Theor Chim Acta (1988) 74: 493-511

Theoretica
Chimica Acta

Vibrational partition functions for H_2O derived from perturbation-theory energy levels

Alan D. Isaacson and Xing-Guo Zhang*

Department of Chemistry, Miami University, Oxford, OH 45056, USA

(Received January 11/Accepted January 12, 1988)

Purely vibrational energy levels and partition functions are calculated using three different potential energy surfaces for the H_2O molecule. Results obtained with perturbation-theory, independent-normal-mode (INM), and harmonic approximations are compared with accurate values. For the cases considered here, the expected improvement that perturbation theory provides over the corresponding harmonic treatment is found to be substantial, while the INM approximation leads to results which are worse than the corresponding harmonic ones. In fact, we show that reliable partition functions for these potential surfaces can be obtained when resonance contributions are removed from the perturbation-theory treatment, and we propose a theoretical criterion for deciding when a particular interaction should be treated as resonant.

Key words: Water — Vibrational energy levels — Partition functions — Perturbation theory

1. Introduction

The efficient calculation of reliable quantum mechanical vibrational partition functions as a function of temperature for a given potential energy surface is a basic problem in chemical physics. One example of a situation where the need for such a calculation arises is the activated complex method for calculating unimolecular and bimolecular reaction rate constants. However, since the direct computation of the quantum mechanical vibrational partition function involves

---

* *Permanent address*: Shanghai Institute of Metallurgy, Academia Sinica, Shanghai 20050, China

solving for the quantum vibrational levels of the given potential, exact calculations are impractical for all but the simplest systems (≤ 3 atoms).

One common alternative is to use the harmonic approximation, for which the energy levels and partition functions are given by simple functions of the normal-mode frequencies [1]. Unfortunately, the harmonic approximation can lead to partition functions and rate constants which are fairly inaccurate [2-7]. A possible improvement to the harmonic approximation involves the inclusion of anharmonicity *within* each normal mode, but neglecting the mode-mode couplings [1, 6]. In this independent-normal-mode (INM) approximation, the energy levels are simply sums of individual normal-mode energies which either can be computed by an accurate one-dimensional calculation or can be modelled in a practical manner, e.g. by a Morse model. However, we show below that the INM approximation can lead to *worse* results than the harmonic approximation. Such behavior indicates that the net anharmonic effect due to the mode-mode couplings is larger but in the opposite direction from that due to the anharmonicities within the normal modes for the cases considered here. Another alternative to the exact solution of the vibrational energies is provided by the standard perturbation-theory treatment of Nielsen [8, 9], which includes the effects of cubic anharmonicity through second order and those of quartic anharmonicity through first order. Although this approach does not necessarily yield accurate excited-state energies [4, 10, 11], the zero-point energy and the *distribution* of excited-state energies (i.e., the density of states) may be accurate enough to provide reliable partition functions, especially at lower temperatures. This is the basic question with which the present study is concerned.

An additional aspect of the present study is the effect of different treatments of vibrational resonances. These resonances, which occur when two or more unperturbed (harmonic) states are close in energy relative to the cubic anharmonic force constant which couples them, lead to a breakdown of perturbation theory. The standard approach in such circumstances is to remove the effects of the resonance from the perturbation-theory results and then to account for the interaction of the affected levels more correctly by diagonalizing the Hamiltonian matrix for these levels [8, 9]. For the numerical examples presented in this paper we show that in order to obtain accurate partition functions it is indeed important to remove resonance effects from the perturbation-theory energy levels, but that diagonalizing the Hamiltonian matrices for the resonant levels is not very important. (We note in passing that a previous application [4] of perturbation theory to obtain the partition functions for H_2O and SO_2 ignored the effects of such resonances.) In addition, we propose an operational criterion for deciding when the effects of resonance may be important.

As a precursor to the calculation of reliable vibrational partition functions in larger molecules and transition-state structures, this paper addresses the issues outlined above as they apply to three potential energy surfaces for H_2O derived from the Hoy-Mills-Strey (HMS) quartic general force field [12], the Romanowski-Bowman (RB) quartic normal-mode force field [13] obtained by the method of program SURVIB [14] from a quartic internal-coordinate force field fit to *ab initio* many-body perturbation-theory calculations [15], and a quartic normal-mode force field obtained from a modified version of the H_2O portion of the Schatz–Elgersma (MSE) potential energy surface for the $OH+H_2$ system [16]. These potentials were chosen because they are different more-or-less realistic descriptions of the vibrational potential energy surface for H_2O that are fairly anharmonic, but in somewhat different ways. In addition, accurate quantal vibrational energies either were available or could be computed without undue effort for these potentials, thus affording a stringent test of the results for various approximations. Although the neglect of terms of order higher than fourth in these normal-mode force fields implies that they may not accurately model the internal-coordinate or analytic potential energy surfaces from which they are derived (see below), their neglect is justifiable in the present study in that (a) vibrational energy levels presented below are computed through fourth order consistently for each method, and (b) for larger and transition-state systems, for which the perturbation-theory approach described below is proposed, reliable potential energy information on normal-mode terms of order higher than fourth is not commonly available. The present study is restricted to a total angular momentum $J=0$ only, and, except for the HMS surface, rotational and Coriolis effects have been omitted.

2. Potential energy surfaces

In applying the standard perturbation-theory treatment of Nielsen [8, 9] to the H_2O molecule, the potential energy is expressed in dimensionless normal-mode coordinates through quartic terms as

$$\begin{aligned} V/hc = {} & \tfrac{1}{2}\sum_i \omega_i q_i^2 + k_{111}q_1^3 + k_{122}q_1q_2^2 + k_{133}q_1q_3^2 + k_{112}q_1^2q_2 \\ & + k_{222}q_2^3 + k_{233}q_2q_3^2 + k_{1111}q_1^4 + k_{1122}q_1^2q_2^2 + k_{1133}q_1^2q_3^2 \\ & + k_{2222}q_2^4 + k_{2233}q_2^2q_3^2 + k_{3333}q_3^4. \end{aligned} \tag{1}$$

Throughout this paper, we use the standard assignment of the symmetric stretch to mode 1, the bend to mode 2, and the asymmetric stretch to mode 3. Thus, terms involving an odd power of q_3 are absent from Eq. (1). In addition, certain quartic terms which do not affect the perturbation-theory energy levels have been omitted from Eq. (1).

