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Ab initio calculations of the vibronically averaged hyperfine coupling constants in the $1^2\Pi_u(X^2B_1, A^2A_1)$ state of the water cation

By M. STAIKOVA, B. ENGELS, M. PERIĆ† and S. D. PEYERIMHOFF
Institute für physikalische und theoretische Chemie, Universität Bonn,
Wegelerstr. 12, D-5300 Bonn 1, Federal Republic of Germany

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The hyperfine coupling constants (hfcc's) A_{iso} and A_{ij} are calculated for all centres of H_2O^+ in its two lowest lying electronic states (X^2B_1, A^2A_1) at various molecular geometries by means of the *ab initio* multireference configuration method. The vibronically averaged values of the hfcc's for the $K = 0$ and $K = 1$ levels in $H_2^{17}O$ in the energy range up to 25000 cm^{-1} are computed. The study shows that the reliable hfcc's of higher vibronic states can only be obtained if the vibronic coupling between the two electronic states is taken into account, while the lowest vibronic states of the X^2B_1 are nearly unaffected by the nuclear motion. Comparisons to the isoelectronic system NH_2 are made.

1. Introduction

In recent years, the H_2O^+ cation has been the subject of great research interest because of its importance for elementary processes in the earth's upper atmosphere and in interstellar space. The spectrum of H_2O^+ has been investigated thoroughly by both experimental and theoretical methods. In a series of papers [1–8] high-resolution emission and absorption experiments, involving the two lowest-lying electronic states X^2B_1 and A^2A_1 have been reported. The ground state of H_2O^+ has been investigated by infrared absorption spectroscopy [9, 10]. High-resolution photoelectron spectra for various isotopomers of H_2O^+ were obtained by Karlsson *et al.* [11], Dixon *et al.* [12] and Reutt *et al.* [13]. Jungen *et al.* [14, 15] derived effective bending potential curves for the two lowest-lying electronic states and applied them in the theoretical treatment of the vibronic coupling in this molecule. Kauppi and Halonen [16] derived the equilibrium structure and a complete three-dimensional potential energy surface for the ground state of the water cation, using experimental vibrational and rotational data.

Smith *et al.* [17], computed the potential surfaces for five electronic states of H_2O^+ using MCSCF, and Fortune *et al.* [18] those for the X^2B_1 and B^2B_2 states employing both self-consistent field (SCF) and MCSCF/configuration interaction (CI) methods. Carter and Meyer [19] calculated vibrational energy levels of H_2O^+ with a Hamiltonian in hyperspherical coordinates. Weis *et al.* [20] presented an extensive *ab initio* calculation of the three-dimensional potential energy and electric dipole moment functions for the electronic ground state of H_2O^+ and Reuter *et al.* [21] reported the results of an *ab initio* investigation of the vibronic structure of H_2O^+, HDO^+ and D_2O^+.

The hyperfine coupling constants (hfcc's) of the ground state of H_2O^+ have been also investigated in several studies. Knight and Steadman [22] reported electron spin

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† Permanent address: University of Belgrade, Faculty of Science, Institute of Physical Chemistry, POB 550, 11000 Belgrade, Yugoslavia.

resonance investigations of H_2O^+, HDO^+, D_2O^+ and $H_2^{17}O^+$ isolated in neon matrix at 4 K, while Strahan *et al.* [23] determined twenty four molecular constants in the ground state of the water cation, including hyperfine parameters, employing laser magnetic resonance (LMR). Theoretical investigations have been performed by Feller and Davidson [24], who used full SD-CI followed by a truncated NO-SDTQ-CI procedure. Further studies were performed by Nakatsuji *et al.* [25] and Momose *et al.* [26] who employed the SAC-CI method and Nakano *et al.* [27] who applied ROHF single CI calculation. However, none of the studies mentioned above investigated the hfcc's taking into account effects arising from the nuclear motion.

The theoretical interest in H_2O^+ concerns the fact that this molecule represents a classical example of the Renner–Teller effect. Here the degenerate state ($^2\Pi_u$), when the molecule is linear, splits on bending into a bent ground and a linear exited state. The ground electronic state X^2B_1 possesses a dominant configuration $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^1$ with an equilibrium bond angle of about 109°, while the upper A^2A_1 state with the main configuration $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^1(1b_1)^2$ has the minimum at a linear geometry.

The present study reports *ab initio* investigations of the hyperfine structure in the two lowest-lying electronic states of H_2O^+, taking into account the vibronic coupling between them. While such effects are small for the lowest vibrational level of the ground state, the vibronic coupling is expected to affect largely the mean values for the hfcc's of the levels in the energy region around the point where both electronic states touch one another at the linear molecular geometry. In the previous papers [28–33] it has been shown that a reliable reproduction of the values for the hfcc's derived by experiment can be achieved only if proper averaging of the corresponding *ab initio* calculated quantities over the vibronic states in question is performed.

