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Anharmonic Rovibrational Numbers and Densities of States for HO_2, H_2CO, and H_2O_2[†]

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Anharmonic vibrational numbers and densities of states are calculated by quantum-corrected Monte Carlo integration of phase space volumes on ab initio potential energy surfaces for HO_2, H_2CO, and H_2O_2. Rotational dependences of the anharmonicity are also determined for H_2CO. The total numbers of states $W(E,J = 0)$ are approximated in analytical form. Using Whitten−Rabinovitch expressions as a reference, anharmonicity factors $F_{\mathrm{anh},\rho}(E,J = 0)$ for the densities of states are also given analytically. The results are used as a benchmark for comparisons with an empirical anharmonicity model (Troe, *J. Chem. Phys.* **1995**, *190*, 381). It was found that some modifications of this model are necessary for applications at high energies. The improved empirical model is intended to serve for estimates of anharmonic densities of states of larger molecular systems at high energies.

1. Introduction

Anharmonic rovibrational densities of states $\rho(E,J)$ of molecules, at the energy E and the total angular momentum with quantum number J, are important quantities in statistical theories of uni- and bimolecular rate processes.[1,2] If accurate ab initio potential energy surfaces are available, in principle exact quantum calculations of the rovibrational energy levels (see, e.g., ref 3) provide an accurate access to $\rho(E,J)$ both in the ranges of stable and of dissociative states. In practice, however, ab initio potentials exist as yet only for a restricted number of small molecular systems and their limited accuracy often requires empirical corrections on the basis of spectroscopic data.[4] In addition, the large computational effort to obtain accurate $\rho(E,J)$ in practical applications appears exaggerated when other relevant factors contributing to the rates are less well characterized. In this situation simpler methods appear desirable which at least provide semiquantitative results for $\rho(E,J)$.

Harmonic vibrational densities of states $\rho_{\mathrm{vib,h}}(E)$ are determined routinely by Beyer−Swinehart state counting algorithms[5−7] or, in smoothed form, by Whitten−Rabinovitch approximations.[1,2,8] In the present work we represent anharmonicity contributions relative to these results, i.e., relative to the Whitten−Rabinovitch expressions. We emphasize, however, that $\rho_{\mathrm{vib,h}}(E)$ determined in this way already contains some anharmonicity when the input parameters are experimental fundamental (in contrast to harmonic) frequencies. Anharmonicity contributions

$$F_{\mathrm{anh},\rho}(E) = \rho_{\mathrm{vib}}(E)/\rho_{\mathrm{vib,h}}(E) \tag{1.1}$$

in the anharmonic vibrational density of states $\rho_{\mathrm{vib}}(E)$ in the past have been proposed in a number of ways which we cannot review at this place (for summaries, see, e.g., refs 1 and 2). However, there is no consensus about which technique in practical applications is most realistic. There appears to be even no simple answer to the question whether $F_{\mathrm{anh},\rho}(E)$ increases or decreases with increasing molecular complexity. It is clear that, at a given energy E, the energy per oscillator decreases with increasing molecular size such that the anharmonicity contribution of each oscillator decreases, but the cumulative effect from large numbers of oscillators may compensate for this effect. One comes to the conclusion that there is some residual anharmonicity, because anharmonicity effects are also observable in the internal energies and heat capacities of crystals at increasing temperatures.

In order to finally study the effects of increasing molecular complexity on $F_{\mathrm{anh},\rho}(E)$, we come back to the empiricial anharmonicity model proposed in ref 9. This approach in a simplified and empiricial way accounts for Morse anharmonicities of stretching vibrations and stretch−bend couplings of bending vibrations. Including only adjacent stretches in the latter couplings, one neglects a large number of other couplings, such as included, e.g., in Dunham expansions of energy terms. However, for molecules of at least moderate complexity, this sacrifice allows one to obtain simple estimates of anharmonicity contributions to $\rho(E,J)$. Nevertheless, the method requires testing by more accurate calculations from systems whose ab initio potentials are available. This is the issue of the present article. Besides, the account for rotational contributions in terms of rotational factors

$$\rho(E, J) = \rho_{\mathrm{vib}}(E)F_{\mathrm{rot}}(E, J) \tag{1.2}$$

such as expressed in ref 10−12, needs to be checked as well.

