

Numerical Laplace transform density of states calculation for medium and large molecules

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(Received 11 June 1992; accepted 24 December 1992)

A novel implementation of the Laplace transform method for the calculation of the density of states of molecules, for which the partition function can be explicitly given is described. It consists of doing the inverse Laplace transform numerically after multiplying the integrand by a smoothing factor. This evaluation is more accurate than the method of steepest descent, and the computation can still be done on a PC in a few minutes. By first order expansion of the partition function in the anharmonic parameters we have been able to calculate the density of states for a model molecule composed by anharmonically coupled anharmonic oscillators, which cannot be treated by the well known Beyer–Swinehart algorithm.

INTRODUCTION

Since the 1950s, with the statistical theory of unimolecular reactions, the density of quantum levels at the activated complex configuration has been one of the relevant inputs in the calculation of reaction rates.¹ More recently, in the related topic of intramolecular vibrational relaxation (IVR), the evaluation of the density of states (DOS) at relatively low energies (with respect to the dissociation energy) has also become necessary for modeling the experimental data.^{2–5}

Several approximated formulas are now available to estimate the DOS of relatively large molecules (more than 20 normal modes), for which a direct count of all the levels is computationally impractical. Forst and Prášil⁶ have tested most of these approximations on two artificial models (model-A for a small molecule and model-B for a large one). In their paper a discussion of each method is given together with the relevant references, and the numerical results for each approximation are compared with those obtained from a direct count. The steepest-descent based formulas are those which are shown to give the most accurate results. Few years later, Beyer and Swinehart⁷ (BS) have introduced an extremely efficient, simple, and accurate algorithm which applies to harmonic molecular models. If an energy step is chosen which divides exactly the normal frequencies of the model, this algorithm gives exact DOS values. Stein and Rabinovitch⁸ (SR) have then extended this method to deal also with all models where the energy levels for each independent degree of freedom can be calculated. This extension is very versatile and accurate, and cases like uncoupled Morse oscillators are treatable. These last two algorithms require a rather large memory size, but the computational effort increases only linearly with (number of modes \times max energy/energy step).

In the present paper we propose a numerical recipe which is related to the steepest-descent approximation. This recipe gives a Gaussian-smoothed DOS which is exact when the partition function of the molecule can be evaluated exactly. Limits are set by numerical precision and integration errors. The smoothing width δ can be adjusted

at will and the computation time is inversely proportional to this parameter, and almost linear with the number of molecular normal modes.

After a detailed description of our numerical recipe, we will first make a comparison with the direct count and the best approximation (steepest descents) reported by Forst and Prášil, for their same model molecules. We will also consider the case of a molecule much larger than model-B, that is $(\text{CF}_3)_3\text{C}-\text{C}\equiv\text{CH}$, with 24 normal modes, of which ten are doubly and four are triply degenerate. For this molecule we use the BS algorithm to generate the exact DOS. These examples will demonstrate the accuracy that can be obtained with the proposed numerical method.

Our approach is computationally convenient when the DOS at given energy values is required and the requested DOS smoothing width is not too small (typically, $\delta > 1 \text{ cm}^{-1}$ is acceptable). However, for all molecular models that can be treated both by our technique and by SR, the SR is superior in that it gives the whole DOS profile with little effort. If the frequencies cannot be exactly divided by an energy step, our results are in general more accurate (if the exact partition function is used), but SR gives values which are sufficiently accurate for most applications. On the other hand, there are models that can be approached much more satisfactorily by our technique than by SR. The typical case is when there is appreciable mode to mode interaction so that it is impossible to list the energy levels associated with each single mode independently of the degree of excitation of the others. In this case, the SR scheme cannot be applied, while the partition function may be numerically evaluated or some good approximations for it can be made, allowing the use of our numerical method. Clearly, the opposite situation can occur if a model with independent modes has a partition function for which an accurate and efficient numerical algorithm cannot be found.

A good example with interacting modes for which it is not possible to properly apply the SR algorithm is the fully anharmonic model of a molecule where all cubic anharmonic parameters are given. Starting from the partition function, it is possible to expand it at the first order in the

anharmonic constants and then convert it to a closed analytical form. We report numerical results for a realistic case (HCCF, as five anharmonically-coupled anharmonic oscillators, of which two are doubly degenerate) and compare them with the direct count values. Even if the first order approximation starts to break down at high energies, these DOS estimates are significantly better than the SR values resulting from considering only the diagonal anharmonic constants, and of the results obtained by considering only the harmonic part of the HCCF potential.