2. Technical details

The isotropic and anisotropic hfcc's describe the interaction between a nuclear spin I and electron spin S. They are determined by the net unpaired electron-spin density at the nucleus and the spatial distribution for the electron-spin density. The former represents a scaler and is defined for a nucleus N as

$$A^N_{\mathrm{iso}} = \frac{8}{3}\pi g_N g \mu_N \mu_B \frac{1}{S}\left\langle \Psi \middle| \sum_{k=1}^{n} \delta(r_{Nk}) s_{zk} \middle| \Psi \right\rangle,$$

where μ_N, g_N are the nuclear magneton and nuclear g factor, respectively. The term g is the g value for the electrons in the free radical, while μ_B is the Bohr magneton. In the present work, g was set to the value of the free electron g_e, equal 2·0. Ψ represents generally the total wavefunction of the system. If instead, only averaging over the electronic coordinates is meant, Ψ is replaced by the electronic wavefunction. The corresponding hfcc's we shall call electronic hfcc's. The anisotropic part which describes the dipole–dipole interaction between the nuclear spin I and the electron spin S represents a tensor. Its Cartesian components are defined in a molecule-fixed coordinate system as

$$A^N_{ij} = g_N g_e \mu_N \mu_B \frac{1}{S}\left\langle \Psi \middle| \sum_{k=1}^{n} \left(\frac{3_{ij} - r^2\delta_{ij}}{r^5}\right)_{Nk} 2 s_{zk} \middle| \Psi \right\rangle,$$

with $i, j = x, y, z$; Nk indicates that A_{ij} is formulated with respect to the centre N.

For comparison with experimental gas phase data the anisotropic part has to be calculated within the principal axis of the tensor of inertia [31].

The molecule is assumed to lie in the *xz* plane, and for the irreducible tensor elements of A the I^r representation is used [34] ($x \equiv b,\ y \equiv c,\ z \equiv a$). In calculations of the electronic hfcc's we neglect the matrix element A_{bc} ($\in B_1$) which is off-diagonal with respect to the two electronic states in question (X^2B_1 and A^2A_1) for both the O and H atoms, as well as $A_{ac}(\in A'')$ for the H atom which connects the states $^2A'$ and $^2A''$ correlating (in the lower C_s point group) to $^2A_1$ and $^2B_1$ of C_{2v} symmetry. The terms $A_{ac}(\in A_2)$ and $A_{ab}(\in B_2)$ for the oxygen atom vanish by symmetry.

The atomic orbital (AO) basis employed in the present study for the oxygen atom consists of the (13s8p) Gaussians in the [8s5p] contraction, proposed by van Duijneveldt [35]; it is augmented by two d functions with exponents $\alpha_d = 2{\cdot}314$ and $0{\cdot}645$ [36] for a better description of the polarization effects, as well as by one additional d function ($\alpha_d = 8{\cdot}0$) which is known to improve the computation of the isotropic hfcc [37, 38]. Finally a diffuse s function $\alpha_s = 0{\cdot}02$ is added to the oxygen AO basis set. For the hydrogen atom the (8s) basis set of van Duijneveldt [35] is used in a [5s] contraction. It is supplemented by two additional s functions ($\alpha_s = 2{\cdot}593,\ 0{\cdot}01$) and three p functions ($\alpha_p = 1{\cdot}848,\ 0{\cdot}649, 0{\cdot}228$) [36].

The calculations are carried out in the standard multireference configuration interaction (MRD-CI) manner, whereas the truncation is made on the basis of the energy selection threshold T [39, 40]. In contrast to the CI treatment applied for the calculation of the potential curves and the electronic transition moments [21] in which the K-shell electrons of the oxygen atom are not correlated and the two highest virtual SCF orbitals are discarded, in the present calculations all electrons are correlated and no virtual orbitals are discarded because it has been found that the correlation effects involving the inner shell electrons are very important for the reliable calculation of the isotropic hfcc [24]. To obtain a faster convergence of the CI expansions, natural orbitals (NOs) are employed as the one-particle basis. The energy threshold of $T = 0{\cdot}15\,\mu E_h$† is used as criterion for selecting the configurations within the MRD-CI procedure. The reference space consists of 22–32 configurations (51–80 SAF). The number of configurations generated by single and double excitations with respect to these reference species is about 1 300 000 and from 17 000 to 28 000 of them are selected according to their contribution to the energy.

