

Infrared Transition Intensities for Water: A Comparison of *ab Initio* and Fitted Dipole Moment Surfaces

A. E. LYNAS-GRAY,* STEVEN MILLER,† AND JONATHAN TENNYSON†

* *Department of Physics, University of Oxford, Keble Road, Oxford OX1 3RH, United Kingdom;*
and † *Department of Physics and Astronomy, University College London,*
Gower Street, London WC1E 6BT, United Kingdom

Four surfaces giving the dipole moment for water as a function of internuclear separations are compared. These surfaces are used to predict intensities for transitions involving $J = 0 - 1$ and Q -branch transitions for $J = 5$ and 10. These intensities are compared with observed transition intensities for H_2^{16}O from the HITRAN database. For reasons of computational efficiency these calculations were performed with a new discrete variable representation (DVR) transition intensity program, DIPOLE3. Our comparisons suggest that the recent *ab initio* dipole moment surfaces of Gabriel *et al.* (*J. Chem. Phys.* **99**, 897–900 (1993)) is the most reliable. These surfaces give accurate linestrengths for transitions whose intensity vary by nine orders of magnitude and promise good extrapolation properties. The calculations also point to a number of transitions which differ significantly from the values tabulated in HITRAN. © 1995 Academic Press, Inc.

1. INTRODUCTION

The high-resolution *infrared* spectrum of water is, for obvious reasons, one of the most thoroughly studied. So, for example, the HITRAN atmospheric linelist (1) catalogs some 30 000 rotation–vibration transitions due to H_2^{16}O . We are interested in the *infrared* absorption spectrum of hot water, particularly as it affects the atmospheres of cool stars. At 2000–4000 K, temperatures typically found in these atmospheres, it has been estimated (2) that up to 10^9 transitions will need to be considered. Our initial calculations (3) have shown that explicit use of a linelist of 6.4×10^6 transitions yielded significant improvements to model atmosphere calculations for the M-dwarf star VB10 and dramatically altered opacity functions (4).

The calculation of reliable *infrared* linelists relies on the availability of three things: potential energy surfaces, dipole moment surfaces, and the means to calculate accurate rotation–vibration spectra. For triatomic molecules the latter problem has been largely solved (5, 6).

In 1991, Fernley *et al.* (7) published a systematic comparison of available potential energy surfaces for water. They suggested that the spectroscopically determined potential due to Jensen (8) was the most reliable. Since then Jensen's potential has been used by a number of workers as the starting point for developing improved potentials (9–11). Indeed the recent potential due to Polyansky *et al.* (11) is of near-experimental accuracy and, in contrast to the earlier potentials, shows excellent extrapolation properties with rotational excitation.

Fernley *et al.* also noted the lack of a reliable dipole moment surface for water. Indeed at that time the best surface appeared to be the *ab initio* calculation due to Rosenberg *et al.* (12) published in 1976. However, this surface has a very limited range, for instance, considering angular displacements of only 3° from equilibrium, and is therefore not suitable for the type of calculation envisaged here. Recently,

however, a number of new dipole moment surfaces for water have been published (13–16). In this work we compare the spectroscopically determined dipole moment surfaces due to Wattson and Rothman (13) with the *ab initio* surface due to Gabriel *et al.* (14) and two *ab initio* surfaces given by Jørgensen and Jensen (15). Further details of these surfaces are given below. The surfaces of Kjaergaard *et al.* (16) were obtained using a lower level of theory and have not been tested.

For all of the surfaces quoted above, their authors computed vibrational band strengths; Jørgensen and Jensen (15), in particular, performed an extensive study which considered some 80 000 vibrational band strengths. In this work we choose to focus on the intensity of individual rotation–vibration transitions. This is because vibration band strengths cannot be directly measured and their calculation necessarily involves approximations (17). Indeed a direct comparison by Gabriel *et al.* (14) shows significant differences between band intensities calculated, as is usual, by using only rotationless wavefunctions and those obtained for the same dipole moment surface by summing over all the relevant rotation–vibration transitions.

So as not to bias our calculations, comparisons were performed starting from states with rotational angular momentum, J , of 0, 1, 5, and 10. There is little accurate data available for such a comparison on transitions with $J \geq 20$.