The values reported here were obtained with a program in compiled QUICK-BASIC, running on an IBM 486 personal computer, which uses the Romberg method to evaluate the inverse Laplace transform integral. The typical computation time is of the order of 10 s per datum. We have also a more efficient version of this program, written in VAX-FORTRAN, which uses the FORTRAN integration routine QDAG.⁹ This software is available from us upon request.

TECHNICAL DETAILS

Our method follows the same trace of the steepest-descents. The DOS is the inverse Laplace-transform of the partition function. In the case of the harmonic model of a molecule, the partition function is given in closed analytical form. The inverse Laplace-transform consists of a line-integral in the complex plane, the integration path being a straight line parallel to the imaginary axis. The problem is therefore reduced to that of approximating the integral of a function which is computationally well defined. In the steepest-descents method, an approximate analytical formula for the integral is given, which depends on the behavior of the integrand at a saddle point. On the other hand, we estimate the integral numerically along part of the integration path, so that the behavior of the integrand away from the saddle point is also accounted for.

The relation between the partition function and the DOS comes from the very definition of vibrational partition function

$$\begin{aligned} Q_v(\beta) &= \sum_{r=0}^{\infty} g_r e^{-\beta E_r} \\ &= \int_0^{\infty} \rho(E) e^{-\beta E} dE \\ &= \prod_{s=1}^N (1 - e^{-\beta \nu_s})^{-1}, \end{aligned} \quad (1)$$

where the summation is over the vibrational energy levels of the molecule, g_r is the degeneracy of the level with energy E_r , and $\rho(E)$ is the corresponding DOS, which is a sum of delta-functions centered at the E_r 's with weights g_r . The last equality follows by considering the molecule as consisting of N harmonic normal modes with frequencies ν_s (and measuring the energy scale from the ground state). All energies will be measured in cm^{-1} , and in particular $\beta = 1/kT$ (cm^{-1}).

The integral form of the partition function makes it evident that it can be considered as the Laplace transform

of the DOS. From the theory of the Laplace transform¹⁰ it follows that, since $\rho(E)$ is zero for $E < 0$ then $Q_v(\beta)$ is an analytical function of the generalized complex variable β in the half complex plane with positive real part ($\beta = x + iy$, $x > 0$). The formula for the inverse Laplace transform is¹⁰

$$\rho(E) = \frac{1}{2\pi i} \int_{x_0 - i\infty}^{x_0 + i\infty} Q_v(\beta) e^{\beta E} d\beta, \quad (2)$$

where the integration path is a straight line parallel to the imaginary axis and lying in the analytical domain of the integrand ($x_0 > 0$). It is important to note that the value of the integral will not depend on where the integration axis is placed, as long as $x_0 > 0$.

Unfortunately, this complex integration does not have a numerically defined limit. The result must be a sum of delta functions, so that the integral is zero for all the values of E except the set of zero measure $\{E_r\}$, where it diverges. This is reflected in the fact that the integrand function irregularly oscillates along the integration path without the average amplitude ever decreasing, since to generate delta functions, arbitrarily large frequencies have to contribute. The question is then, what happens if the integral is evaluated on some finite interval $[x_0 - iy_0, x_0 + iy_0]$? The result is that the delta functions in $\rho(E)$ are replaced by peaks with a width of the order of $1/y_0$ and therefore the details of the DOS as a function of the energy are partially lost. To be more precise, if the integral is "sharply cut" at the edges of the interval, the delta functions are converted to $\sin[y_0(E - E_r)]/(E - E_r)$ profiles. The effect is the same as when suppressing the high frequencies in the Fourier-transform of some time-dependent signal; the fast time variations are smoothed-out. Since the harmonic or even the anharmonic approximations of the molecular potential are already not sufficiently good to give the exact location of the energy levels, the averaging of the fine details of the DOS does not lead to a real loss of information. Even in a case where the exact partition function could be evaluated numerically, the smoothed density of levels still remains a useful piece of information about the system.