The normal-coordinate force constants for the three potential energy surfaces used in the present study are listed in Table 1. For the HMS surface, the force constants are the same as those used in a previous application [4] of perturbation theory to obtain the vibrational partition function for H_2O, and were computed from the curvilinear internal-coordinate quartic force field of [12] using a computer program described elsewhere [17]. For the RB surface, the force constants for the potential given in Eq. (1) were derived from the mass-weighted cartesian normal-coordinate force constants of the quartic force field for H_2O given in the

Table 1. Dimensionless normal-coordinate force constants (in cm^{-1}) for H_2O

	HMS	RB	MSE
ω_1	3831.94	3846.07	3865.32
ω_2	1648.88	1684.47	1687.44
ω_3	3942.55	3954.87	3975.43
k_{111}	−302.70	−306.12	537.93
k_{112}	53.18	40.99	−222.40
k_{122}	167.54	151.38	−221.52
k_{133}	−928.37	−919.54	947.29
k_{222}	−63.62	−43.01	129.89
k_{233}	138.92	136.35	−161.17
k_{1111}	31.90	31.65	52.24
k_{1122}	−85.67	−75.87	6.50
k_{1133}	201.49	191.10	174.88
k_{2222}	2.09	−2.30	7.40
k_{2233}	−101.22	−91.85	−63.10
k_{3333}	35.44	32.10	33.64

manual to the POLYMODE program [13]. This normal-mode force field was obtained from the quartic curvilinear internal-coordinate force field fit by Bartlett et al. [15] to their D-MBPT(∞) set of *ab initio* many-body perturbation-theory energies. Note that the full quartic force field given in [13] contains some quartic terms which do not appear in Eq. (1), and have been omitted in the present study. The force constants $F2$, $F3$, and $F4$ in [13] are given in atomic units with respect to the mass-weighted normal coordinates. To convert these into the dimensionless normal-coordinate force constants in cm^{-1} needed here [8, 9, 12], we used the relations

$$\bar{\omega}_i = (2F2_i)^{1/2}, \tag{2}$$

$$\omega_i = \bar{\omega}_i r, \tag{3}$$

$$k_{ijk} = F3_{ijk}(\bar{\omega}_i\bar{\omega}_j\bar{\omega}_k)^{-1/2} r, \tag{4}$$

and

$$k_{iijj} = F4_{iijj}(\bar{\omega}_i\bar{\omega}_j)^{-1} r, \tag{5}$$

where $\bar{\omega}_i$ is the frequency of mode i in atomic units and $r = 219474.627$ cm^{-1}/a.u.

The force constants for the MSE surface were derived from a modified version of the H_2O asymptotic region of the analytic Schatz–Elgersma potential energy surface for the $OH + H_2$ system [16] as follows. Using a program described elsewhere [6], the equilibrium geometry X_0 in mass-weighted cartesians was located and a normal-mode analysis was performed. Third and fourth derivatives of the potential energy with respect to the mass-weighted normal coordinates were then found efficiently from second and third numerical derivatives of the analytic gradient of the potential ∇V along the normal-mode directions $\boldsymbol{L}_i$, i.e.

$$D_3 V_{iij} = \frac{1}{\delta^2}[\nabla V(\boldsymbol{X}_0 + \delta \boldsymbol{L}_i) + \nabla V(\boldsymbol{X}_0 - \delta \boldsymbol{L}_i) - 2\nabla V(\boldsymbol{X}_0)] \cdot \boldsymbol{L}_j \tag{6}$$

and

$$\begin{aligned} D_4 V_{iijj} = \frac{1}{2\delta^3}[&\nabla V(\boldsymbol{X}_0 + \delta \boldsymbol{L}_i + \delta \boldsymbol{L}_j) - 2\nabla V(\boldsymbol{X}_0 + \delta \boldsymbol{L}_j) + \nabla V(\boldsymbol{X}_0 - \delta \boldsymbol{L}_i + \delta \boldsymbol{L}_j) \\ &- \nabla V(\boldsymbol{X}_0 + \delta \boldsymbol{L}_i - \delta \boldsymbol{L}_j) + 2\nabla V(\boldsymbol{X}_0 - \delta \boldsymbol{L}_j) - \nabla V(\boldsymbol{X}_0 - \delta \boldsymbol{L}_i - \delta \boldsymbol{L}_j)] \cdot \boldsymbol{L}_j, \end{aligned} \tag{7}$$

where $i \leq j$, for a small step size δ (typically 0.0001 a.u.). These derivatives were converted into mass-weighted normal-coordinate force constants by the relations

$$\begin{aligned} &F3_{iii} = \tfrac{1}{6} D_3 V_{iii}, \qquad F3_{iij} = \tfrac{1}{2} D_3 V_{iij}, \\ &F4_{iiii} = \tfrac{1}{24} D_4 V_{iiii}, \quad \text{and} \quad F4_{iijj} = \tfrac{1}{4} D_4 V_{iijj}, \end{aligned} \tag{8}$$

where $i \neq j$, and then transformed into dimensionless normal-coordinate force constants through the use of Eqs. (4) and (5). However, we then found that the quartic force field of Eq. (1) with force constants obtained in this manner, i.e. from the true derivatives of the potential energy at the equilibrium geometry, does not adequately model the actual analytic potential energy in a large enough region about the equilibrium geometry to allow convergence to a valid ground-state energy in the vibrational SCF calculations described below. For example, even though the actual Schatz-Elgersma potential energy surface increases monotonically along the mode 2 direction, the quartic force field of Eq. (1) with force constants derived from the derivatives of the potential at the equilibrium geometry possesses a maximum of only 7.35 kcal/mol (2570 cm^{-1}) at a distance $q_2 = 3.241$ in this direction. Although we were unable to eliminate the problem of maxima within the vibrational well, we improved the fit to the actual Schatz-Elgersma surface and obtained sufficiently high barriers in a larger region about the equilibrium geometry by varying the values of most of the cubic and quartic force constants in Eq. (1). The best set of force constants we obtained were determined as follows. Keeping the frequencies fixed, we chose k_{111} and k_{1111} by a fit of Eq. (1) to the actual potential at the points $(q_1, q_2, q_3) = (\pm 6.63545, 0, 0)$, k_{222} and k_{2222} by a fit at $(0, \pm 8.76843, 0)$, k_{3333} by a fit at $(0, 0, 5.38343)$, k_{233} and k_{2233} by a fit at $(0, \pm 8.76843, 5.38343)$, and k_{112}, k_{122}, and k_{1122} by a fit at the three points $(6.63545, \pm 8.76843, 0)$ and $(-6.63545, -8.76843, 0)$. The resulting set of modified force constants are listed in Table 1. The potential energy surface of Eq. (1) obtained with these force constants rises monotonically along each normal-mode direction, but has a barrier of about 14 kcal/mol (5000 cm^{-1}) in the $(q_1 > 0, q_2 < 0)$ quadrant. This barrier is high enough to allow the VSCF-CI calculation described below to converge for several of the lowest vibrational levels, and this is sufficient for the partition function calculations presented herein. Note that since the present study is concerned with the accuracy of the vibrational partition functions for a *given* potential energy surface rather than the computation of accurate vibrational partition functions for the H_2O molecule, the fact that the set of cubic and quartic force constants for the MSE surface are somewhat different from those for the HMS and RB surfaces is not a problem. In fact, it is advantageous in that it allows the tests of the accuracy of the various approximations discussed below to be carried out for more than one kind of anharmonic behavior.