Our empirical method, such as described in refs 4, 9 and 13, has been tested for only few systems before. It seemed to provide good results for total numbers of vibrational states $W(E,J = 0)$ of NO_2, see refs 9 and 14, and for HOCl, see ref 15, while problems were noted for H_3^+. More elaborate comparisons between the empirical and ab initio results have begun to be made for the HO_2 system in refs 4 and 13. It was observed that the empirical method in its simplest form overestimates $F_{\mathrm{anh},\rho}(E)$ at large energies but that this failure could be corrected for by modifications of the method. For this reason, further studies appear necessary. We provide these in the present work comparing empirical calculations of anharmonic vibrational densities of states with ab initio calculations, at first for HO_2 and then for the formaldehyde and hydrogen peroxide systems. In these cases sufficiently accurate and complete potential energy surfaces are available such that a reliable comparison can be

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made. The analysis shows that the individual complexities of the potentials can be considerable and that one cannot hope for a really quantitative, generally applicable, empirical method of the type proposed in ref 9. Nevertheless, we show that at least semiquantitative agreement between empirical and ab initio results for anharmonicity factors can be obtained. This opens the way to estimates of anharmonicity of at least moderately complex molecular systems by employing the empirical method of ref 9 in a somewhat modified form.

2. Determination of Anharmonicity Factors

In the following we determine the anharmonicity factors $F_{\mathrm{anh},\rho}(E,J)$ by the two methods outlined in refs 4 and 13. First, we use the empirical method of ref 9 in its simplest form. E.g., we represent the energy levels $E(n_1,n_2,n_3) = E_1(n_1) + E_2(n_2) + E_3(n_1,n_2,n_3)$ of a triatomic molecule by two local mode stretching vibrations (s1 and s2) with Morse oscillator energy levels

$$E_1(n_1) = h\,\nu_{s1}(n_1 + 1/2) - (h\,\nu_{s1})^2(n_1 + 1/2)^2/4D_1 \tag{2.1}$$

and

$$E_2(n_2) = h\,\nu_{s2}(n_2 + 1/2) - (h\,\nu_{s2})^2(n_2 + 1/2)^2/4D_2 \tag{2.2}$$

where ν_{s1} and ν_{s2} are harmonic, local mode, stretching frequencies, and D_1 and D_2 are effective Morse dissociation energies of the two stretches. The local mode bending (b3) energy levels are first represented by harmonic values

$$E_3(n_1, n_2, n_3) = h\,\nu_b(n_3 + 1/2) \tag{2.3}$$

with a bending frequency ν_b coupled to the adjacent stretching frequencies through

$$\nu_b = \nu_{b3}[(1 - cE_1/D_1)(1 - cE_2/D_2)]^{0.41} \tag{2.4}$$

where c denotes some fit parameter; see below. For applications including higher energies, the harmonic levels are replaced by hindered rotor levels in the form

$$E_3(n_1, n_2, n_3) = h\,\nu_b(n_3 + 1/2) - \mathrm{B}(n_3 + 1/2)^2\pi(1 - \pi/4) \tag{2.5}$$

at $E_3 \leq V_0$ and

$$E_3(n_1, n_2, n_3) = (h\,\nu_b)^2(1 - 4/\pi^2)/4B + (n_3 + 1/2)^2 B \tag{2.6}$$

at $E_3 \geq V_0$ where $V_0 = (h\ \nu_b)^2/4B$ and B is an effective rotational constant (in energy units). We recommend to use $B = (B_1B_2)^{1/2}$ where B_1 and B_2 are the rotational constants of the two moieties (in energy units) linked by the bending. The local mode frequencies ν_{s1}, ν_{s2}, and ν_{b3} are empirically fitted in such a way that the experimental fundamentals $E(1,0,0)$, $E(0,1,0)$, and $E(0,0,1)$ are exactly reproduced. The Morse dissociation energies D_1 and D_2 are first determined from the thermodynamic values $\Delta H_0°$ and the zero point energies before (E_z) and after dissociation (E_{zi})[4,9] (i.e., $D_i = \Delta H_{0i}° + E_z - E_{zi}$). If special features of the potential are known, which differ from "normal" Morse potentials, these may be represented by modification of D_1 and D_2, see below. Energy levels in the dissociation continuum are omitted.[4] The empirical form of eq 2.4 was suggested on the basis of an analysis of dissociation/recombination rate coefficients. Equation 2.4 is empirical and to some extent intuitive; it, therefore, needs checking such as given below. E.g., our application to HO_2 in refs 4 and 9 suggested that the reduction of the parameter c in eq 2.4 to a value of 0.5 provided better results. However, below we show that retaining $c = 1$ and modifying D_1 and D_2 is more realistic. After approximate positions of the energy levels are determined through eqs 2.1, 2.2, 2.5, and 2.6, the number of states $W(E)$ is obtained by state counting. Analytical approximate representation of $W(E)$ after fitting to a continuous expression and differentiation with respect to E finally leads to the density of states $\rho(E) = \mathrm{d}W(E)/\mathrm{d}E$.