In practice, we will proceed in the opposite direction, and instead of "cutting" the integral in some way, we apply a Gaussian smoothing (with $1/e$ half-width given by δ) to the DOS function. What we obtain is a weight function which effectively produces a smooth cut of the integral. If we want to preserve the total number of states, the Gaussian function to be convoluted to the DOS [as given in Eq. (2)] must be normalized to one. This smoothed DOS turns out to be numerically well-behaved. We have

$$\begin{aligned} \bar{\rho}_{\delta}(E) &= \int_{-\infty}^{+\infty} \rho(E') \frac{e^{-(E-E')^2/\delta^2}}{\sqrt{\pi}\delta} dE' \\ &= \frac{1}{2\pi i} \int_{x_0 - i\infty}^{x_0 + i\infty} Q_v(\beta) \int_{-\infty}^{+\infty} e^{\beta E'} \frac{e^{-(E-E')^2/\delta^2}}{\sqrt{\pi}\delta} \\ &\quad \times dE' d\beta, \end{aligned} \quad (3)$$

where the order of integration has been inverted. Integrating in dE' gives a factor $\exp(\beta E + \delta^2 \beta^2/4)$. Then, the in-

tegral over β can be split into an integral over $[x_0 - i\infty, x_0]$ plus one over $[x_0, x_0 + i\infty]$, which turn out to be the complex conjugate of each other. By summing the two parts back together

$$\begin{aligned}\bar{\rho}_\delta(E) &= \frac{1}{\pi i} \int_{x_0}^{x_0 + i\infty} \text{Re}[F_\delta(E, \beta)] d\beta \\ &= \frac{1}{\pi} \int_0^\infty \text{Re}[F_\delta(E, x_0 + iy)] dy,\end{aligned}\quad (4)$$

$$F_\delta(E, \beta) = Q_v(\beta) \exp(\beta E + \delta^2 \beta^2 / 4).$$

The fact that $F_\delta(E, \beta)$ is well-behaved, so that it can be integrated numerically, follows from

$$\exp(\delta^2 \beta^2 / 4) = \exp \frac{\delta^2}{4} (x^2 - y^2) \times \exp \frac{\delta^2}{2} ixy, \quad (5)$$

where the exponent $-\delta^2 y^2 / 4$ gives a cutoff of the order of δ^{-1} , since it makes the integrand vanish very rapidly when y becomes larger than a few times δ^{-1} .

Along the integration path, along which only the imaginary part of β varies, the factors $(1 - e^{-\nu\beta})^{-1}$ in the partition function resemble the transmission function of an étalon, with peaks regularly spaced, characterized by a width decreasing with E (see discussion below). Every time y is almost a common multiple of the wavelengths corresponding to the frequencies ν_n , a beat note, or recurrence, is generated. One recurrence is obviously at $\beta = x_0$ ($y_0 = 0$), where all factors start with zero phase. We will denote the position of these recurrences by their coordinate along the integration axis, y_0, y_1, y_2, \dots . The separation between recurrences depends on how well the ratios between all the normal frequencies are approximated by small integers. This becomes increasingly unlikely for large molecules with many normal frequencies.

The dependence of the width of the recurrences and their intensity on the energy is a consequence of the following argument for the choice of a particular integration axis. It can be easily seen that there must be only one minimum of the integrand function along the real axis. Since the value of the integral does not depend on x_0 and the strongest recurrence is always on the real axis, if x_0 is chosen to minimize this initial recurrence, then the oscillations in the integrand are also minimized. In fact, if the integration is started from a point x_0 where the integrand is not at a minimum, more oscillations of the integrand will be needed to compensate for the initial larger contribution and result in the same value of the integral. In such a case, the increased round off errors make the numerical evaluation of the integral more inaccurate.

The position of this "optimal" x_0 depends on the energy. In the limit of large E , x_0 is inversely proportional to E (see the Appendix). As a result, also the width of the peaks in the étalonlike factors considered above tends to be inversely proportional to E . Therefore the recurrences become narrower and their intensity decreases (except for the exact ones, such as y_0), when E increases.