3. Energy levels

The lowest energy levels for the HMS, RB, and MSE potentials, measured from the bottom of the potential well, are presented in Tables 2-4, respectively. The accurate levels for the HMS potential have been computed by Carney et al. [18, 19]. For the accurate levels for the RB surface, we performed a vibrational SCF-CI calculation using the POLYMODE program [13, 20]. In this calculation we used the *virtual* basis [21, 22] obtained from a VSCF calculation on the ground state, in which the Coriolis interaction and Watson terms were omitted and each vibrational modal was expanded as a linear combination of 25 harmonic oscillator functions. For the CI calculation, configurations (i.e. products of modals) $|v_1 v_2 v_3\rangle$ were included for $v_1 = 0, \dots, 8$, $v_2 = 0, \dots, 11$, and $v_3 = 0, 2, 4,$

Table 2. Energy levels (in cm^{-1}) for the HMS surface

State v_1	v_2	v_3	Acc.[a]	p.t.[b]	p.t. +corr. ($p = 0.25$)[c]	p.t. +corr. ($p = 0.25$) +diag'n.[d]	p.t. +corr. ($p = 0.20$)[e]	p.t. +corr. ($p = 0.20$) +diag'n.[f]	INM[g]	H[h]
0	0	0	4 652	4 634	4 629	4 629	4 649	4 649	4 717	4 712
0	1	0	6 249	6 232	6 227	6 227	6 247	6 247	6 368	6 360
0	2	0	7 811	7 795	7 803	7 789	7 823	7 809	8 007	8 009
1	0	0	8 369	8 290	8 272	8 286	8 345	8 302	8 480	8 543
0	0	1	8 473	8 388	8 384	8 384	8 403	8 403	8 775	8 654
0	3	0	9 336	9 325	9 360	9 318	9 380	9 338	9 634	9 658
1	1	0	9 952	9 871	9 827	9 868	9 900	9 883	10 130	10 192
0	1	1	10 055	9 965	9 960	9 960	9 980	9 980	10 454	10 303
0	4	0	10 828	10 822	10 896	10 816	10 915	10 837	11 249	11 307
1	2	0	11 498	11 419	11 362	11 410	11 435	11 425	11 769	11 841
0	2	1	11 602	11 508	11 517	11 497	11 537	11 517	12 121	11 952
2	0	0	12 072	11 860	11 829	11 860	11 955	11 864	12 193	12 375
1	0	1	12 173	11 878	11 860	11 879	12 039	11 880	12 537	12 486
0	0	2	12 278	12 047	12 042	12 042	12 009	12 067	12 929	12 596

[a] Accurate ([18, 19])

[b] Perturbation theory without resonance corrections

[c] Perturbation theory with correction for k_{122} resonance

[d] Perturbation theory with correction for k_{122} resonance and diagonalization for affected states

[e] Perturbation theory with corrections for k_{122} and k_{133} resonances

[f] Perturbation theory with corrections for k_{122} and k_{133} resonances and diagonalization for affected states

[g] Accurate levels for the independent-normal-mode surface containing only the diagonal force constants

[h] Harmonic

Table 3. Energy levels (in cm^{-1}) for the RB surface[a]

State			Acc.[b]	p.t.	p.t. + corr ($p = 0.25$)	p.t. + corr ($p = 0.25$) + diag'n.	p.t. + corr ($p = 0.20$)	p.t. + corr ($p = 0.20$) + diag'n.	INM	H
v_1	v_2	v_3								
0	0	0	4 683	4 656	4 652	4 652	4 671	4 671	4 754	4 743
0	1	0	6 293	6 276	6 271	6 271	6 291	6 291	6 423	6 427
0	2	0	7 871	7 862	7 869	7 856	7 889	7 876	8 076	8 112
1	0	0	8 383	8 321	8 304	8 317	8 376	8 331	8 526	8 589
0	0	1	8 467	8 401	8 397	8 397	8 416	8 416	8 801	8 698
0	3	0	9 410	9 413	9 445	9 409	9 464	9 428	9 710	9 796
1	1	0	9 942	9 926	9 885	9 921	9 957	9 935	10 195	10 273
0	1	1	10 002	9 973	9 969	9 969	9 988	9 988	10 470	10 382
0	4	0	10 903	10 931	10 999	10 930	11 018	10 950	11 327	11 480
1	2	0	11 472	11 497	11 444	11 485	11 516	11 498	11 848	11 958
0	2	1	11 505	11 511	11 519	11 503	11 538	11 522	12 122	12 066
2	0	0	12 047	11 896	11 877	11 892	11 991	11 898	12 245	12 435
1	0	1	12 109	11 894	11 867	11 895	12 053	11 891	12 573	12 544
0	0	2	12 209	12 046	12 041	12 041	12 009	12 066	12 936	12 652

[a] See Table 2 for a description of the method used for each column

[b] Accurate (present work)

6, 8 or 1, 3, 5, 7, 9, depending on the symmetry of the states desired, yielding a total of 540 configurations for each symmetry. That the *virtual* modals obtained with the ground state as the reference state for the VSCF calculation provide a good basis set for describing excited states in the CI calculation has been observed elsewhere [23]. In the present study, we demonstrated the validity of this approach for the RB surface by performing the same VSCF-CI calculations using the full quartic force field of [13], which contains certain quartic terms omitted from the RB surface, and including the Watson and Coriolis interaction terms. The energy levels obtained by this approach were found to be in very good agreement with accurate ones [22] obtained from individual large-scale VSCF-CI calculations, in which each state of interest was used for the VSCF reference state [23]. In fact, for the 24 energies listed in [22], the largest errors obtained with the present approach were 22 and 9 cm^{-1} for the highly excited $|131\rangle$ and $|032\rangle$ states, respectively; the other 22 levels agreed within 6 cm^{-1}, with 18 of them agreeing within 1 cm^{-1}.

The accurate levels for the MSE surface were computed by the same VSCF-CI procedure described for the RB surface. However, owing to the barrier in the $q_1 - q_2$ plane discussed above, levels with more than around 5000 cm^{-1} of energy available in these modes could not be converged either in the number of SCF basis functions or in the number of CI configurations. The lowest eight converged energy levels are listed in Table 4, along with several unconverged levels whose values are given in parentheses. (In some cases, the largest CI coefficient in the expansion for two unconverged levels corresponded to the same configuration.)