All the calculations presented here used rotation–vibration wavefunctions calculated using high-accuracy variational calculations and Hamiltonians with kinetic operators which are exact with the Born–Oppenheimer approximation. The use of such wavefunctions with arbitrarily defined dipole moment surfaces necessarily leads to the calculation of many multidimensional integrals which have to be evaluated numerically. To make this procedure computationally tractable we have developed a new program, DIPOLE3, which calculates rotation–vibration transition dipole moments within the discrete variable representation (DVR). The theory for this is given below.

2. DIPOLE TRANSITION CALCULATIONS

Our rotation–vibration wavefunctions are represented using basis sets in three internal coordinates (r_1, r_2, θ); in the present work these are Radau coordinates. The radial basis functions are represented by Morse oscillator-like functions (18), denoted $|m\rangle$ and $|n\rangle$ respectively, and the angular coordinate by associated Legendre functions $|j, k\rangle$, where k is the projection of the rotational angular momentum onto the body-fixed z axis. Wavefunctions are therefore stored coefficients of this basis set expansion. In particular, $d_{k'j'm'n}^{Jp\ell}$ gives the coefficient of basis function $|m, n, j, k\rangle$ for the wavefunction of the ℓ th state with rotational angular momentum J and rotational parity p .

Miller *et al.* (19) derived a general formula for the dipole transition linestrength

$$S(f-i) = \frac{1}{4} [(2J'+1)(2J''+1)] \\ \times \left[\sum_{\nu=-1}^{+1} \sum_{\lambda=|\nu|} \sum_{k=p''}^{J''} \sum_{j'=j''} a(\nu, \nu+k, \lambda) [(2j'+1)(2j''+1)]^{1/2} \right. \\ \times \begin{pmatrix} J' & 1 & J'' \\ -k-\nu & \nu & k \end{pmatrix} \begin{pmatrix} j' & \lambda & j'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j' & \lambda & j'' \\ -k-\nu & \nu & k \end{pmatrix} \\ \left. \times \sum_{m''n''} \sum_{m'n'} B_{\lambda,\nu}^{m''m'n''} \times d_{k'j'm'n}^{Jp'\ell'} d_{k''j''m''n''}^{J''p''\ell''} [(-1)^{J'+J''+1} + (-1)^{p''+p'}] \right]^2, \quad (1)$$

where

$$\begin{aligned} a(0, n, \lambda) &= 1, & 0 \leq n \leq J', \\ a(\pm 1, 0, \lambda) &= -[\lambda(\lambda + 1)]^{1/2}, \\ a(\pm 1, n, \lambda) &= -[\lambda(\lambda + 1)/2]^{1/2}, & 0 < n \leq J', \\ a(\nu, n, \lambda) &= 0, & n < 0, n > J', \nu = 0, \pm 1. \end{aligned}$$

and the radial integrals are given by

$$B_{\lambda, \nu}^{m'n'n''} = \langle m'n' | C_{\lambda, \nu}(r_1, r_2) | m''n'' \rangle. \quad (2)$$

$C_{\lambda, \nu}$ is obtained by performing an (associated) Legendre polynomial expansion of the $\nu = 0$ and $\nu = 1$ dipole moment surfaces at each value of (r_1, r_2) (18, 19).

Usually (18, 19) matrix elements (2) are evaluated using Gauss-Laguerre quadrature in two dimensions and the results fed into Eq. (1). However for calculations, such as the present one, where large basis set expansions are used and high values of J considered, the seven-dimensional summation implied by this procedure becomes computationally very expensive. To avoid this problem we have used the more advantageous properties of the discrete variable representation (DVR) to evaluate the radial integrals.

In the radial coordinates, the DVR is related to the basis set expansion via the transformations

$$T_m^\alpha = (w_\alpha)^{1/2} |m_\alpha\rangle \quad (3)$$

and

$$T_n^\beta = (w_\beta)^{1/2} |n_\beta\rangle, \quad (4)$$

where (α, β) and (w_α, w_β) are the points and weights of the appropriate Gauss-Laguerre quadrature scheme (5, 20). Using these transformations, the radial matrix elements become

$$B_{\lambda, \nu}^{\alpha'\beta'\alpha''\beta''} = \sum_{m'n'} T_{m'}^{\alpha'} T_{n'}^{\beta'} B_{\lambda, \nu}^{m'n'n''} T_{m''}^{\alpha''} T_{n''}^{\beta''} = \delta_{\alpha'\alpha''} \delta_{\beta'\beta''} C_{\lambda, \nu}(\alpha', \beta'). \quad (5)$$

These matrix elements are diagonal as a consequence of the so-called quadrature approximation (5, 21). We can therefore define

$$b_{\lambda, \nu}^{\alpha\beta} = B_{\lambda, \nu}^{\alpha\beta\alpha\beta}. \quad (6)$$

Similarly, wavefunction coefficients can be transformed to a radial DVR using

$$c_{k|\alpha\beta}^{j\rho\ell} = \sum_{mn} T_m^\alpha T_n^\beta d_{k|mn}^{j\rho\ell} \quad (7)$$

where the new coefficients, c , explicitly give the amplitude of the wavefunction at the grid point (α, β) .