In the limit of large molecules and high energy, for all values of the cutoff δ^{-1} smaller than the position of the

first recurrence y_1 , the integral is dominated by the behavior of the integrand very close to the zero recurrence, which has the shape of a sharp and narrow peak without "wiggles" at its tails. In this case, the steepest-descent approximation gives a result which is a good estimate of a DOS smoothed with an energy resolution δ larger than $1/y_1$. On the other hand, in the case of small molecules and low energies, where the zero recurrence has many wiggles at its tails, the steepest-descent approximation accounts just for the central peak, yielding less accurate values, which should correspond to a very coarsely smoothed DOS. These considerations indicate the general conditions for the steepest descent to perform well, but they also suggest that in some unfortunate cases the steepest descents could produce a bad DOS estimate, in particular when the frequencies are such that y_1 is small and the corresponding recurrence strong. The problem is that the steepest descents method does not give any control on the effective smoothing width. Finally, it should be noted that the particular structure of the integrand implies a general property for the DOS at sufficiently high energies. That is, if the average level-spacing is of the order of $1/y_1$ (as it is made plausible in the Appendix), the value of the smoothed DOS is practically constant as the smoothing width varies from the average level-spacing up to a value close to E , which approximately corresponds to the width of the zero recurrence.

To numerically evaluate the integral which gives the smoothed DOS, we have developed a program which requires as an input the frequencies that define the molecular harmonic model, and then the energy at which the DOS has to be calculated, the Gaussian smoothing factor δ and the desired numerical accuracy. The program finds the correct value of x_0 by minimizing numerically the integrand function along the positive real axis, and sets a finite integration interval large enough that the neglected part is virtually zero. For this, it is convenient to use $[x_0, x_0 + i10/\delta]$. The integral on this interval is then evaluated to the requested accuracy using some standard integration routine. We have a version written in QUICK-BASIC for IBM-PC's, which uses a robust but slow Romberg integration scheme, and a VAX-FORTRAN version which uses a more efficient globally adaptive Gauss integration subroutine (QDAG) from the Fortran library.

It should be noticed that since the integration interval is inversely proportional to δ , while the density of integration points should approximately remain constant for the same accuracy, the computation time is linear in the requested energy resolution, as stated earlier. With respect to the accuracy, the computation time increases only in a logarithmic fashion. Besides these facts, since the integral with a smaller δ has to account for more oscillations in the partition function, the integration procedure should become numerically unstable and inaccurate results are to be expected in the limit of very high energy resolution.

In practice, using numerical double precision (real*8), we have found that even with 1 cm^{-1} resolution the integration does not have problems to converge to the correct value (obtained by exact count). However, the cpu time on

a VAX-3400 system is of the order of 10 min to get one value of the DOS for the molecule $(\text{CF}_3)_3\text{C}-\text{C}\equiv\text{CH}$, whose frequencies are listed in Table III. Therefore, it appears that the limiting factor is the computation time rather than the numerical accuracy.

HARMONIC CASE: COMPARISON WITH OTHER APPROXIMATIONS

To test our technique in exactly the same way as in Ref. 6 and to be able to make a comparison with the results of other approximations reported there, we have to include the presence of "free rotors" in the partition function. The free rotor coordinates of subsystems in the molecule are independent of the other vibrational degrees of freedom and the partition function can be factorized as $Q_{vr}=Q_vQ_r$. To avoid including the moment of inertia in the calculations, the rotational partition function is reduced to (notations slightly differ from Ref. 6)

$$Q'_r(\beta) = Q_r(\beta)/C_I = \beta^{-R/2} \quad (6)$$

$$C_I = \left(\frac{2}{\pi^2}\right)^{R/2} \prod_{s=1}^R \sigma_s^{-1} I_s^{d_s/2} \Gamma\left(\frac{d_s}{2}\right),$$

where R is the number of free rotors, σ_s is the symmetry number, and d_s the dimension ($d_s=1$ or 2) of the s th rotational mode. In this way, the reduced partition function used in Eq. (4) to obtain what we will call "reduced DOS," is

$$Q'_{vr}(\beta) = Q_v Q'_r = Q_v(\beta) \beta^{-R/2}. \quad (7)$$

As noted in Ref. 6, the case $R'=R+2$ gives the total number of states for a molecule with R free rotors. In general this is a property of the Laplace-transform, since the transform of an integral is equal to the transform of the integrand, divided by the independent variable. Therefore, by including the parameter R in our program we are now able to deal both with free rotors and with the total number of states. Note that the units of the calculated DOS for a given value of R are given by $(\text{cm}^{-1})^{R/2-1}$. If the true DOS is needed, the result of the calculation should be scaled by C_I .