To improve the truncated wavefunction obtained in the MRD-CI calculation, a perturbation-like B_k method is applied [38, 41, 42]. A corrected vector, which contains the relaxation of the most important coefficient due to the neglected configurations, is used to calculate the hfcc's. The contribution of the B_k correction to the recovery of the error in the computed isotropic hfcc's is particularly large for the electronic states in which the values for A_{iso} are determined solely by spin-polarization effects. In the framework of the B_k treatment all coefficients in the CI expansion with the magnitude $\geqslant 0{\cdot}01$ (about 500 SAF) as well as those of the configurations generated by single excitations from the leading reference configuration are corrected.

The approach employed for the calculations of the vibronic wavefunction is described elsewhere [43]. The large-amplitude bending vibrations are treated employing the semi-rigid-bender Hamiltonian [44, 45]. The vibronic wavefunctions are represented by expansions in the eigenfunctions of a two-dimensional harmonic

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† $1\,E_h \approx 4{\cdot}359\,75 \times 10^{-18}$ J.

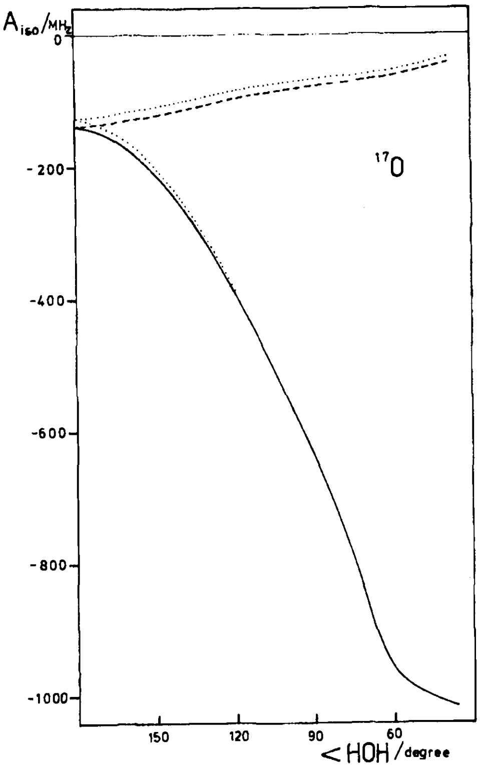

Figure 1. Bond angle dependence of the electronic mean values for the isotropic hfcc of ^{17}O in the electronic ground state X^2B_1 (dashed line) and the first excited A^2A_1 state (full line). Dotted line represents the results obtained without B_k correction.

oscillator. The vibronically-averaged hfcc's are calculated as integrals over these basis functions [32].

The electronic hfcc's are calculated as a function of the H–O–H bond angle Θ at optimized R_{OH} bond length taken from [21]. In this way the leading part of the stretch–bend interaction is incorporated in an effectively one-dimensional large-amplitude bending treatment. The equilibrium geometries assumed in the presented study correspond to the $R_{OH} = 1{\cdot}010$ Å and $\Theta = 108{\cdot}9$ at the ground state and $R_{OH} = 0{\cdot}9966$ Å and $\Theta = 180°$ at the excited state. These geometry parameters are within the range of values derived from experimental data that have been found [12, 17, 21, 23] to deviate in the ground state from each other by 0·008 Å in R_{OH} and by 1·2° in the bond angle.

3. Results and discussion

The results of the calculations of the electronic isotropic hfcc's of ^{17}O and ^{1}H are shown in figure 1 and figure 2, respectively; the components of the anisotropic hf tensor are displayed in figures 3 and 4.

In figure 1 the comparison between the values for $A_{iso}(^{17}O)$ calculated with both the truncated MRD-CI wavefunction and the vector corrected by the B_k method is also given. It can be seen that the improvement of the wavefunction shifts the values of A_{iso} in the X^2B_1 state about 10 MHz downwards. A similar trend, as expected, is

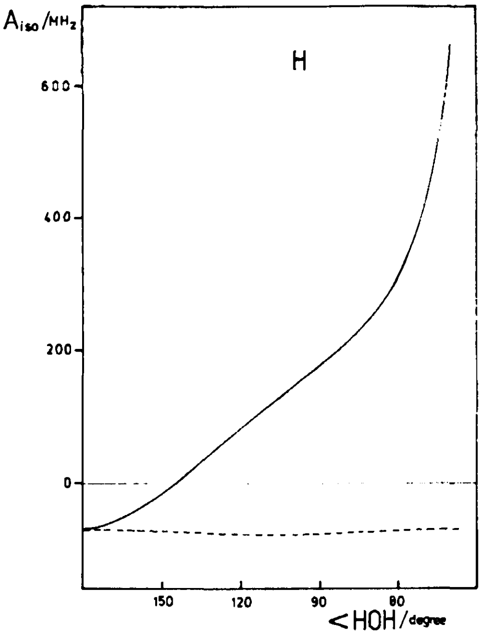

Figure 2. Bond angle dependence of the electronic mean values for the isotropic hfcc of hydrogen in the X^2B_1(dashed line) and the A^2A_1 state (full line) of the water cation.

found for $A_{iso}(^1H)$ in the ground state, the B_k correction amounts in this case to approximately 4 MHz. For the isotropic hfcc's of the A^2A_1 state as well as the anisotropic hfcc's for both states the differences are insignificant except for nearly linear geometries.

