})$	114.4°	114.1°	120.0°
out-of-plane angle	13.9°	14.3°	0.0°
Energy (hartrees)	-76.32970	-76.33808	-76.33637

Table II. Theoretical harmonic vibrational frequencies (in cm^{-1}) and infrared intensities (given in parentheses in $\frac{(\text{debye})^2}{\text{amu}}$) for H_3O^+ and three isotopically substituted forms. As noted in the text, the predicted harmonic OH stretching frequencies are expected to be $\sim 12.3\%$ above the (yet-to-be-observed) fundamentals. Note that results obtained with the double zeta plus polarization (DZ+P) basis set are given above those from the larger extended (Ext) basis set.

Normal Mode						
Species	$\nu_1(a_1)$	$\nu_2(a_1)$	$\nu_3(e)$	$\nu_4(e)$		
H_3O^+	3831(1.0)	814(13.8)	3948(13.5)	1794(3.2)		
	3868(1.2)	803(14.5)	4004(14.8)	1788(3.2)		
D_3O^+	2722(0.6)	617(6.6)	2907(7.0)	1304(1.3)		
	2749(0.7)	609(6.9)	2950(7.7)	1299(1.3)		
H_2DO^+	a'	a'	a''	a'	a''	a'
	2843(4.4)	753(11.5)	3948(13.5)	3874(5.8)	1774(3.4)	1509(1.7)
	2879(4.8)	743(12.0)	4004(14.8)	3919(6.5)	1768(3.4)	1503(1.7)
HD_2O^+	a'	a'	a'	a''	a'	a''
	2781(2.1)	686(9.0)	3913(9.9)	2908(7.2)	1625(2.7)	1332(1.2)
	2811(2.3)	677(9.4)	3964(10.9)	2950(7.9)	1620(2.7)	1326(1.2)

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