In Tables I(a) and I(b), our numerical approximation is applied to model-A (small molecule) and to model-B (large molecule) for the same energies and number of rotors as in Forst and Prášil.⁶ The data are normalized to the corresponding exact-count values taken from Ref. 6 and compared to the results of the steepest-descents approximation (listed as "FP"), which is the best analytic approximation available.

In Table II, we compare results for $(\text{CF}_3)_3\text{C}-\text{C}\equiv\text{CH}$, with 24 normal modes, of which ten are doubly and four are triply degenerate. This molecule is one of the large acetylenic systems which are of current interest for investigations on internal vibrational redistribution phenomena. The normal frequency values that we used have been estimated by one of our collaborators by considering similar systems. The BS algorithm gives exact results if the energy partitions exactly divide the harmonic frequencies.^{7,8} Therefore, in our case we obtained the exact count values

TABLE I. (a) Comparison of calculated "reduced" DOS against direct count values (DC) for model-A ("small") molecule from Ref. 6. To obtain the real density it is necessary to multiply the listed values by the factor C_I in Eq. (6), which contains the moment of inertia and geometrical information on the molecule. FP are the steepest-descents results by Forst and Prášil (Ref. 6) and RL are the results of our numerical recipe for $\delta=10 \text{ cm}^{-1}$. Frequencies for model-A are listed in Table III.

R	Energy (cm^{-1})	DC ($\text{cm}^{1-R/2}$)	FP/DC	RL/DC
2	1 000	2.0000×10^0	1.058	1.0000
	2 000	5.0000×10^0	1.082	1.0000
	3 000	1.1000×10^1	1.042	1.0000
	4 000	2.1000×10^1	1.031	1.0000
	5 000	3.5000×10^1	1.077	1.0000
	10 000	2.9100×10^2	1.024	0.9973
	20 000	3.7300×10^3	1.019	0.9995
3	1 000	4.8043×10^1	1.116	0.9999
	2 000	1.6235×10^2	1.016	1.0000
	3 000	3.8135×10^2	1.029	1.0000
	4 000	7.7103×10^2	1.047	1.0000
	5 000	1.4328×10^3	1.051	1.0000
	10 000	1.4690×10^4	1.024	0.9998
	20 000	2.4627×10^5	1.017	1.0000
4	1 000	1.1200×10^3	1.113	1.0000
	2 000	4.6240×10^3	1.017	1.0000
	3 000	1.2280×10^4	1.033	1.0000
	4 000	2.7270×10^4	1.047	1.0000
	5 000	5.4996×10^4	1.041	1.0000
	10 000	7.1024×10^5	1.023	1.0000
	20 000	1.5574×10^7	1.016	1.0000
5	1 000	2.4777×10^4	1.079	1.0000
	2 000	1.2230×10^5	1.029	1.0000
	3 000	3.7583×10^5	1.032	1.0000
	4 000	9.2473×10^5	1.039	1.0000
	5 000	2.0058×10^6	1.035	1.0000
	10 000	3.2933×10^7	1.022	1.0000
	20 000	9.4669×10^8	1.015	1.0000

by the BS algorithm with 1 cm^{-1} partitions. To allow for a fair comparison with the numerical DOS values, the density on these partitions was smoothed with a Gaussian filter of $1/e$ half-width, equal to the value of δ in our calculations (20 cm^{-1}). The numerical results were converged to 1×10^{-8} relative accuracy, and this is indeed the degree of agreement with the exact smoothed values. The computation time on a VAX-3400 is ~ 30 s per datum, but it would be only a few seconds if less accuracy would be required. The BS computation time for the whole density profile and the smoothing was ~ 7 s on the same computer. In Table II are also reported the values for the total number of states (SUM), which were obtained numerically by setting the number of free rotors $R=2$. For these SUM values the agreement does not appear to be as good as for the DOS. We have not been able to understand the origin of this discrepancy.

The normal frequencies of all these molecular models are listed in Table III.