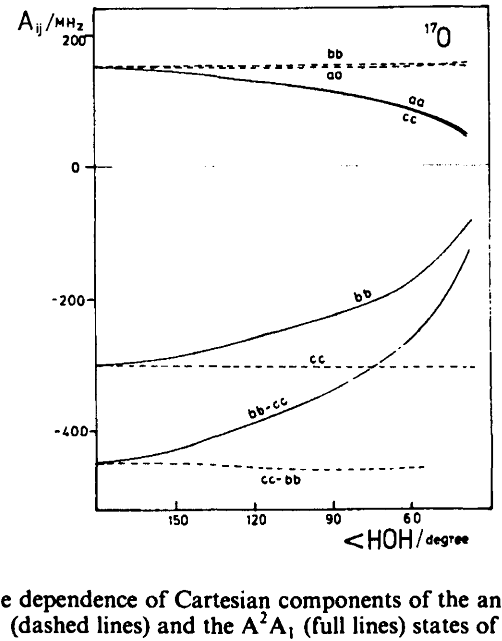

Figure 3. Bond angle dependence of Cartesian components of the anisotropic hf tensor for ^{17}O in the X^2B_1 (dashed lines) and the A^2A_1 (full lines) states of H_2O^+. The results for the ± (bb–cc) irreducible tensor components are also given.

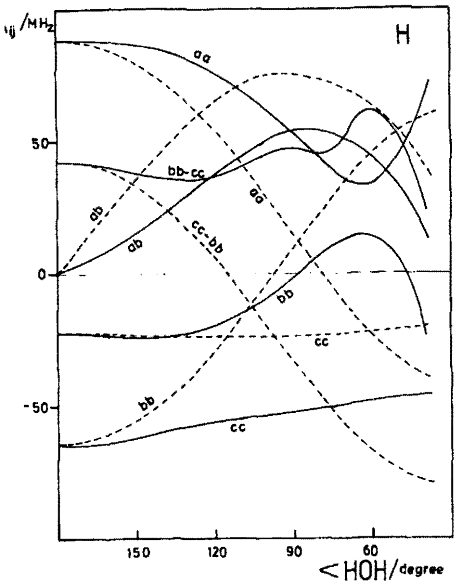

Figure 4. Components of the electronic mean values of the anisotropic hf tensor for hydrogen in the X^2B_1 and the A^2A_1 (full lines) state of H_2O^+.

From figure 1 it can be seen that the values of A_{iso} exhibit a very different dependence on the bending angle in the ground and the excited state. In the former the difference between the A_{iso} at the linear geometry ($\Theta = 180°$) and at the smallest angle of the computation ($\Theta = 40°$) is 93 MHz (−138 MHz against −45 MHz), while in the latter one the difference is larger than 900 MHz. The different behaviour in both states is easily understandable by taking into account the characters of the singly-occupied orbitals. The $1b_1$ orbital, partially populated in the ground state, represents at all values of the bond angle essentially an oxygen 2p orbital with the node in the molecular plane. Therefore the isotropic hfcc's of all centres are determined solely by spin-polarization effects. The size of the polarization effects in the X^2B_1 are found to be larger than those in the ground state of the NH_2 molecule [30]. At a linear geometry the $3a_1$ orbital which is singly occupied in the A^2A_1 state possesses a pure π character so that, as found for the X^2B_1 state, the direct contribution to the isotropic hfcc's of all centres is zero. If the molecule is bent it obtains more and more σ character from which a strong increase of the direct contribution to the isotropic hfcc's results. Because of this feature the difference between the values of A_{iso} at $\Theta = 180°$ and $\Theta = 160°$ is relatively small (about 40 MHz); with decreasing bond angle the angular dependence of $A_{iso}(^{17}O)$ becomes continuously stronger. Similar behaviour has been found for $A_{iso}(^{14}N)$ in the isoelectronic NH_2 [30]. The relatively stronger increase of the absolute values of $A_{iso}(^{17}O)$ in the H_2O^+ molecule compared to $A_{iso}(^{14}N)$ in the NH_2 molecule is due to the differences in the g_N factors of both isotopes.