Inserting these radial DVR expressions into the formula for the transition line-strengths gives

$$\begin{aligned}
S(f-i) &= \frac{1}{4}[(2J' + 1)(2J'' + 1)] \\
&\times \left[\sum_{\nu=-1}^{+1} \sum_{\lambda=|\nu|}^{J'} \sum_{k=p'}^{J''} a(\nu, \nu + k, \lambda) [(2j' + 1)(2j'' + 1)]^{1/2} \right. \\
&\times \begin{pmatrix} J' & 1 & J'' \\ -k-\nu & \nu & k \end{pmatrix} \begin{pmatrix} j' & \lambda & j'' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} j' & \lambda & j'' \\ -k-\nu & \nu & k \end{pmatrix} \\
&\left. \times \sum_{\alpha\beta} b_{\lambda,\nu}^{\alpha\beta} \times c_{k'j'\alpha\beta}^{j'p'\ell'} c_{k''j''\alpha\beta}^{j''p''\ell''} [(-1)^{J'+J''+1} + (-1)^{p'+p''}] \right]^2. \quad (8)
\end{aligned}$$

It is immediately apparent that the dimensionality of the summations has been reduced from seven to five by the transformations. In practical applications we have found that evaluating expression (8) instead of (1) has saved a factor of up to 80 in CPU time.

A program to calculate dipole transition intensities, DIPOLE3, has been written as part of our upgraded 3D DVR program suite (22). For this and related work we wrote a small program explicitly to transform our wavefunction coefficients from radial basis sets to radial DVR using transformation (6). Future studies will probably be performed using the DVR directly.

3. DIPOLE MOMENT SURFACES

Expansions of the water dipole as derivatives with respect to normal coordinate at the equilibrium geometry are well developed; see, for example, Flaud *et al.* (23). However, as in the case of potential energy surfaces represented by force constants, it remains unclear how best to continue these expansions away from equilibrium. We have therefore chosen only to consider dipole functions which explicitly give values for the components of the dipole as a function of the internal coordinates. We have identified four such dipole moment surfaces which would appear to be accurate enough to warrant detailed investigation.

Watson and Rothman (WR) (13) adjusted the parameters in their dipole function using the $Q(1)$ transitions up to $10\,000\text{ cm}^{-1}$ of H_2^{16}O . They took their experimental data from HITRAN. They started their fit from the *ab initio* data of Ermler and Krone (24), but noted many of the coefficients changed significantly from the *ab initio* values. WR's fitting procedure adjusted 29 parameters but did not appear to consider the possibility that some of these parameters might be correlated or poorly determined by the data. This consideration may well adversely affect the extrapolation properties of WR's dipole moment surfaces.

Jørgensen and Jensen (JJ) (15) used the *ab initio* CASSCF scheme to compute two dipole moment surfaces. Both surfaces used a basis comprising 101 contracted Gaussian type orbitals (GTOs) but differ in the level of electron correlation included in the calculation. Their first surface (JJ1) used a CASSCF scheme with 924 configurations in their multiconfiguration expansion. Their second surface (JJ2) augmented this CASSCF calculation with a multireference configuration interaction (CI) calculation. Readers are referred to the original paper for further details.