In the standard second-order perturbation-theory scheme of Nielsen [8], the

Table 4. Energy levels (in cm^{-1}) for the MSE surface[a]

State v_1	v_2	v_3	Acc.[b,c]	p.t.	p.t. + corr. ($p=0.25$)	p.t. + corr. ($p=0.25$) + diag'n.	p.t. + corr. ($p=0.20$)	p.t. + corr. ($p=0.20$) + diag'n.	INM	H
0	0	0	4 796	4 793	4 783	4 783	4 804	4 804	4 716	4 764
0	1	0	6 404	6 403	6 394	6 394	6 414	6 414	6 350	6 452
0	2	0	7 893	7 921	7 937	7 911	7 957	7 932	7 928	8 139
1	0	0	8 403	8 428	8 393	8 419	8 469	8 443	8 152	8 629
0	0	1	8 883	8 871	8 861	8 861	8 882	8 882	8 788	8 740
0	3	0	(9 160 9 335)	9 347	9 413	9 352	9 433	9 374	9 452	9 826
1	1	0	(9 944)	10 044	9 959	10 020	10 034	10 044	9 786	10 317
0	1	1	10 522	10 506	10 497	10 497	10 517	10 517	10 422	10 427
0	4	0	(10 537)	10 681	10 822	10 718	10 842	10 740	10 921	11 514
2	0	0	(11 029)	11 630	11 570	11 713	11 701	11 775	11 160	12 495
0	5	0	(11 354 12 256)	11 923	12 163	12 012	12 184	12 035	12 336	13 201
1	2	0	(11 691 12 088)	11 567	11 458	11 419	11 533	11 472	11 365	12 004
0	2	1	12 069	12 049	12 065	12 050	12 086	12 071	12 001	12 114
1	3	0	(12 834 13 298)	12 998	12 873	12 888	12 964	12 879	12 889	13 692
1	0	1	12 906	12 907	12 889	12 813	13 058	12 889	12 224	12 605
0	0	2	(12 931)	12 839	12 829	12 829	12 795	12 846	12 951	12 715

[a] See Table 2 for a description of the method used for each column

[b] Accurate (present work)

[c] Values in parentheses represent unconverged levels. In some cases, the same configuration had the largest coefficient in two CI eigenvectors

vibrational energy levels are approximated by

$$E_{v_1 v_2 v_3}/hc = \sum_i \omega_i (v_i + \tfrac{1}{2}) + \sum_{j \geq i} \sum x_{ij} (v_i + \tfrac{1}{2})(v_j + \tfrac{1}{2}), \tag{9}$$

where

$$x_{ii} = \frac{1}{4}\left[6k_{iiii} - \frac{15k_{iii}^2}{\omega_i} - \sum_{j \neq i} \left(\frac{k_{iij}^2}{\omega_j} \right) \left(\frac{8\omega_i^2 - 3\omega_j^2}{4\omega_i^2 - \omega_j^2} \right) \right] \tag{10}$$

and

$$x_{ij} = k_{iijj} - 2k_{iij}^2 \left(\frac{\omega_i}{4\omega_i^2 - \omega_j^2} \right) - 2k_{ijj}^2 \left(\frac{\omega_j}{4\omega_j^2 - \omega_i^2} \right)$$

$$- \frac{3k_{iii}k_{ijj}}{\omega_i} - \frac{3k_{jjj}k_{iij}}{\omega_j} - \sum_{k \neq i,j} \frac{k_{iik}k_{kjj}}{\omega_k}$$

$$-\frac{1}{2}\sum_{k\neq i,j} k_{ijk}^2\omega_k\left[\frac{\omega_k^2-\omega_i^2-\omega_j^2}{(\omega_i+\omega_j+\omega_k)(\omega_i+\omega_j-\omega_k)(\omega_i-\omega_j+\omega_k)(\omega_i-\omega_j-\omega_k)}\right] \tag{11}$$

for $j > i$. (In this paper, we are following the conventions of [9]; our anharmonicity constants x_{ij} are equal to $x_{ij}+x_{ji}$ in the notation of [8].)

When two or more unperturbed vibrational levels are close in energy relative to the interaction force constant that couples them, perturbation theory breaks down. Such a near degeneracy, which is commonly referred to as a Fermi resonance, leads to a near singularity in certain terms in Eqs. (10) and (11). Following the method of Nielsen [8, 9], the resonant interaction is first removed from the perturbation-theory treatment, leading to nonsingular terms in Eqs. (10) and (11) for that particular interaction force constant. The resulting corrected anharmonicity constants yield vibrational energy levels that Harding and Ermler [14] term "deperturbed". In the present study, the perturbed levels are then approximated by the solutions of the eigenvalue problem that arises from the direct coupling of these deperturbed levels by the appropriate interaction force constant. This approach to the combination of resonant and non-resonant anharmonic effects is consistent with the method described by Papousek and Aliev [24], but is somewhat different from that proposed by Schlegel, Wolfe, and Bernardi [25], in which the level shifts obtained by solving the eigenvalue problem associated with the direct coupling of the unperturbed levels are simply added to the deperturbed levels. In the present study, we found that the two approaches generally lead to similar results. For example, in the case of the HMS surface there is a Fermi resonance involving modes 1 and 2, since $2\omega_2 \approx \omega_1$ (i.e. $\omega_1 - 2\omega_2 =$ 534 cm^{-1}, which is relatively small for an interaction force constant $k_{122} =$ 168 cm^{-1}). The energy levels in the column of Table 2 labelled "p.t." thus contain improper contributions from the terms in the anharmonicity constants involving the denominator $(4\omega_2^2-\omega_1^2)$. When such contributions are removed by the replacements [8, 9]

$$-\left(\frac{k_{122}^2}{4\omega_1}\right)\left(\frac{8\omega_2^2-3\omega_1^2}{4\omega_2^2-\omega_1^2}\right) \to -k_{122}^2\left[\frac{1}{2\omega_1}+\frac{1}{8(2\omega_2+\omega_1)}\right] \tag{12}$$

in x_{22} and

$$-2k_{122}^2\left(\frac{\omega_2}{4\omega_2^2-\omega_1^2}\right) \to -k_{122}^2\left[\frac{1}{2(2\omega_2+\omega_1)}\right] \tag{13}$$

in x_{12}, we get the deperturbed levels listed in the column labelled "p.t.+corr. ($p = 0.25$)". Many of the deperturbed levels are strongly coupled by the interaction term in the potential that involves k_{122}, and this coupling is then included by solving the appropriate eigenvalue problem. The results of this procedure are listed in the column labelled "p.t.+corr. ($p = 0.25$)+diag'n." As a specific example, the two energy levels arising from the pair of states $|020\rangle$ and $|100\rangle$, which exhibit Fermi resonance because of the k_{122} interaction term discussed here, are found by diagonalizing the 2×2 matrix [8, 9]

$$\begin{pmatrix} E^d_{020} & \frac{1}{2}k_{122} \\ \frac{1}{2}k_{122} & E^d_{100} \end{pmatrix}, \tag{14}$$

where E^d_{020} and E^d_{100} are the deperturbed energies of the $|020\rangle$ and $|100\rangle$ states, respectively, with all quantities in cm^{-1}. We note in passing that if the unperturbed (harmonic) energies for the $|020\rangle$ and $|100\rangle$ states were used in place of the deperturbed energies in Eq. (14) and the resulting level shifts added to the deperturbed levels, as proposed by Schlegel et al. [25], we would obtain level energies of 7790 cm^{-1} and 8285 cm^{-1}, in very good agreement with the results given in Table 2. In a similar fashion, the three energy levels arising from the trio of states $|040\rangle$, $|120\rangle$, and $|200\rangle$ are found by diagonalizing the 3×3 matrix [8, 9]

$$\begin{pmatrix} E^d_{040} & \sqrt{\frac{3}{2}}k_{122} & 0 \\ \sqrt{\frac{3}{2}}k_{122} & E^d_{120} & \sqrt{\frac{1}{2}}k_{122} \\ 0 & \sqrt{\frac{1}{2}}k_{122} & E^d_{200} \end{pmatrix}, \tag{15}$$

and so on.