The results obtained for the hydrogen show a similar dependence on the bond angle as those for $A_{iso}(^{17}O)$ (figure 2). Starting from $\Theta = 180°$ the hfcc value in the ground state changes from −76 to −81 MHz at the equilibrium geometry ($\Theta = 109°$) and to −79 MHz at $\Theta = 40°$. The minimum is found near the equilibrium geometry. The dependence on the bending angle is weaker than for the oxygen centre. For

Table 1. Comparison of the values for the isotropic hfcc's of ^1H and ^{17}O (in MHz) in the ground state X^2B_1 obtained in previous theoretical (at assumed equilibrium $R_{OH} = 0{\cdot}999$ Å and $\theta = 110{\cdot}5°$) and experimental studies with the results for the lowest lying $v_2 = 0$, $K = 0$ vibronic level computed in the present work (ETG, even-tempered Gaussians; P, e.g. no contraction)

	Ref.	Method	AO Basis	$A_{iso}(^{17}O)$	$A_{iso}(^1H)$
theor.	[24]	SD-CI	(10s,5p,1d/8s,1p)/[8s,4p,1d/6s,1p]	−57·7	−66·7
		SDTQ-CI	—	−78·5	−78·8
	[26]	SAC-CI	Dunning(9s,5p/4s)/[4s,2p/2s]	−64·7	−73·1
		—	Huzinaga(9s,5p/4s)/P	−48·8	−58·8
		—	ETG(10s,5p,1d/8s,1p)/ [8s,4p,1d/6s,1p]	−54·4	−56·95
		—	ETG(10s,5p,1d/8s,1p)/P	−53·4	−56·5
		—	ETG(11s,5p,1d/9s,1p)/P	−54·5	−57·3
	[25]	SAC-CI	STO1	−86·4	−72·1
		—	STO2	−81·1	−67·3
		—	STO3	−73·3	−67·5
		—	STO4	−77·5	−67·7
		—	STO5	−73·3	−67·5
		—	STO6	−78·9	−75·6
	present work(1)	MRDCI/Bk	(13 + 1s,8p,3d/8 + 2s,3p)/ [8 + 1s,5p,3d/5 + 2s,3p]	−90·4	−81·0
expt.	[22]			+/−83·2	+/−73·1
	[23]				+/−75·7

(1) calculated for $R_{OH} = 1{\cdot}010$ Å and $\theta = 108{\cdot}9°$.

the excited state the value for $A_{iso}(^1H)$ increases from −76 MHz at $\theta = 180°$ to 648 MHz at the smallest bond angle considered. The sharp rise at very small bond angles is likely a consequence of the presence of the third electronic state, which strongly couples with the A^2A_1 state [21]. This electronic state is completely ignored here, because the small bond angle region does not play an essential role for the vibronical averaging.

The calculated values of $A_{ij}(^{17}O)$ are given in figure 3. The very weak bond angle dependence of the anisotropic tensor elements at the X^2B_1 can be easily explained, as for NH_2, by the nature of the $1b_1$ orbital. The shape of this orbital does not change significantly during the bending because it is predominently build by the oxygen p_x atomic orbital being perpendicular to the molecular plane. The values of $A_{ij}(^{17}O)$ in the A^2A_1 state possess stronger dependences on θ than those found for X^2B_1. The variations arise from the change in the nature of the $3a_1$ orbital.

The values of the components of the anisotropic hf tensor $A_{ij}(^1H)$ for hydrogen (figure 4) show a more complicated functional dependency on the bending angle θ than those for oxygen. The behaviour with respect to θ in the ground state can be explained by the relative position between the unpaired electron and the hydrogen centre, as for the $A_{ij}(^1H)$ in the NH_2 molecule [30]. For the excited state the dependence of the components of the anisotropic hf tensor on the bending angle is stronger than for the X^2B_1 which as for the oxygen centre can be attributed to the additional effect of the change in character of the singly occupied $3a_1$ orbital.

In table 1 the experimental values are summarized together with the results of the calculation of the isotropic hfcc, taken from the literature. The results of the present paper for the lowest-lying level $v_2 = 0$, $K = 0$ of the ground electronic state are also given. Although in previous theoretical studies vibronic averaging has not been carried out, a comparison of the values for hfcc's at the equilibrium geometry with the experimental results as well as with those in the present work is reasonable because the effects arising from nuclear motion are not significant for the lowest vibrational level. As can be seen from table 1 the SD-CI calculations of Feller and Davidson [24] underestimate the values for the isotropic hfcc's for H and ^{17}O, particularly for the latter nucleus. These results were substantially improved by taking into account an estimate of the effect of triple (T) and quadruple (Q) substitutions as well as by correction for the basis set error. Momose *et al.* [26] investigated the influence of the AO basis, particularly of the various contraction schemes employed to calculate the isotropic hfcc's in their symmetry adapted cluster expansion configuration interaction (SAC-CI) computations. The results for oxygen are again appreciably below the experimentally derived value, as well as those for hydrogen with the exception of the value obtained using the Dunning's AO basis. The overall error is about 30–40% for the oxygen centre and 20–23% for hydrogen. The very good results for the [4s2p/2s] Dunning contraction is fortuitous as already pointed out by Engels and Peyerimhoff [46] for the nitrogen atom.