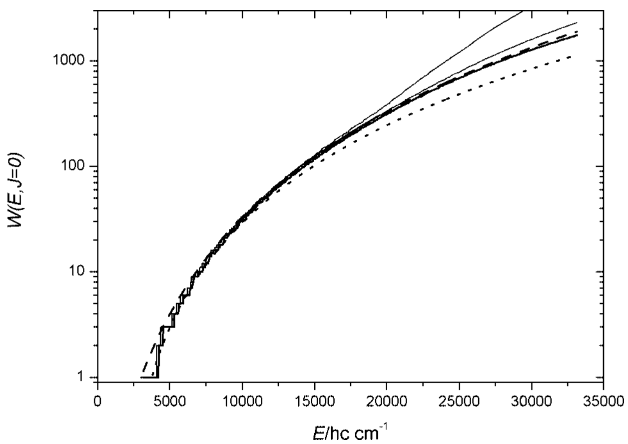

Figure 1. Number of vibrational states $W(E,J = 0)$ for HO_2, see text (curves from bottom to top: dotted line, harmonic oscillator Whitten−Rabinovitch expression; bold full line, optimum anharmonic empirical model ($c = 1$, hindered rotor bend, modified D_i); dashed line, optimum fit to quantum-corrected phase space volume on corrected XXZLG ab initio potential[4,17] (step functions at left: quantized XXZLG and quantized optimum empirical results); lower light line, anharmonic empirical model ($c = 0.5$, hindered rotor bend, unmodified D_i); upper light line, anharmonic empirical model ($c = 1$, hindered rotor bend, unmodified D_i); E = energy above the potential minimum).

Second, if an analytical representation of the ab initio potential energy surface is available, we determine the number $W(E,J)$ of rovibrational molecular states by quantum-corrected Monte Carlo integration of the phase space volume. In this case, the classical phase space volume is calculated and then quantum-corrected by means of the Whitten−Rabinovitch approximation[8] for harmonic levels such as suggested in ref 16. By comparison with filter diagonalization quantum results, the procedure was also checked for HO_2 in ref 4. The phase space integration is unique for the bound states. In the range of dissociative states, however, some decision about the limits of the phase space to include has to be made. The choice of the limits in ref 13 was shown to be relatively arbitrary as long as not too large energies E were considered. In the simplest way, the analytical continuation of the expression for $W(E)$, such as derived from bound states up to the lowest dissociation energy, was shown to be adequate. In the present work, more complicated situations were also analyzed; see below.

3. Anharmonicity Factors for HO_2

Before a comparison with four-atom systems like H_2CO and H_2O_2 is made, we revisit anharmonicity factors for HO_2. First, in Figure 1 we show the number of vibrational states $W(E,J = 0)$ for HO_2 such as obtained by phase space integration with the ab initio XXZLG potential[17] (after the minor corrections for experimental fundamentals and dis-

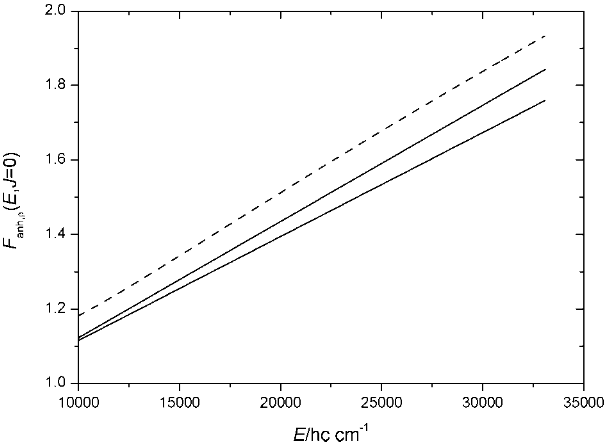

Figure 2. Anharmonicity factor $F_{\mathrm{anh},\rho}(E,J = 0)$ for HO_2, see text (curve from bottom to top: lower line, empirical model ($c = 1$, harmonic oscillator bend, modified D_i); middle line, optimum empirical model ($c = 5$, hindered rotor bend, modified D_i); upper dashed line, quantum-corrected phase space integration results on corrected XXZLG ab initio potential[4,17]).