In the usual application of perturbation theory to obtain vibrational energy levels that are compared with spectroscopic data, Fermi resonances are detected from large shifts of levels from their expected values. The present theoretical study, however, required a simple criterion for determining when Fermi resonances are present based only on the parameters of the potential energy surface. This was done by assuming that a Fermi resonance exists whenever the ratio $|k_{ijj}/(\omega_i-2\omega_j)|$ exceeded the minimum value p. Since Fermi resonances occur in some linear triatomics for values of this ratio as low as 0.22 [26], we list in Tables 2–4 results obtained with two different values of p: $p=0.25$, for which only the k_{122} interaction is assumed to be resonant; and $p=0.20$, for which both the k_{122} and k_{133} interactions are assumed resonant. [Although $2\omega_3-\omega_1$ is very large ($>4000\ \mathrm{cm}^{-1}$), the k_{133} force constant is also very large ($>900\ \mathrm{cm}^{-1}$). Thus, although the $|100\rangle$ and $|002\rangle$ states are not very close in energy, the strong coupling between them can be treated as a Fermi resonance.]

One further comment regarding the perturbation-theory levels is in order. The expressions for the anharmonicity constants given above, and hence the perturbation-theory energy levels, do not include Coriolis interactions. However, in order to compare the perturbation-theory results with the accurate levels for the HMS surface given in [18] and [19], it was necessary to include these contributions into the x_{ij}'s. For the HMS surface, we found that the only nonnegligible contribution from Coriolis couplings increased the value of x_{23} by 26.77 cm^{-1}; this amount has been included in x_{23} for all of the perturbation-theory results in Table 2.

For the purposes of comparison, harmonic results for the vibrational energy levels are also listed in the last column of Tables 2–4. These were obtained from the relation

$$E^H_{v_1v_2v_3}/hc = \sum_i \omega_i(v_i + \tfrac{1}{2}). \tag{16}$$

In addition, the second-to-last column of Tables 2–4 gives the results of accurate calculations in the INM approximation. For these calculations, only the diagonal terms in the potential of Eq. (1) were retained, and accurate energy levels for the INM versions of the HMS, RB, and MSE surfaces were obtained with the POLYMODE program [13, 20] using the same procedure described above for the accurate levels of the RB surface, except that the Watson and Coriolis interaction terms were included for the HMS case. No convergence problems arose in the calculations of a sufficient number of energy levels to obtain converged partition functions since the only maximum in these potentials occurs at 22 500 cm^{-1} (64.4 kcal/mol) in the bending mode of the RB surface.

4. Partition functions

We consider both the partition function with the zero of energy at the bottom of the potential well,

$$Q(T) = \sum_{v_1}\sum_{v_2}\sum_{v_3} \exp(-E_{v_1v_2v_3}/kT), \tag{17}$$

as well as the partition function with the zero of energy at the ground-state level E_{000},

$$\tilde{Q}(T) = \sum_{v_1}\sum_{v_2}\sum_{v_3} \exp[-(E_{v_1v_2v_3} - E_{000})/kT]. \tag{18}$$

The former, which is mostly determined by the energy of the ground-state level, is important for the calculation of equilibrium constants and for the activated complex method for obtaining reaction rate constants from potential energy surfaces, while the latter is sensitive to the energies of the excited levels.

The partition functions obtained from the energy levels described in the previous section were calculated at five temperatures between 200 and 2400K, and the results for the three potential surfaces studied in this paper are presented in Table 5. The values for the partition functions computed from the accurate and uncorrected perturbation-theory levels for the HMS surface were taken from previous work [4, 27], while all of the other values were obtained by direct summation in Eq. (17). Note that $\tilde{Q}(T)$ can be obtained from $Q(T)$ by

$$\tilde{Q}(T) = Q(T) \exp(E_{000}/kT), \tag{19}$$

where E_{000} is the appropriate ground-state energy. Because the low-energy levels for H_2O are fairly widely spaced, only the ground-state level needs to be included in the summation in Eq. (17) for three-figure accuracy up to 298K, the lowest two levels up to 600K, the lowest five levels up to 1000K, and the lowest 40 levels up to 2400K. This was verified both by including a large number of extra levels

Table 5. Partition functions for H_2O

Surface	Method[a]		T(K)				
			200	298.15	600	1000	2400
$\tilde{Q}(T)$							
HMS	Accurate		1.00	1.00	1.02	1.12	2.04
	p.t.		1.00	1.00	1.02	1.12	2.07
	p.t. + corr.	($p = 0.25$)	1.00	1.00	1.02	1.12	2.07
	p.t. + corr. + diag'n.	($p = 0.25$)	1.00	1.00	1.02	1.12	2.07
	p.t. + corr.	($p = 0.20$)	1.00	1.00	1.02	1.12	2.06
	p.t. + corr. + diag'n.	($p = 0.20$)	1.00	1.00	1.02	1.12	2.06
	INM		1.00	1.00	1.02	1.11	1.95
	Harmonic		1.00	1.00	1.02	1.11	1.95
RB	Accurate		1.00	1.00	1.02	1.12	2.05
	p.t.		1.00	1.00	1.02	1.12	2.05
	p.t. + corr.	($p = 0.25$)	1.00	1.00	1.02	1.12	2.05
	p.t. + corr. + diag'n.	($p = 0.25$)	1.00	1.00	1.02	1.12	2.05
	p.t. + corr.	($p = 0.20$)	1.00	1.00	1.02	1.12	2.04
	p.t. + corr. + diag'n.	($p = 0.20$)	1.00	1.00	1.02	1.12	2.05
	INM		1.00	1.00	1.02	1.11	1.94
	Harmonic		1.00	1.00	1.02	1.11	1.93
MSE	Accurate		1.00	1.00	1.02	1.12	2.1
	p.t.		1.00	1.00	1.02	1.12	2.02
	p.t. + corr.	($p = 0.25$)	1.00	1.00	1.02	1.12	2.02
	p.t. + corr. + diag'n.	($p = 0.25$)	1.00	1.00	1.02	1.12	2.04
	p.t. + corr.	($p = 0.20$)	1.00	1.00	1.02	1.12	2.13
	p.t. + corr. + diag'n.	($p = 0.20$)	1.00	1.00	1.02	1.12	2.04
	INM		1.00	1.00	1.02	1.12	2.04
	Harmonic		1.00	1.00	1.02	1.10	1.92
$Q(T)$[b]							
HMS	Accurate		2.92 (−15)	1.78 (−10)	1.46 (−5)	1.39 (−3)	1.26 (−1)
	p.t.		3.32 (−15)	1.94 (−10)	1.52 (−5)	1.43 (−3)	1.29 (−1)
	p.t. + corr.	($p = 0.25$)	3.44 (−15)	1.99 (−10)	1.54 (−5)	1.44 (−3)	1.29 (−1)
	p.t. + corr. + diag'n.	($p = 0.25$)	3.44 (−15)	1.99 (−10)	1.54 (−5)	1.44 (−3)	1.29 (−1)
	p.t. + corr.	($p = 0.20$)	2.98 (−15)	1.80 (−10)	1.47 (−5)	1.40 (−3)	1.27 (−1)
	p.t. + corr. + diag'n.	($p = 0.20$)	2.98 (−15)	1.80 (−10)	1.47 (−5)	1.40 (−3)	1.27 (−1)
	INM		1.82 (−15)	1.30 (−10)	1.25 (−5)	1.25 (−3)	1.15 (−1)
	Harmonic		1.90 (−15)	1.34 (−10)	1.26 (−5)	1.26 (−3)	1.16 (−1)
RB	Accurate		2.34 (−15)	1.53 (−10)	1.36 (−5)	1.33 (−3)	1.24 (−1)
	p.t.		2.83 (−15)	1.74 (−10)	1.44 (−5)	1.38 (−3)	1.26 (−1)
	p.t. + corr.	($p = 0.25$)	2.93 (−15)	1.78 (−10)	1.46 (−5)	1.39 (−3)	1.26 (−1)