Nakatsuji and Izawa [25] compared the results for the isotropic hfcc's obtained employing Gaussian (GTO) and Slater type orbitals (STO). The values generated using GTOs are similar to those published in [26], i.e. they underestimate generally the experimental findings. An appreciably better agreement with the experiment is achieved in calculation with the STO basis sets. However, although the authors claim that the variationally better function (i.e. that one corresponding to the lower energy) gives more reliable hfcc's, this trend cannot be clearly seen from table 1 in which the basis sets (STO1–STO6) are classified according to an improvement of the calculated energy. The results of Nakano *et al.* [27] who employed the ROHF SCI method accompanied with the use of various sets of GTOs are similar to those published in [26], they are therefore not included in table 1.

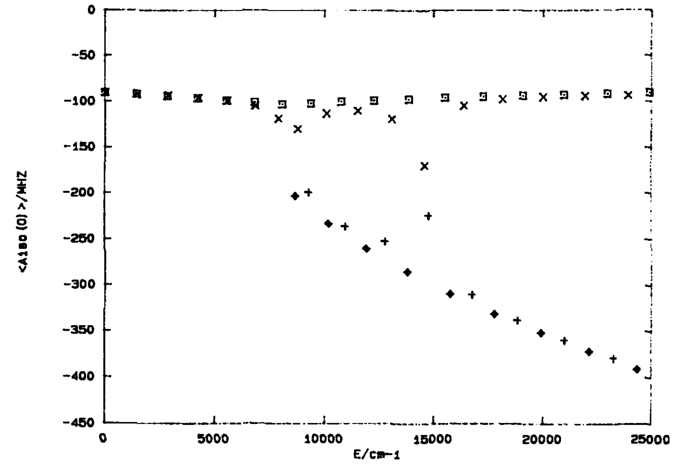

Figure 5. Computed vibronic mean values for the isotropic hfcc's of ^{17}O in H_2O^+. □: $K = 0$ vibronic levels of the X^2B_1 state; ◇: $K = 0$ levels of the A^2A_1 state; ×: $K = 1$ levels belonging predominantly to the X^2B_1 state; +: $K = 1$ levels of predominantly A^2A_1 state.

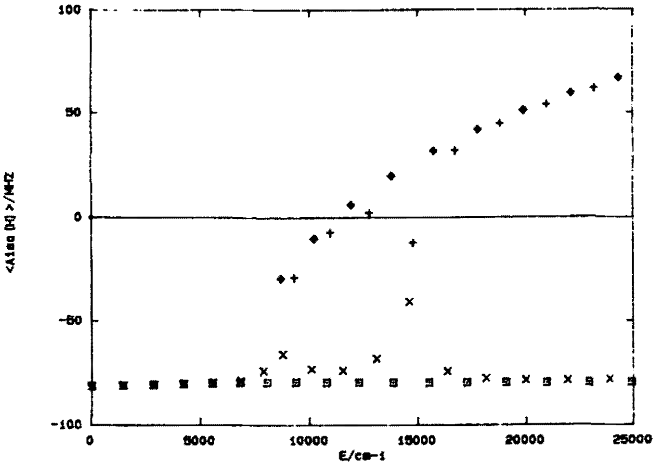

Figure 6. Vibronic mean values for the isotropic hfcc of hydrogen in $H_2^{16}O^+$. For a key to notation see figure 5.

The results of the present study are in a good agreement with the experiment. While our results for the hfcc's obtained with the truncated CI vectors underestimate the experimental findings, the values computed by applying the B_k correction (presented in table 1) slightly overestimate them (6–8%), in contrast to our experience with similar systems [28, 31, 32]. It should be noted that in the present case the vibronic averaging as well as the averaging over the stretching coordinates has an insignificant effect on the values for the isotropic hfcc's in the lowest vibrational level of H_2O^+ so that the two results given in table 1 are practically identical to the electronic mean values, computed at the equilibrium geometry which we determined ($R_{OH} = 1{\cdot}010\,\text{Å}$ and $\Theta = 108{\cdot}9°$ [21]).

From the theoretical side the calculation of the anisotropic tensor is much simpler than the treatment of the isotropic interaction. The tensor element A_{aa} given in the present work ($v_2 = 0$, $K = 0$: $A_{aa} = 40{\cdot}5\,\text{MHz}$) shows an excellent agreement with experimental data given by Strahan *et al.* ($A_{aa} = 39{\cdot}2 \pm 1{\cdot}6\,\text{MHz}$). A similar agreement is found for A_{bb} and A_{cc}, where the theoretical values of $-24{\cdot}7$ MHz and $16{\cdot}2$ MHz compares excellently to $-21{\cdot}9 \pm 1{\cdot}9$ MHz and $-17{\cdot}3 \pm 1{\cdot}9$ MHz given by Strahan *et al.* [23]. (Note that in [23] the A_{bb} and A_{cc} were interchanged.)