sociation energies are applied such as described in ref 4). In analytical form our results for $W(E,J = 0)$ like in ref 4 are fitted by

$$W(E,J=0) = [(E + hc\ 1345.05\ \mathrm{cm}^{-1})/hc\ 4347.26\ \mathrm{cm}^{-1}]^{3.643} \quad (3.1)$$

In applying the empirical method of ref 9, like in ref 4 we observed that $W(E,J = 0)$ with the parameter $c = 1$ in eq 2.4 was reasonably well represented up to the first dissociation energy $E = D_1 = hc$ 18960 cm^{-1}. However, $W(E,J)$ was increasingly overestimated for higher energies; see Figure 1. It was suggested in ref 4 to cure this problem by empirically reducing the parameter c in eq 2.4 from unity to a value of 0.5. This procedure, however, was found to be of success only for a limited energy range such as also illustrated in Figure 1. The origin of this problem then was identified by inspecting the ab initio potential. Both in the direction of the H−OO stretching (see Figure 1 of ref 18 and of the HO−O stretching (see Figure 4 of ref 19) the potential is stiffer than that represented by a Morse potential and shows signs of avoided crossings. For this reason, tentatively $D_1 = hc$ 18960 cm^{-1} was assumed to correspond to the dissociation products $H + O_2(^1\Delta)$ and $D_2 = hc$ 23560 cm^{-1} to correspond to the dissociation products $HO + O(^1D)$. Thus, keeping the parameter c equal to unity, excluding all stretching levels above the dissociation energies for $H + O_2(^3\Sigma)$ and $HO + O(^3P)$, and representing the bend by a harmonic oscillator, the empirical method works by far better. Apart from the accurate positions of individual energy levels at low energies, the derived $W(E,J = 0)$ now agrees well with the accurate results. Even better results, agreeing within 5% with the accurate $W(E,J = 0)$, are obtained when the harmonic bend is replaced by a hindered rotor with an effective rotational constant $B = [B(O_2)B(OH)]^{1/2}$; see below. The comparison with $W(E,J = 0)$ for harmonic oscillators, calculated with the Whitten−Rabinovitch approximation, shows the effects of anharmonicity in $W(E,J = 0)$. One may represent this by an anharmonicity factor $F_{\mathrm{anh},W}(E,J)$. Instead, in the following we only consider $F_{\mathrm{anh},\rho}(E,J)$ which is obtained by smoothing, i.e., by representing the step function $W(E,J)$ in the analytical form of eq 3.1 and by differentiating this expression with respect to the energy.

Figure 2 illustrates our results for $F_{\mathrm{anh},\rho}(E,J = 0)$. They are represented in analytical form by

$$F_{\mathrm{anh},\rho}(E,J=0) = 1 + (E - hc\ 4543\ \mathrm{cm}^{-1})/hc\ 30268\ \mathrm{cm}^{-1} \quad (3.2)$$

(A slightly different expression optimized for a range of J values was presented in refs 4 and 13). The accurate results from the XXZLG potential (corrected as mentioned above) are compared with data from the empirical method. In the latter the use of the effective dissociation energies D_1 and D_2 is essential. We show results for harmonic and hindered rotor bending levels with the effective rotational constant $B = [B(O_2)B(OH)]^{1/2}$ and the modified D_i indicated above. The agreement of the latter results with the accurate values looks satisfactory. However, it should be kept in mind that the empirical method in this case required nonempirical insight into the shape of the potential along the H−OO and HO−O stretchings. Without this modification, the overestimates of $W(E,J = 0)$ illustrated in Figure 1 would have limited the quality of the empirical prediction of anharmonicity.