Table 5—continued

Surface	Method[a]		T(K)				
			200	298.15	600	1000	2400
	p.t. + corr. + diag'n.	($p = 0.25$)	2.93 (−15)	1.78 (−10)	1.46 (−5)	1.39 (−3)	1.26 (−1)
	p.t. + corr.	($p = 0.20$)	2.54 (−15)	1.62 (−10)	1.39 (−5)	1.35 (−3)	1.24 (−1)
	p.t. + corr. + diag'n.	($p = 0.20$)	2.54 (−15)	1.62 (−10)	1.39 (−5)	1.35 (−3)	1.24 (−1)
	INM		1.40 (−15)	1.09 (−10)	1.14 (−5)	1.18 (−3)	1.12 (−1)
	Harmonic		1.52 (−15)	1.15 (−10)	1.17 (−5)	1.20 (−3)	1.12 (−1)
MSE	Accurate		1.04 (−15)	8.90 (−11)	1.04 (−5)	1.13 (−3)	1.2 (−1)
	p.t.		1.06 (−15)	9.04 (−11)	1.04 (−5)	1.14 (−3)	1.14 (−1)
	p.t. + corr.	($p = 0.25$)	1.14 (−15)	9.46 (−11)	1.07 (−5)	1.15 (−3)	1.15 (−1)
	p.t. + corr. + diag'n.	($p = 0.25$)	1.14 (−15)	9.46 (−11)	1.07 (−5)	1.15 (−3)	1.16 (−1)
	p.t. + corr.	($p = 0.20$)	9.81 (−16)	8.56 (−11)	1.02 (−5)	1.12 (−3)	1.19 (−1)
	p.t. + corr. + diag'n.	($p = 0.20$)	9.81 (−16)	8.56 (−11)	1.02 (−5)	1.12 (−3)	1.14 (−1)
	INM		1.84 (−15)	1.31 (−10)	1.25 (−5)	1.26 (−3)	1.21 (−1)
	Harmonic		1.30 (−15)	1.04 (−10)	1.11 (−5)	1.17 (−3)	1.10 (−1)

[a] See Table 2 for a description of the methods used for the energy levels

[b] Power of 10 in parentheses

in Eq. (17), and, in the harmonic case, by comparing with the standard analytic result:

$$Q(T) = \prod_{i=1,2,3} \frac{\exp(-hc\omega_i/2kT)}{[1 - \exp(-hc\omega_i/kT)]}. \tag{20}$$

Because many of the x_{ij} anharmonicity coefficients in Eq. (9) are negative, the levels obtained from Eq. (9) will actually decrease for sufficiently high quantum numbers. For the temperature range considered in this paper, we have verified that the partition function calculations converged at quantum numbers for which the levels are still increasing.

For the partition functions computed from the accurate levels for the MSE surface, three-figure accuracy was obtained up to 1000K using only converged levels. For 2400K, excited unconverged levels were included in the partition function. Various sets of levels obtained from different VSCF-CI calculations were similar enough in their distribution to yield two-figure agreement in $Q(2400)$, so this value is listed in Table 5 only to two digits.

5. Discussion

5.1. *Energy levels*

The results in Table 2 for the 14 lowest-energy levels for the HMS surface show that the errors caused by the perturbation-theory approach generally increase as the degree of excitation increases, as expected. Without corrections for resonance, perturbation theory predicts values for the 14 lowest-energy levels which are too low by an average of 94 cm^{-1}, with a ground-state energy that is too low by 18 cm^{-1} and 13 lowest-energy excited levels with errors in the range −6 to −295 cm^{-1}. Correcting the perturbation-theory results for only the k_{122} resonance yields an *increase* in the average absolute error to 112 cm^{-1}, with an error in the ground-state energy of −23 cm^{-1} and those for the excited levels in the range −313 to +68 cm^{-1}. Improving the approximations to the resonant excited levels by solving the appropriate eigenvalue problems slightly improves the average absolute error to 99 cm^{-1}, with the errors ranging from −12 to −294 cm^{-1}. However, when corrections to the perturbation-theory results are made for both the k_{122} and k_{133} resonances, the average absolute error is reduced to 73 cm^{-1}, with an error in the ground-state energy of only −3 cm^{-1} and errors in the 13 excited levels in the range −269 to +87 cm^{-1}. Solving the appropriate eigenvalue problems for the resonant levels actually increases the average absolute error to 85 cm^{-1}, with errors in the range −293 to +9 cm^{-1}; generally speaking, only the energies for the states in which only the bending mode is excited are improved by diagonalization. For comparison, we note that the 14 lowest harmonic levels for the HMS surface are (not surprisingly) all too high by an average of 260 cm^{-1}, with an error of +60 cm^{-1} in the ground state and errors in the 13 excited states in the range +111 to +479 cm^{-1}.

Similar trends can be observed in the energy-level results for the RB surface listed in Table 3. The errors caused by perturbation theory again generally increase with the degree of excitation. Without corrections for resonance, the average absolute error for the 14 levels listed in Table 3 is 58 cm^{-1}, with an error of −27 cm^{-1} for the ground-state level and errors in the range −215 to +28 cm^{-1} for the 13 excited levels. Correcting the perturbation-theory results for only the k_{122} resonance again increases the average absolute error, to 75 cm^{-1}, with an error of −31 cm^{-1} for the ground state and errors in the range −242 to +96 cm^{-1} for the 13 excited levels. Improving the approximations to the resonant excited levels by solving the appropriate eigenvalue problems decreases the average absolute error to 60 cm^{-1}, with errors in the range −214 to +27 cm^{-1}. Correcting the perturbation-theory results for both the k_{122} and k_{133} resonances reduces the average absolute error to 48 cm^{-1}, with an error of −12 cm^{-1} for the ground state and errors in the range −200 to +115 cm^{-1} for the 13 excited states. Solving the appropriate eigenvalue problems for the resonant levels in this case increases the average absolute error, to 54 cm^{-1}, with errors in the range −218 to +47 cm^{-1}. The 14 lowest harmonic levels for the RB surface are again all too high, with errors ranging from +60 cm^{-1} for the ground state to +577 cm^{-1}, yielding an average error of +347 cm^{-1}.