The final surface we consider is the *ab initio* one due to Gabriel *et al.* (GRRCH) (14). These workers used a 130 contracted GTO basis and the coupled electron pairs approximation (CEPA-1). The main differences between this calculation and those of JJ is that GRRCH's basis contains basic functions with higher angular momentum

TABLE I
Comparison of Observed (from HITRAN (*I*)) and Calculated
Linestrengths and Frequencies for $R(0)$ Transitions

ω / cm^{-1}	E'' / cm^{-1}	$S(f - i) / D^2$			$\nu_1 \nu_2 \nu_3$	$JK_a K_c$
		WR	HITRAN	JJ1		
obs	obs	GRRCH		JJ2	upper	upper
calc	calc				lower	lower
37.14	0.00	3.42(+0)	3.45(+0)	3.65(+0)	000	1 1 1
37.08	0.00	3.40(+0)		3.64(+0)	000	0 0 0
1634.97	0.00	1.52(-2)	1.50(-2)	1.70(-2)	010	1 1 1
1634.52	0.00	1.51(-2)		1.69(-2)	000	0 0 0
3196.09	0.00	5.31(-5)	4.88(-5)	8.29(-5)	020	1 1 1
3196.44	0.00	6.31(-5)		6.37(-5)	000	0 0 0
3693.29	0.00	1.71(-4)	1.76(-4)	3.56(-4)	100	1 1 1
3692.76	0.00	1.31(-4)		3.66(-4)	000	0 0 0
4717.47	0.00	8.99(-8)	1.00(-7)	8.18(-9)	030	1 1 1
4718.28	0.00	2.18(-7)		2.78(-8)	000	0 0 0
5274.16	0.00	5.23(-6)	6.65(-6)	8.21(-6)	110	1 1 1
5273.55	0.00	6.84(-6)		8.57(-6)	000	0 0 0
5354.87	0.00	7.11(-4)	3.79(-4)	3.25(-4)	011	1 0 1
5355.75	0.00	3.77(-4)		3.00(-4)	000	0 0 0
6194.79	0.00	6.07(-9)	1.36(-9)	1.59(-8)	040	1 1 1
6194.61	0.00	3.74(-9)		2.03(-7)	000	0 0 0
6818.31	0.00	5.01(-7)	5.63(-7)	1.13(-6)	120	1 1 1
6818.37	0.00	5.81(-7)		9.59(-7)	000	0 0 0
6895.15	0.00	1.58(-5)	1.20(-5)	6.99(-6)	021	1 0 1
6897.19	0.00	1.31(-5)		7.30(-6)	000	0 0 0
7236.81	0.00	1.95(-5)	2.21(-5)	3.36(-5)	200	1 1 1
7238.08	0.00	2.25(-5)		3.38(-5)	000	0 0 0
7273.00	0.00	9.83(-5)	1.31(-4)	2.01(-4)	101	1 0 1
7274.24	0.00	1.61(-4)		2.56(-4)	000	0 0 0
7479.64	0.00	9.86(-7)	6.25(-7)	4.72(-7)	002	1 1 1
7479.70	0.00	1.35(-6)		2.89(-7)	000	0 0 0
8323.29	-1.00	6.70(-8)	6.70(-8)	3.04(-8)	130	1 1 1
8322.75	0.00	8.75(-8)		3.12(-8)	000	0 0 0

on both the O and H atoms, and the CEPA method probably yields a greater proportion of the electron correlation than the CASSCF-CI method of JJ.

We note that JJ, for both their surfaces, used a functional form which forces the dipole to display qualitatively correct behaviour for linear geometries. The dipole moment surfaces of WR and GRRCH are both expressed as power series expansions about equilibrium and thus do not behave correctly at linearity. When Fernley *et al.* (7) compared potential energy surfaces, they found that surfaces they considered which did not give the correct saddle point behavior at linearity gave erratic results for states with significant bending excitation. Our results below show no such analogous behavior for the dipole moment surfaces, probably because the transitions contained in HITRAN are not sensitive to linear geometries. However, the possibility of unreliable results for states with significant bending excitation must be borne in mind.