4. Anharmonicity Factors for H_2CO

Besides HO_2, we have chosen the H_2CO system because an analytical representation of the ab initio potential is available[20−22] and the potential shows complexities for the larger energies that are typical for polyatomic molecules. We have used this potential before for classical trajectory calculations of the rate of the reaction $H + HCO \rightarrow H_2 + CO$ in ref 23. We also calculated with it dissociative lifetimes of H_2CO in ref 24 in relation to thermal dissociation and photolysis rates.[25,26] In this system the problem of the phase space boundary of dissociative states is of some interest, because the dissociation proceeds via complex elimination, simple bond fission, and roaming atom mechanisms. In order to handle this situation properly, we started classical trajectories from each phase point in the range of dissociative states of the phase space such as demonstrated in ref 23. Only those phase points then were included in the phase space volume contributing to $W(E,J)$, for which the trajectories propagated in the direction of both positive and negative time showed properties corresponding to bound H_2CO complexes. Apart from this detail, $W(E,J)$ was again determined by Monte Carlo integration of the phase space volume and subsequent quantum-correction using the Whitten−Rabinovitch approximation; see section 2. The resulting $W(E,J = 0)$ (divided by the symmetry number $\sigma = 2$) is shown in Figure 3 and compared with harmonic oscillator results, again obtained with the Whitten−Rabinovitch approximation (using fundamental frequencies of H_2CO which introduces some anharmonicity). $W(E,J = 0)$ in smoothed analytical form is represented by

$$W(E,J=0) = [(E + hc\ 186.30\mathrm{cm}^{-1})/hc\ 6799.34\ \mathrm{cm}^{-1}]^{6.661} \quad (4.1)$$

The accurate numbers of states $W(E,J = 0)$ from the quantum-corrected phase space integration shown in Figure 3 is compared with results from our empirical method. For the four-atom system H_2CO we represent the three stretches corresponding to the fundamentals (2811 (s1), 1756 (s2), and 2861 cm^{-1} (s3)) by Morse oscillators such as characterized by eq 2.1 with dissociation energies $\Delta H_0°/hc = 35970$ ($CO + H + H$), 62260 ($O + CH_2$), and 31040 cm^{-1} ($H + HCO$), respectively. The three bends (1500 (b1), 1251 (b2), and 1170 cm^{-1} (b3)), are again coupled to the adjacent stretches. When the bends are treated as harmonic oscillators, their levels are given by $E_{bi} = h\,\nu_{bi}\,(n_{bi} + 1/2)F_1F_3$ where $F_i = (1 - cE_i/D_i)^{0.41}$ and where E_i are the energies of the stretching vibrations s_1 and s_3. This

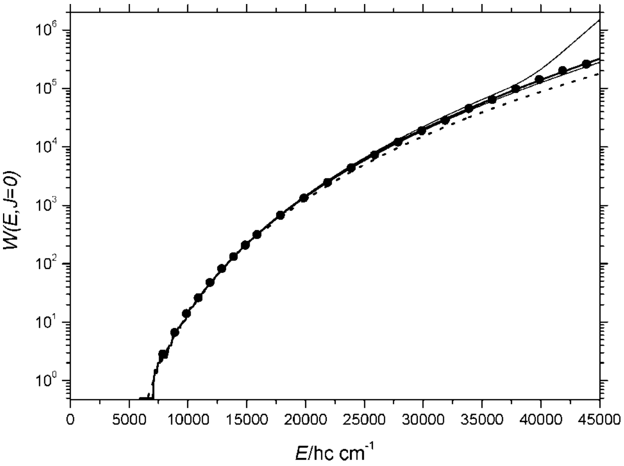

Figure 3. Number of vibrational states $W(E,J = 0)$ for H_2CO, see text (curves from bottom to top: dotted line, harmonic oscillator Whitten−Rabinovitch expression; lower light full line, anharmonic empirical model ($c = 0.5$, harmonic oscillator bends, unmodified D_i); bold full line, optimum anharmonic empirical model ($c = 1$, harmonic oscillator bends, modified D_i); line with filled circles and steps at left, quantum-corrected phase space volume on ab initio potential from ref 20; upper light full line, anharmonic empirical model ($c = 1$, harmonic oscillator bends, unmodified D_i); E = energy above the potential minimum).