Due to different anharmonic behavior, the energy-level results for the MSE surface given in Table 4 exhibit somewhat different trends from those noted above for the other two surfaces employed in the present study. Here we consider only the 8 energy levels listed in Table 4 for which the accurate values are converged. First, the errors in the perturbation-theory approach do not clearly increase with an increasing degree of excitation. Second, the perturbation-theory results obtained without corrections for resonance are generally better than those obtained with such corrections. To be specific, without corrections for resonance the errors range from -20 to $+28\ \mathrm{cm}^{-1}$, with an average absolute error of $13\ \mathrm{cm}^{-1}$ and an error in the ground-state energy of only $-3\ \mathrm{cm}^{-1}$. Correcting the perturbation-theory results for only the k_{122} resonance increases the average absolute error to $18\ \mathrm{cm}^{-1}$, with an error in the ground-state energy of $-13\ \mathrm{cm}^{-1}$ and errors in the range -25 to $+44\ \mathrm{cm}^{-1}$ for the excited levels. Solving the appropriate eigenvalue problems for the resonant levels generally increases the errors, especially for the $|101\rangle$ state, leading to an average absolute error of $27\ \mathrm{cm}^{-1}$ with errors in the range -93 to $+18\ \mathrm{cm}^{-1}$. Correcting the perturbation-theory results for both the k_{122} and k_{133} resonances further increases the average absolute error to $40\ \mathrm{cm}^{-1}$, with errors in the range -5 to $+152\ \mathrm{cm}^{-1}$, but with an error in the ground-state energy of only $+8\ \mathrm{cm}^{-1}$. In this case solving the appropriate eigenvalue problems for the resonant levels improves all of them, yielding errors in the range -17 to $+40\ \mathrm{cm}^{-1}$, with an average absolute error of $15\ \mathrm{cm}^{-1}$. A third difference between the results for the MSE surface and those for the other two surfaces employed in this study concerns the harmonic levels listed in Table 4. For the MSE surface several of the harmonic levels have energies below the accurate values. In fact, the error in the ground state is $-32\ \mathrm{cm}^{-1}$, while the errors in the other states range from -301 to $+246\ \mathrm{cm}^{-1}$ with an average absolute error of $142\ \mathrm{cm}^{-1}$.

5.2. *Partition functions*

The value for $\tilde{Q}$, the partition function with the zero of energy placed at the ground-state level, is sensitive to the distribution of excited-state level energies. Since these distributions are similar for the various sets of perturbation-theory levels and for the accurate levels considered in this study, the values in Table 5 for $\tilde{Q}$ obtained from the perturbation-theory levels agree to within about 1% with those obtained from the accurate levels. [For the MSE surface, the distributions of excited levels obtained with different perturbation-theory treatments are different enough to display some differences in $\tilde{Q}(2400)$. Because the accurate values for the excited levels were not converged, the slight lack of agreement with the accurate value for $\tilde{Q}(2400)$ should not be taken seriously.] On the other hand, the harmonic levels generally rise much faster than the accurate values, so that the $\tilde{Q}$ values in Table 5 obtained from the harmonic levels are somewhat smaller at higher temperatures than the accurate values.

The value for Q, the partition function with the zero of energy placed at the bottom of the vibrational well, is additionally quite sensitive to the value of the ground-state energy. Given the good agreement between the accurate and perturbation-theory results for $\tilde{Q}$ discussed above, the errors in our perturbation-theory results for Q are mostly due to errors in the ground-state energies, so that the errors in the Q values decrease as the temperature increases. In addition, since the ground-state level is not resonant, values of $Q(T)$ obtained with corresponding sets of non-diagonalized and diagonalized resonant levels are generally the same to at least three figures. From Table 5, it is clear that the improvements in the energy levels (especially the ground state) obtained from perturbation theory lead to $Q(T)$ values that are much more accurate than the harmonic results for the cases studied here. Even without any corrections for resonance, the errors in the perturbation-theory results for $Q(T)$ for the HMS surface range from +14% at 200K to +2% at 2400K while the errors in the harmonic values for this surface range from −35% at 200K to −8% at 2400K. A similar comparison for the RB surface gives uncorrected-perturbation-theory errors that range from +21% at 200K to +2% at 2400K, while the errors in the harmonic results range from −35% at 200K to −10% at 2400K; corresponding numbers for the MSE surface are +2% at 200K to +1% at 1000K (p.t.) vs +25% at 200K to +4% at 1000K (harmonic). Correcting the perturbation-theory levels for only the k_{122} resonance yields $Q(T)$ values that are somewhat less accurate than those obtained without resonance corrections. The ranges of the errors in the perturbation-theory results in Table 5 with the correction only for the k_{122} resonance for the HMS, RB, and MSE surfaces are +18% at 200K to +2% at 2400K, +25% at 200K to +2% at 2400K, and +10% at 200K to +2% at 1000K, respectively. On the other hand, correction of the perturbation-theory levels for both the k_{122} and k_{133} resonances leads to substantially better $Q(T)$ values for the HMS and RB surfaces than those obtained without such corrections: the errors range from +2% at 200K to +1% at 2400K for the HMS surface and from +8% at 200K to <1% at 2400K for the RB surface. However, for the MSE surface the errors range from −6% at 200K to −1% at 1000K when corrections are made for both the k_{122} and k_{133} resonances, which are somewhat larger than the errors obtained without corrections for resonance. The anomalies of the MSE surface were discussed above; the accuracy of the perturbation-theory ground-state level obtained without resonance corrections could be fortuitous. In any event, it is important to note that the perturbation-theory approach with corrections for both the k_{122} and k_{133} resonances leads to the best overall agreement with the accurate values of $Q(T)$ for the three surfaces studied; except for an error of 8% at 200K for the RB surface, the errors obtained with this approach are within 6% from 200K to 2400K.

5.3. Independent-normal-mode results

The results for the INM energy levels given in Tables 2–4 show that including the diagonal anharmonic terms in the normal-mode potential of Eq. (1) while neglecting the mode–mode couplings is a poorer approximation than the harmonic model for the three potential energy surfaces for the H_2O molecule employed in this study. Specifically, the INM ground-state and average absolute errors for the converged levels listed in Tables 2–4 are +65 and 287 cm^{-1}, +71 and 336 cm^{-1}, and −80 and 171 cm^{-1} for the HMS, RB, and MSE surfaces, respectively; the corresponding harmonic errors are +60 and 260 cm^{-1}, +60 and 347 cm^{-1}, and −32 and 142 cm^{-1}. For the HMS and RB surfaces, the increase in the INM ground-state energies over the harmonic ones arises from the fact that the positive anharmonic contribution due to the asymmetric stretch dominates. For the MSE surface, the negative anharmonic contribution due to the symmetric stretch dominates, causing the INM ground state to be lower than the harmonic one. In all three cases, however, the net accurate anharmonic effects for the full potentials are in the opposite direction from those obtained with the INM approximation.