FULL ANHARMONIC CASE: COMPARISON WITH THE EXACT COUNT

In general, the vibrational energy in the anharmonic approximation can be written as

TABLE I. (b) Same as in Table I(a) with Forst and Prášil (Ref. 6) model-B ("large") molecule. The smoothing factor used for the RL values is $\delta = 10 \text{ cm}^{-1}$. Frequencies for model-B are listed in Table III.

R	Energy (cm^{-1})	DC ($\text{cm}^{1-R/2}$)	FP/DC	RL/DC
2	1 000	5.0000×10^0	0.660	0.9935
	2 000	2.0000×10^1	0.808	0.9750
	3 000	7.0000×10^1	0.883	0.9995
	4 000	2.0600×10^2	0.972	0.9985
	5 000	6.2000×10^2	0.927	0.9516
	10 000	3.6773×10^4	1.014	0.9900
3	20 000	1.0523×10^7	1.013	0.9993
	1 000	5.4292×10^1	1.324	0.9907
	2 000	3.7189×10^2	1.076	0.9955
	3 000	1.6126×10^3	1.034	0.9994
	4 000	5.5460×10^3	1.039	0.9997
	5 000	1.7028×10^4	1.025	0.9953
4	10 000	1.3377×10^5	1.016	0.9993
	20 000	4.7741×10^8	1.011	0.9999
	1 000	1.0680×10^3	1.400	1.0000
	2 000	8.7530×10^3	1.094	0.9998
	3 000	4.1168×10^4	1.062	1.0000
	4 000	1.5427×10^5	1.049	1.0000
12	5 000	5.0094×10^5	1.034	0.9997
	10 000	4.7830×10^7	1.018	1.0000
	20 000	2.1241×10^{10}	1.010	1.0000
	1 000	8.3333×10^{12}	0.997	1.0005
	2 000	3.0522×10^{14}	1.030	1.0002
	3 000	3.5886×10^{15}	1.025	1.0001
	4 000	2.5795×10^{16}	1.021	1.0000
	5 000	1.3829×10^{17}	1.019	1.0000
	10 000	6.8149×10^{19}	1.015	1.0000
	20 000	1.8559×10^{23}	1.009	1.0000

TABLE II. Comparison of exact smoothed DOS and sum of states (SUM) with values calculated with our numerical method (RL) for $(\text{CF}_3)_3\text{C}-\text{C}\equiv\text{CH}$. The normal frequencies of this molecule are listed in Table III. The exact DOS and SUM have been obtained using the BS algorithm, (Refs. 7 and 8) with energy partitions of 1 cm^{-1} which divide the normal frequencies exactly. The smoothing has been done with a Gaussian of 20 cm^{-1} $1/e$ half-width, which is the value of δ used in the numerical DOS and SUM calculations.

E/cm^{-1}	BS DOS	BS SUM	RL DOS	RL SUM
			BS	BS
100	$1.778\,776\,033 \times 10^{-2}$	$4.046\,748\,543 \times 10^0$	1.000 000 00	0.999 973 36
200	$3.252\,281\,664 \times 10^{-1}$	$2.027\,906\,333 \times 10^1$	1.000 000 00	1.000 026 06
300	$8.299\,223\,412 \times 10^{-1}$	$6.419\,931\,443 \times 10^1$	1.000 000 00	0.999 948 95
400	$1.896\,621\,728 \times 10^0$	$2.108\,841\,148 \times 10^2$	1.000 000 00	1.000 003 43
500	$6.057\,455\,947 \times 10^0$	$5.617\,724\,850 \times 10^2$	1.000 000 00	0.999 991 78
600	$1.207\,080\,347 \times 10^1$	$1.419\,150\,637 \times 10^3$	1.000 000 00	0.999 991 07
700	$2.812\,641\,580 \times 10^1$	$3.358\,877\,712 \times 10^3$	1.000 000 00	0.999 996 18
800	$5.919\,996\,115 \times 10^1$	$7.531\,565\,739 \times 10^3$	1.000 000 00	0.999 995 50
900	$1.210\,232\,660 \times 10^2$	$1.615\,957\,726 \times 10^4$	1.000 000 00	0.999 994 99
1 000	$2.345\,592\,338 \times 10^2$	$3.344\,835\,491 \times 10^4$	1.000 000 00	0.999 996 39
2 000	$6.634\,483\,432 \times 10^4$	$1.295\,305\,337 \times 10^7$	1.000 000 00	0.999 997 92
3 000	$5.395\,732\,990 \times 10^6$	$1.292\,752\,302 \times 10^9$	1.000 000 00	0.999 998 61
4 000	$2.201\,598\,181 \times 10^8$	$6.138\,868\,682 \times 10^{10}$	1.000 000 00	0.999 998 97
5 000	$5.666\,426\,498 \times 10^9$	$1.784\,823\,481 \times 10^{12}$	1.000 000 00	0.999 999 19
6 000	$1.040\,832\,446 \times 10^{11}$	$3.632\,867\,616 \times 10^{13}$	1.000 000 00	0.999 999 34
7 000	$1.472\,202\,415 \times 10^{12}$	$5.617\,504\,951 \times 10^{14}$	1.000 000 00	0.999 999 45
8 000	$1.687\,261\,819 \times 10^{13}$	$6.967\,718\,673 \times 10^{15}$	1.000 000 00	0.999 999 53
9 000	$1.624\,579\,101 \times 10^{14}$	$7.204\,170\,262 \times 10^{16}$	1.000 000 00	0.999 999 59
10 000	$1.349\,919\,007 \times 10^{15}$	$6.387\,974\,290 \times 10^{17}$	1.000 000 00	0.999 999 64