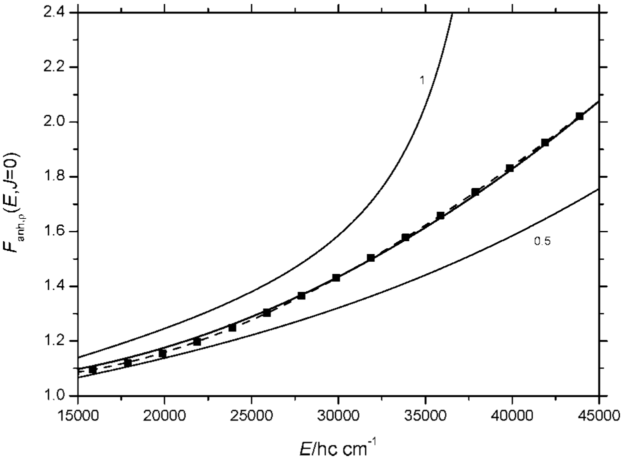

Figure 4. Anharmonicity factor $F_{anh,\rho}(E,J = 0)$ for H_2CO, see text (curves from bottom to top: lower light line, empirical model ($c = 0.5$, harmonic oscillator bends, unmodified D_i); dashed line with filled squares, quantum-corrected phase space integration on ab initio potential from ref 20; bold full line: optimum empirical model ($c = 1$, harmonic oscillator bends, modified D_i); upper light line, empirical model ($c = 1$, harmonic oscillator bends, unmodified D_i); E energy above the potential minimum).

approach generalizes eqs 2.3 and 2.4. As for HO_2, one observes that the choice of $c = 1$ leads to relatively good agreement with the accurate results only up to the first dissociation energy. At higher energies this choice again overestimates $W(E,J = 0)$. (States above the dissociation energies are not included in the empirical determination of $W(E,J = 0)$). Following the experiences made with HO_2, see section 3, the problem would be overcome if larger effective Morse dissociation energies would be used. However, inspecting the ab initio potential we found no evidence for how much the D_i of the stretches might be increased. Therefore, tentatively and by analogy to HO_2, we increased D_3 (corresponding to the dissociation products H + HCO) by the energy hc 9290 cm^{-1} of the first electronically excited state of HCO. Support for this choice comes from a comparison of the empirical stretching levels with spectroscopic levels and $W(E,J = 0)$ from experimental Dunham coefficients[27−30] such as derived for the low energy range (vibrational levels up to about *hc* 12000 cm^{-1}). Representing the experimental H−COH stretching levels in the form of Morse levels, these studies indeed result in larger effective values of D_3 than obtained from the $\Delta H_0°$ given above. With D_3 increased by *hc* 9290 cm^{-1} and $c = 1$, the empirical method then gives $W(E,J = 0)$, which is in good agreement with the quantum-corrected phase space integration results; see Figure 3.

Anharmonicity factors $F_{anh,\rho}(E,J = 0)$ are illustrated in Figure 4. They are represented analytically by

$$F_{anh,\rho}(E,J=0) = 1 + [(E - hc\ 7017\text{cm}^{-1})/hc\ 36419\ \text{cm}^{-1}]^{1.8} \tag{4.2}$$

The comparison of $F_{anh,\rho}(E,J = 0)$ from the phase space integration and from the described modified empirical model appears quite satisfactory.

We have also investigated rotational dependences of the anharmonicity factors $F_{anh,\rho}(E,J)$. First, we have verified that the effect of rotations on harmonic numbers and densities of states indeed can very well be described by the method of rotational factors outlined in refs 10−12 (approximately representing H_2CO by a prolate symmetric top). Second, we have compared $F_{anh,\rho}(E,J)$ with $F_{anh,\rho}(E,J = 0)$ in the phase space integration results. Figures 5 and 6 show the results for $J = 20$ and 50, respectively. One observes that the rotational effects of $F_{anh,\rho}(E,J)$ are only small such that $F_{anh,\rho}(E,J)$ can well be approximated by $F_{anh,\rho}(E,J = 0)$. The deviations appear negligible for practical applications.

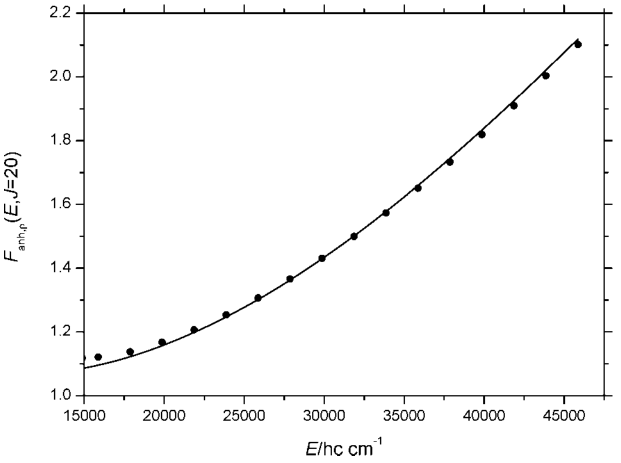

Figure 5. Anharmonicity factor $F_{anh,\rho}(E,J = 20)$ for H_2CO (filled circles, quantum-corrected phase space integration on ab initio potential; full line, phase space results for $J = 0$, see Figure 4; E = energy above the potential minimum).