TABLE I—Continued

ω / cm^{-1}	E'' / cm^{-1}	$S(f-i) / D^2$			$v_1 v_2 v_3$	$lK_a K_c$
		WR GRRCH	HITRAN	JJ1 JJ2		
8799.64	-1.00	2.26(-8)	1.55(-7)	1.04(-9)	210	1 1 1
8801.17	0.00	2.27(-7)		1.33(-9)	000	0 0 0
8830.23	-1.00	1.35(-5)	9.30(-6)	6.42(-6)	111	1 0 1
8832.94	0.00	1.13(-5)		4.35(-6)	000	0 0 0
40.22	1594.75	3.31(+0)	3.32(+0)	3.52(+0)	010	1 1 1
40.18	1594.34	3.28(+0)		3.52(+0)	010	0 0 0
1601.35	1594.75	3.14(-2)	3.51(-2)	3.51(-2)	020	1 1 1
1602.10	1594.34	3.14(-2)		3.49(-2)	010	0 0 0
2098.55	1594.75	3.47(-4)	4.60(-4)	3.80(-4)	100	1 1 1
2098.42	1594.34	3.32(-4)		3.77(-4)	010	0 0 0
2184.75	1594.75	1.15(-3)	7.31(-4)	5.63(-4)	001	1 0 1
2185.23	1594.34	6.48(-4)		5.24(-4)	010	0 0 0
3122.72	1594.75	1.45(-4)	1.33(-4)	2.35(-4)	030	1 1 1
3123.94	1594.34	1.84(-4)		1.98(-4)	010	0 0 0
3679.41	1594.75	1.08(-4)	1.57(-4)	2.59(-4)	110	1 1 1
3679.21	1594.34	7.42(-5)		2.72(-4)	010	0 0 0
3760.13	1594.75	4.30(-3)	4.71(-3)	6.21(-3)	011	1 0 1
3761.41	1594.34	5.40(-3)		6.35(-3)	010	0 0 0
6802.74	1594.75	4.69(-5)	3.48(-5)	2.51(-5)	031	1 0 1
6805.05	1594.34	3.81(-5)		2.61(-5)	010	0 0 0
44.46	3151.63	3.18(+0)	2.52(+0)	3.38(+0)	020	1 1 1
44.39	3152.05	3.16(+0)		3.38(+0)	020	0 0 0
1565.84	3151.63	4.89(-2)	4.18(-2)	5.46(-2)	030	1 1 1
1566.23	3152.05	4.93(-2)		5.43(-2)	020	0 0 0

4. CALCULATIONS AND DISCUSSION

The calculations were performed using the H_2^{16}O wavefunctions produced for previous astronomically motivated studies (3, 4). These calculations were performed in Radau coordinates and used the spectroscopically determined potential of Jensen (8). The wavefunctions were expanded in terms of Morse oscillator-like functions for the stretches and (associated) Legendre functions for the bends using previously optimized parameters (7). Rotationally excited states were generated using the two-step variational method of Tennyson and Sutcliffe (25) and were performed using the TRIATOM program suite (18).

Tables I and II compare the present results for all the $P(1)$ and $R(0)$ transitions of H_2^{16}O with those tabulated in HITRAN. The HITRAN line intensities are thought to be less than 10% in error in most cases, although in a few cases errors of up to 50% are expected (1). In the case of our previous comparison of potential energy surfaces it was possible to give a reliable quantitative measure of the performance of each surface by comparing the standard deviation of (observed - calculated) band origins and term values. The variation in transition intensities over nearly ten orders of magnitude makes such measures, which would be entirely dominated by the errors in the

TABLE II
Comparison of Observed (from HITRAN (*I*)) and Calculated
Linestrengths and Frequencies for *P*(1) Transitions