The results of the calculation of the vibronic mean values for the isotropic hfcc of (^{17}O) in $H_2^{17}O^+$ and (^1H) in $H_2^{17}O^+$ in the $K = 0$ and $K = 1$ rovibronic states are graphically presented in figures 5 and 6 and all calculated numbers in the energy range up to $25\,000\,\text{cm}^{-1}$ are summarized in tables 2 and 3. Bent notation of the vibronic levels is employed [32]. Averaging over the stretching coordinates is not performed because it has been found that is causes only a small change (i.e. $\leqslant 1\%$) of the values for hfcc's if the molecule is assumed to be in the zeroth stretching state. The $K = 0$ vibronic levels are unambiguously attributed to one of the two electronic states in question and in this case the variation of the vibronically averaged hfcc is caused predominantly by the geometry variation of the corresponding electronic mean values. The values of $A_{iso}(^{17}O)$ for $K = 0$ of the X^2B_1 state (figure 5) show only weak dependence on the vibrational quantum number. For the $K = 0$ states of the electronically excited state A^2A_1 the large influence of the bending angle Θ on $A_{iso}(^{17}O)$ is reflected in the sharp increase of the absolute value for $A_{iso}(^{17}O)$ as a function of the

Table 2. Calculated vibronic mean values for the isotropic hfcc and aa component of the anisotropic hf tensor in the $K = 0$ level. The superscripts $-$ and $+$ correspond to the X^2B_1 and A^2A_1 electronic states, respectively. Hfcc's in MHz.

	$H_2^{17}O^+$			$H_2^{16}O^+$		
	(E/hc)	^{17}O		(E/hc)	H	
v_2	$/cm^{-1}$	A_{iso}	A_{aa}	$/cm^{-1}$	A_{iso}	A_{aa}
0^-	0	−90·4	148	0	−81·4	40·5
1^-	1432	−92·1	148	1435	−81·1	42·4
2^-	2835	−94·1	148	2841	−80·7	44·2
3^-	4204	−96·4	148	4212	−80·3	46·1
4^-	5527	−99·0	148	5539	−80·0	48·0
5^-	6805	−101	148	6820	−79·7	49·6
6^-	8067	−103	148	8085	−79·5	49·6
0^+	8666	−203	143	8668	−29·6	86·9
7^-	9373	−102	148	9396	−79·5	47·6
1^+	10188	−233	141	10196	−10·0	85·4
8^-	10770	−100	148	10798	−79·6	44·7
2^+	11914	−260	139	11929	6·38	83·8
9^-	12264	−98·7	148	12298	−79·6	41·8
3^+	13777	−285	137	13798	20·1	82·2
10^-	13848	−97·2	148	13887	−79·7	39·2
11^-	15513	−95·9	148	15558	−79·7	36·9
4^+	15741	−309	135	15769	31·9	80·4
12^-	17255	−94·7	148	17305	−79·7	34·8
5^+	17789	−331	133	17824	42·1	78·7
13^-	19068	−93·5	148	19124	−79·7	33·0
6^+	19910	−352	132	19952	51·2	77·0
14^-	20950	−92·4	148	21013	−79·7	31·4
7^+	22098	−372	131	22146	59·4	75·3
15^-	22900	−91·3	148	22969	−79·7	29·9
8^+	24346	−391	130	24402	67·0	73·7
16^-	24916	−90·3	148	24991	−79·6	28·6

increasing vibrational quantum number v_2. The situation is quite different for the $K \neq 0$ levels (particularly for $K = 1$). In the vicinity of the barrier to linearity they are strongly shared between both upper and lower potential surfaces. The amount of mixing found for a given vibronic state is reflected in the average values of A_{iso}. Vibronic states below 7000 cm^{-1} possess practically only X^2B_1 character because the Renner–Teller interaction is negligible in the region below the barrier to linearity. Between roughly 7000 and 15 000 cm^{-1} the coupling of the both electronic states with one another is significant and the values for the hfcc's in the $K = 1$ vibronic states (figure 5) deviate from the smooth curves connecting the values for hfcc's in the $K = 0$ states. The larger influence of the Renner–Teller effect in the vicinity of the barrier to linearity is found for $v_2 = 7^-$ where the $K = 0$ and the $K = 1$ value of $A_{iso}(^{17}O)$ differ by about 30 MHz ($A_{iso}(^1H) \sim 15$ MHz). The absolute size of the difference is similar to the effects found for the NH_2 molecule.