5. Anharmonicity Factors for H_2O_2

H_2O_2 was chosen as the second four-atom system to be analyzed in the present work. Again an accurate ab initio calculation of the potential energy surface[31] and suitable analytical representations of the potential[31,32] are available. This system shows the complication of a hindered rotor/torsion around the central O−O bond which is relevant already at low energies. In order to separate the high-energy anharmonicities considered so far from the low-energy anharmonicity of this torsion, several alternative procedures may be chosen. First, one may represent the reference numbers and densities of states by the Whitten−Rabinovitch approximation with harmonic tor-

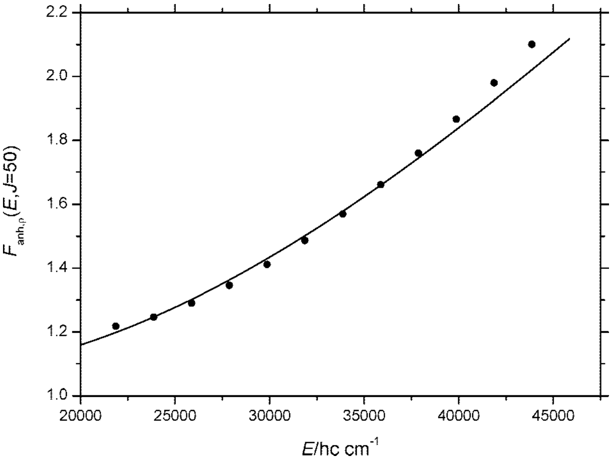

Figure 6. As in Figure 5, for $F_{anh,\rho}(E,J = 50)$.

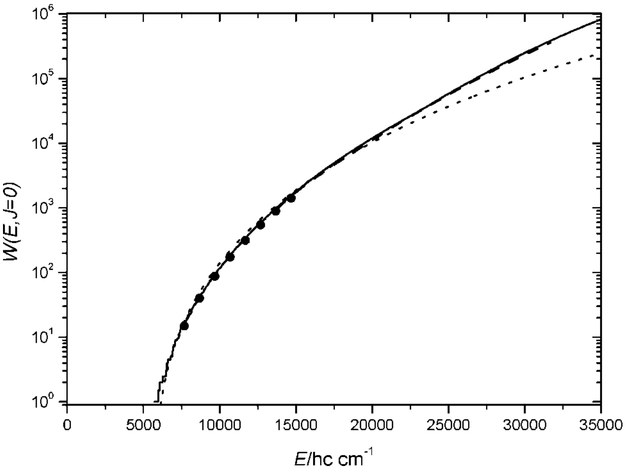

Figure 7. Number of vibrational states $W(E,J = 0)$ for H_2O_2, see text (curves from bottom to top: dotted line, reference Whitten−Rabinovitch expression (free rotor torsion, see text); filled circles and step function, quantum-corrected phase space volume on ab initio potential from ref 31; dashed line, analytical fit to the phase space results; full line, empirical model (hindered rotor torsional levels, $c = 1$, hindered rotor bends, unmodified D_i); E = energy above the potential minimum).

sional levels corresponding to the fundamental torsional frequency. Second, one may employ the Whitten−Rabinovitch approximation including a free rotor torsion.[1,28] Third, one may convolute the correct hindered rotor/torsion density of states with the Whitten−Rabinovitch expression for the number of harmonic oscillator levels of the remaining modes. For simplicity, here we have chosen the second possibility to represent reference numbers and densities of states relative to which anharmonic values are expressed. Analyzing the torsional levels,[31] the best corresponding free rotor number of levels is obtained when the effective rotational constant is chosen as twice the rotational constant of OH. Working with the corresponding reference Whitten−Rabinovitch expression for $W(E,J = 0)$, one observes an overestimate of $W(E,J = 0)$ at low energies. This is of no relevance here, however.

Figure 7 shows our quantum-corrected Monte Carlo integration results of the phase space volume. The calculated $W(E,J = 0)$ are analytically represented by

$$W(E, J = 0) = [(E + hc\ 606.92\ \mathrm{cm}^{-1})/hc\ 5520.91\ \mathrm{cm}^{-1}]^{7.165} \tag{5.1}$$

At energies above hc 15000 cm^{-1} the calculated $W(E,J = 0)$ exceeds the described Whitten−Rabinovitch reference results.