ω / cm^{-1}	E'' / cm^{-1}	$S(f-1) / D^2$			$v_1 v_2 v_3$	$JK_a K_c$
		WR GRRCH	HITRAN	JJ1 JJ2		
3732.13	23.79	1.34(-3)	1.70(-3)	2.12(-3)	001	0 0 0
3732.16	23.80	1.75(-3)		2.18(-3)	000	1 0 1
5307.47	23.79	2.42(-4)	1.30(-4)	1.12(-4)	011	0 0 0
5308.32	23.80	1.30(-4)		1.04(-4)	000	1 0 1
1557.61	37.14	6.27(-3)	6.15(-3)	6.97(-3)	010	0 0 0
1557.26	37.09	6.23(-3)		6.97(-3)	000	1 1 1
3114.49	37.14	2.00(-5)	1.86(-5)	3.13(-5)	020	0 0 0
3114.96	37.09	2.42(-5)		2.46(-5)	000	1 1 1
3619.92	37.14	9.27(-5)	9.24(-5)	1.70(-4)	100	0 0 0
3619.44	37.09	7.53(-5)		1.74(-4)	000	1 1 1
4629.66	37.14	4.87(-8)	4.40(-8)	3.97(-8)	030	0 0 0
4630.66	37.09	8.30(-8)		1.36(-8)	000	1 1 1
5197.84	37.14	2.03(-6)	2.26(-6)	2.89(-6)	110	0 0 0
5197.26	37.09	2.54(-6)		2.97(-6)	000	1 1 1
6096.88	37.14	9.3(-10)	8.5(-10)	5.47(-9)	040	0 0 0
6097.09	37.09	1.89(-9)		6.73(-9)	000	1 1 1
6737.96	37.14	1.90(-7)	2.12(-7)	4.23(-7)	120	0 0 0
6738.02	37.09	2.28(-7)		3.37(-7)	000	1 1 1
2137.37	1618.56	3.67(-4)	2.35(-4)	1.75(-4)	001	0 0 0
2137.81	1618.16	2.03(-4)		1.62(-4)	010	1 0 1
3712.71	1618.56	1.56(-3)	1.70(-3)	2.22(-3)	011	0 0 0
3713.96	1618.16	1.94(-3)		2.27(-3)	010	1 0 1
1516.66	1634.97	1.34(-2)	1.48(-2)	1.49(-2)	020	0 0 0
1517.53	1634.52	1.34(-2)		1.48(-2)	010	1 1 1
2022.08	1634.97	1.23(-4)	1.46(-4)	1.35(-4)	100	0 0 0
2022.01	1634.52	1.18(-4)		1.33(-4)	010	1 1 1
3031.82	1634.97	5.43(-5)	5.00(-5)	8.77(-5)	030	0 0 0
3033.23	1634.52	6.97(-5)		7.50(-5)	010	1 1 1
3600.01	1634.97	6.70(-5)	8.40(-5)	1.35(-4)	110	0 0 0
3599.83	1634.52	5.17(-5)		1.40(-4)	010	1 1 1
1470.70	3196.09	2.18(-2)	1.74(-2)	2.42(-2)	030	0 0 0
1471.31	3196.44	2.19(-2)		2.40(-2)	020	1 1 1

strong transitions, unhelpful. Similarly a comparison of percentage errors would be dominated by the errors in the very weak transitions.

To obtain meaningful comparisons over the entire range of line intensities we have therefore chosen to plot observed against calculated on a logarithmic scale. Figure 1 presents the data of Tables I and II in this fashion; Figs. 2 and 3 give a comparison of the *Q*(5) and *Q*(10) lines, respectively, with all those found in the HITRAN database. In these figures perfect agreement is represented by the diagonal line. The scatter about this line is a measure of the accuracy of each surface.

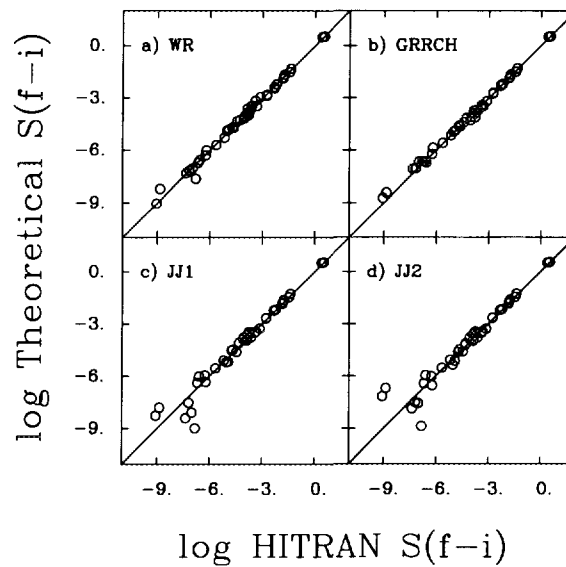


FIG. 1. Comparison of calculated linestrengths, in D^2 , for $J = 0-1$ with all the transitions on the HITRAN database. The calculations used the dipole moment surfaces of (a) Watson and Rothman (WR) (13); (b) Gabriel *et al.* (GRRCH) (14); (c) Jørgensen and Jensen (JJ1) (15), CASSCF calculation; and (d) Jørgensen and Jensen (JJ2) (15), CASSCF-CI calculation.