Above the barrier particularly strong coupling can be found if two $K = 1$ vibronic levels lying accidentally close to one another. In the present work this was found for $v_2 = 11^-$ and $v_2 = 3^+$. It should be stressed, however, that these local interactions cannot be described reliably in pure *ab initio* calculations of the present kind because

Table 3. Calculated vibronic mean values for the isotropic hfcc, *aa* and *bb–cc* component of the anisotropic hf tensor in the $K = 1$ level. The superscripts – and + correspond to the X^2B_1 and A^2A_1 component electronic states, respectively. Hfcc's in MHz.

	$H_2^{17}O^+$				$H_2^{16}O^+$			
	(E/hc)	^{17}O			(E/hc)	H		
v_2	$/cm^{-1}$	A_{iso}	A_{aa}	$A_{bb}-A_{cc}$	$/cm^{-1}$	A_{iso}	A_{aa}	$A_{bb}-A_{cc}$
0^-	29	-90·4	148	-455	29	-81·4	40·4	-9·21
1^-	1465	-92·0	148	-454	1469	-81·1	42·3	-6·98
2^-	2876	-93·7	148	-454	2882	-80·7	44·0	-4·92
3^-	4253	-96·2	148	-454	4262	-80·3	45·8	-2·84
4^-	5586	-99·1	148	-453	5598	-79·8	47·9	-0·404
5^-	6844	-105	148	-453	6857	-78·6	51·9	3·97
6^-	7894	-119	148	-450	7907	-74·0	61·1	13·6
7^-	8773	-130	147	-447	8788	-65·6	60·3	12·5
0^+	9282	-199	143	-433	9290	-29·3	79·0	31·2
8^-	10085	-113	147	-451	10109	-73·3	50·1	2·41
1^+	10949	-236	140	-424	10962	-6·87	81·1	34·5
9^-	11527	-110	147	-451	11557	-74·2	46·0	-1·65
2^+	12757	-252	139	-420	12777	3·36	78·0	32·8
10^-	13078	-119	147	-449	13112	-69·1	45·3	-2·09
11^-	14604	-170	144	-438	14640	-36·0	55·6	9·93
3^+	14783	-224	140	-426	14815	-17·1	63·6	18·9
12^-	16359	-105	147	-451	16407	-73·9	37·9	-9·34
4^+	16747	-310	135	-407	16780	31·6	77·5	36·8
13^-	18147	-97·7	148	-453	18200	-77·6	34·5	-12·8
5^+	18828	-338	133	-401	18867	44·9	77·1	39·2
14^-	19999	-95·3	148	-453	20058	-78·4	32·5	-14·7
6^+	20983	-360	132	-396	21028	54·1	75·7	40·4
15^-	21917	-94·0	148	-453	21983	-78·5	30·9	-16·2
7^+	23201	-379	130	-392	23258	61·9	74·0	41·3
16^-	23902	-93·5	148	-453	23973	-78·3	29·6	-17·4

the amount of mixing of two vibronic levels with one another is extremely dependent on the position of the theoretically unperturbed vibrational species, belonging to different electronic states and coupled via the Renner–Teller effect. Since the error in computing the high vibrational levels may exceed some hundred wave-numbers, it is clear that values for the vibronically averaged hfcc's in the states assigned to 11^- and 3^+ should be looked upon only as an illustration of what happens when two $K \neq 0$ levels lie as close as 180 cm^{-1} to one another.

Far above the barrier the behaviour of the vibronically-averaged values for hfcc's becomes again regular (practically the same as that of their $K = 0$ counterparts), the only exceptions being caused by possible local interactions mentioned above. Similar trends as found for $A_{iso}(^{17}O)$ can be seen in the bending quantum number dependence of the isotopic hfcc's of hydrogen (tables 1 and 2, figure 6).

In tables 2 and 3 the elements of the dipolar tensors for both ^{17}O and ^{1}H centres are summarized. We present the results for vibronically averaged values of the irreducible components of the anisotropic hf tensor which can be extract from experiments (see [32]). We have also computed the vibronic mean values for the hfcc's in other isotopomers of the water cation ($H_2^{16}O^+$, $HD^{16}O^+$ and $D_2^{16}O^+$). The tables with these results can be obtained upon request.

4. Conclusions

In the present study electronic mean values for the hfcc's in the X^2B_1 and the A^2A_1 states of H_2O^+ are calculated as a function of the bond angle Θ. The vibronically-averaged hfcc's are then computed for $K = 0$ and $K = 1$ vibronic states employing the *ab initio* bending potential curves. The study shows that consideration of the Renner–Teller effect plays an important role for a quantitative description of the hfcc's.

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