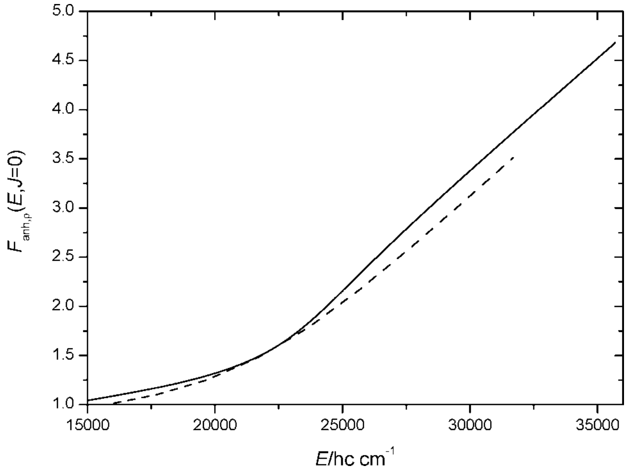

Figure 8. Anharmonicity factor $F_{anh,\rho}(E,J = 0)$ for H_2O_2 (dashed line, quantum-corrected phase space integration on ab initio potential from ref 31; full line, empirical model (hindered rotor torsion, $c = 1$, hindered rotor bends, unmodified D_i); E = energy above the potential minimum).

Without further considering the artifacts of the reference results at lower energies, we only focus attention on the anharmonicity at larger energies.

The phase space results in Figure 7 are compared with results from our empirical method. In this case, the three stretches are treated again as Morse oscillators, the two bends are coupled to the adjacent stretches through eq 2.4, and they are treated as hindered rotors through eqs 2.5 and 2.6 with $B = B(\mathrm{OH})$. The torsion finally is treated as a one-dimensional hindered rotor whose torsional frequency through eq 2.4 is coupled to the adjacent O−O and O−H stretches. Without further modifying the effective dissociation energy of the O−O stretch, the agreement of the empirical and the phase space integration results is very good such as shown in Figure 7. This agreement appears somewhat unexpected, because the potential along the O−O bond at large bond extensions has a “reef”.[31,32] However, raising the effective dissociation energy by the energy of the first electronically excited state of OH analogous to the procedure empirically applied for HO_2 and H_2CO would not have led to noticeable modifications of the results.

Figure 8 shows the anharmonicity factors $F_{anh,\rho}(E,J = 0)$. They are not given for low energies, because here the free-rotor Whitten−Rabinovitch reference number of states is oversimplified. Therefore, only above about hc 15000 cm^{-1} the results become meaningful. Here, they approach an analytical expression of the form

$$F_{anh,\rho}(E, J = 0) \approx 0.693 + 2.47y + [6.11y^2 + 0.484]^{1/2} \tag{5.2}$$

with $y = (E - hc\ 21000\ \mathrm{cm}^{-1})/hc\ 20000\ \mathrm{cm}^{-1}$. The results from our empirical method without modification of the dissociation energies nearly agree with the phase space integration results.

6. Conclusions

The present quantum-corrected Monte Carlo integration of the phase space volumes on ab initio potentials for HO_2, H_2CO, and H_2O_2 illustrates the increasing contribution of anharmonicity to vibrational numbers and densities of states when the energy increases. On the other hand, there are only small rotational dependences of the anharmonicity. As long as complete and accurate potentials are not available for larger molecules, one may try to specify anharmonicity effects for larger molecules by empirical models. One such model is the one described here, slightly modifying the original version from ref 9. However, because of its empirical character, it needs comparisons with benchmark calculations such as given in the present work. We found that the original model works reasonably well up to the first dissociation energy. However, it overestimates the anharmonicity at larger energies. Empirically using larger effective Morse dissociation energies, the performance of the empirical model could be markedly improved. However, this modification requires at least some nonempirical insight into the potential, either from ab initio calculations or from spectroscopic observations such as Dunham parameters. Generalizing such modifications, one may proceed and employ the empirical model for estimates of high-energy anharmonicity effects in larger molecules. We have done preliminary calculations of this type and found that the calculational effort up to large molecular sizes is still tolerable. However, such calculations so far could not be checked against results based on ab initio potentials.

Despite the satisfactory performance of the described empirical model, it is clear that it cannot be accurate. However, in view of the need for realistic estimates of anharmonicity effects in statistical unimolecular rate theories, the limitations of our approach may appear tolerable for practical applications.

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