It is clear from the figures that all four surfaces perform well and that the amount of scatter, particularly for linestrengths greater than about $10^{-3} D^2$, is pleasingly small. For the $J = 5$ and 10 transitions and some of the weaker lines, there are a few cases

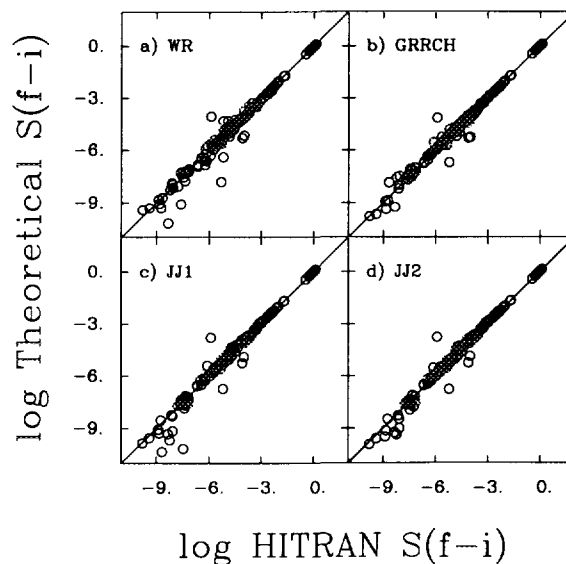


FIG. 2. Comparison of calculated linestrengths, in D^2 , for Q -branch transitions with $J = 5$ with all the transitions on the HITRAN database. Dipole moment surfaces used as in Fig. 1.

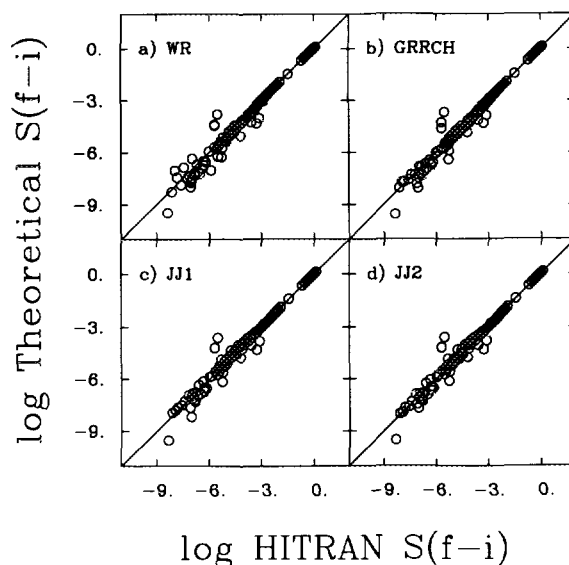


FIG. 3. Comparison of calculated line strengths, in D^2 , for Q -branch transitions with $J = 10$ with all the transitions on the HITRAN database. Dipole moment surfaces used as in Fig. 1.

where all four dipole functions give similar significant disagreements with the results of from HITRAN. There are three possible causes for this: (i) that the potential energy surface used causes significant errors in our wavefunctions, (ii) that the wavefunctions themselves are not sufficiently well converged, and (iii) that the HITRAN data are in error. In particular, the latter possibility can arise because many of the "observed" intensities for water in HITRAN have not actually been directly measured, but obtained from observed band dipoles using Hönl-London factors. Which of these possibilities is the actual one will have await further work using a more accurate potential, such as (11), and better converged basis sets.

Comparing the four functions, we note that all appear to be in good agreement for the strong transitions. For the weaker lines it is apparent that both JJ1 and JJ2 give a significantly larger scatter than WR and GRRCH. The GRRCH results also seem to show less scatter than the WR ones. As, for reasons discussed above, we would also trust the extrapolation properties of the GRRCH surfaces more than those due to WR, we recommend this surface for future work.

5. CONCLUSION

Linestrength calculations have been performed using four recent and accurate water dipole moment surfaces. The results of these calculations have been compared with extensive datasets of observed results obtained from HITRAN (1). In general all four surfaces give satisfactory results; however, the *ab initio* surface of Gabriel *et al.* (GRRCH) (14) appears to give the best answers.

It is interesting to note that GRRCH produced their surface using a level of theory that, according to the authors, yields band origins up to 30 cm^{-1} away from experiment. This is about two orders of magnitude worse than we would expect from a spectroscopically determined potential. However, the *ab initio* dipole moment surfaces would appear to be marginally more accurate than the spectroscopically determined one due

to Wattson and Rothman (WR) (13) with which we compared it. Indeed for the stronger bands GRRCH reproduced the most observed linestrengths with an error of between 2 and 10%, figures which are comparable with typical experimental errors.

It is our plan to use the GRRCH dipole moment surfaces, one of the improved water potential energy surfaces (e.g., Ref. (11)), and our new 3D DVR program suite (22) to calculate a new, accurate and extensive linelist for H₂¹⁶O. The results of these calculations will be reported elsewhere.

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