As expected, the ground-state errors in the INM results lead to larger errors in the values for $Q(T)$ listed in Table 5 than the harmonic approximation does. For the HMS surface, the INM errors range from −38% at 200K to −9% at 2400K, compared to the range of harmonic errors of −35% at 200K to −8% at 2400K. A similar comparison for the RB surface gives INM errors in the range −40% at 200K to −10% at 2400K vs harmonic errors in the range −35% at 200K to −10% at 2400K; corresponding numbers for the MSE surface are +77% at 200K to +12% at 1000K (INM) vs +25% at 200K to +4% at 1000K (harmonic).

6. Summary

In this paper, we have presented purely vibrational energy levels and partition functions calculated from three rather different quartic normal-mode potential energy surfaces for the H_2O molecule derived from the Hoy–Mills–Strey quartic general force field [12], the Romanowski–Bowman quartic normal-mode force field [13] obtained from a fit to *ab initio* data [15], and a quartic normal-mode force field for a modified version of the H_2O portion of the Schatz–Elgersma analytic potential energy surface for the $OH+H_2$ system [16]. By comparison with accurate results obtained from vibrational CI calculations, we have determined to what degree a standard second-order perturbation-theory treatment provides better results for these potential energy surfaces than the corresponding harmonic treatment, and we have shown that results obtained with the independent-normal-mode approximation are *worse* than the harmonic ones for the cases studied here. In addition, we found that removing resonance contributions from the perturbation-theory treatment generally leads to substantial improvements in the energy levels and partition functions computed in this study. Here we define the resonance interactions as those for which the ratio $|k_{ijj}/(\omega_i - 2\omega_j)|$ exceeds 0.20; this is consistent with the values of this ratio for several known vibrational resonances [26]. In fact, the deperturbed ground-state energy and the distribution of the deperturbed excited levels computed by this approach provided quite reliable zero-point energies and partition functions: for the three potential energy surfaces employed here, the largest error in the ground-state energy is 12 cm^{-1} and the maximum error in $Q(T)$ is 8% for the range 200–2400K. We also found that correcting the resonant deperturbed levels by solving the appropriate eigenvalue problems neither systematically improves the energies of the resonant levels nor significantly affects the partition functions for the potential energy surfaces and the temperature range considered here.

The direct summation of Boltzmann factors involving energy levels computed from second-order perturbation theory with the removal of resonance contributions thus provides an efficient and reliable approach to the calculation of vibrational partition functions for the H_2O molecule. Another case for which second-order perturbation theory has already been shown to provide a reliable zero-point energy and partition functions [4] is the Kuchitsu-Morino force field [28] for SO_2, which is much less anharmonic than H_2O. For this system, the value of the ratio $|k_{ijj}/(\omega_i - 2\omega_j)|$ is 0.10 for both the k_{122} and k_{133} interactions, indicating that neither of these interactions need to be treated as resonant. Indeed, second-order perturbation theory without corrections for resonance gives a zero-point energy that is within 1 cm^{-1} of the accurate value and partition functions that are within 1% of the accurate values from 200 to 2000K [4]. Because accurate (i.e. VSCF-CI) calculations are quite practical for triatomic molecules, the major value of this approach is that it is easily extended to larger systems as well as to the bound vibrational degrees of freedom in transition-state structures, for which accurate calculations are not practical. The reliability of this approach in such cases, especially those with low-frequency modes and a high density of low-lying levels, is currently under investigation. An additional consideration for larger systems concerns the magnitude of an additive constant which has been left out of the perturbation-theory energy levels of Eq. (9) because it is claimed to be very small [9]. A preliminary investigation has shown that this constant term can significantly improve the perturbation-theory ground-state energy for larger systems and even provides some improvement for the H_2O results presented herein. The details will be published in the near future.

Acknowledgments. The authors wish to thank Drs. H. Romanowski, J. Bowman, and D. G. Truhlar for helpful discussions. This work was carried out on Miami University's VAX 11/750 computer facility, and we are most grateful for the computer time. One of us (X-G.Z.) is indebted to the Ohio Board of Regents Research Challenge Program for financial support.

References and notes

1. Truhlar DG, Isaacson AD, Garrett BC (1985) Baer M (ed) The theory of chemical reaction dynamics, vol 4. CRC Press, Boca Raton p 1; this reference also contains a discussion of how normal-mode frequencies are obtained for a reacting complex
2. Garrett BC, Truhlar DG (1979) J Am Chem Soc 101:4534
3. Garrett BC, Truhlar DG (1979) J Phys Chem 83:1915
4. Isaacson AD, Truhlar DG, Scanlon K, Overend J (1981) J Chem Phys 75:3017
5. Isaacson AD, Truhlar DG (1981) J Chem Phys 75:4090
6. Isaacson AD, Truhlar DG (1982) J Chem Phys 76:1380
7. Isaacson AD, Truhlar DG (1984) J Chem Phys 80:2888
8. Nielsen HH (1959) Encycl Phys 37/1:173
9. Califano S (1976) Vibrational states. Wiley, London
10. Truhlar DG, Olsen RW, Jeannotte AC, Overend J (1976) J Am Chem Soc 98:2373
11. Carney GD, Sprandel LL, Kern CW (1978) Adv Chem Phys 37:305
12. Hoy AR, Mills IM, Strey G (1972) Mol Phys 24:1265
13. Romanowski H, Bowman JM (1985) "POLYMODE: program 496", QCPE Bull 5(2):64
14. Harding LB, Ermler WC (1985) J Comput Chem 6:13
15. Bartlett RJ, Shavitt I, Purvis III GD (1979) J Chem Phys 71:281
16. Schatz GC, Elgersma H (1980) Chem Phys Lett 73:21
17. Pariseau MA, Suzuki I, Overend J (1965) J Chem Phys 42:2335
18. Carney GD, Kern CW (1975) Int J Quantum Chem Symp 9:317

19. Carney GD, Curtiss LA, Langhoff SR (1976) J Mol Spectrosc 61:371
20. Romanowski H, Bowman JM, Harding LB (1985) J Chem Phys 82:4155
21. Christoffel KM, Bowman JM (1982) Chem Phys Lett 85:220
22. Romanowski H, Bowman JM (1984) Chem Phys Lett 110:235
23. Romanowski H, private communication
24. Papousek D, Aliev MR (1982) Molecular vibrational-rotational spectra. Elsevier, New York, pp 160–163
25. Schlegel HB, Wolfe S, Bernardi F (1977) J Chem Phys 67:4181
26. Nakagawa T, Morino Y (1968) J Mol Spectrosc 26:496; Nakagawa T, Morino Y (1969) Bull Chem Soc Jpn 42:2212
27. Isaacson AD, Truhlar DG, unpublished work
28. Kuchitsu K, Morino Y (1965) J Chem Soc Jpn 38:814