$$E(\{n_s\}_s) = \sum_{s=1}^N \nu_s(n_s + \frac{1}{2}) + \sum_{r,s} X_{rs}(n_r + \frac{1}{2})(n_s + \frac{1}{2})$$

$$= E_0 + \sum_s \nu_s n_s + \sum_{r,s} X_{rs}(n_r + n_s n_s). \quad (8)$$

Conventionally, doubly-degenerate modes (e.g., $\nu_r = \nu_s$ and $X_{rr} = X_{ss}$) are described by using other quantum numbers, linearly related to the ones we use, that is $n'_r = n_r + n_s$, $l_r = n_r - n_s$, and the summations are restricted to $r < s$. It can be easily verified that our anharmonic constants are related to the conventional ones (X'_{rr} and g_{rr}) by the linear relations $X_{ss} = X_{rr} = X'_{rr} + g_{rr}$ and $X_{rs} = X'_{rr} - g_{rr}$. The relations for the off-diagonal terms with another doubly degenerate mode (e.g., $\nu_t = \nu_u$, $X_{tt} = X_{uu}$, $X_{rt} = X_{su}$ and $X_{ru} = X_{st}$) are $X_{rt} = (X'_{rt} + g_{rt})/2$ and $X_{ru} = (X'_{rt} - g_{rt})/2$. For the off-diagonal term with another nondegenerate mode w is $X_{rw} = X'_{rw}/2$.

By dropping the zero-point energy E_0 and expanding the exponential in the partition function in powers of the anharmonic constants

$$\mathcal{Q}_{v,a}(\beta) = \sum_{\{n_s\}_s} e^{-\beta \sum_s \nu_s n_s} \left[1 - \beta \sum_{r,s} X_{rs}(n_r + n_s n_s) + O(\beta^2 X_{rs}^2) \right]. \quad (9)$$

The first summation is the usual harmonic partition function. The term linear in the anharmonic constants gives

TABLE III. Molecular parameters in wave numbers. Degeneracies are given in parentheses. model-A and model-B are taken from Forst and Prášil (Ref. 6), the $(\text{CF}_3)_3\text{C}-\text{C}\equiv\text{CH}$ values are estimated by considering similar molecules, and the HCCF parameters are taken from Ref. 11.

Model-A					
ν_1 (1)	3788	ν_2 (1)	3774	ν_3 (1)	1440
ν_4 (1)	1296	ν_5 (1)	880		
Model-B					
ν_1 (6)	3034	ν_2 (1)	2000	ν_3 (4)	1415
ν_4 (4)	983				
$(\text{CF}_3)_3\text{C}-\text{C}\equiv\text{CH}$					
ν_1 (1)	3328	ν_2 (1)	2100	ν_3 (1)	1305
ν_4 (2)	1275	ν_5 (3)	1248	ν_6 (1)	1140
ν_7 (2)	1109	ν_8 (2)	921	ν_9 (1)	861
ν_{10} (1)	753	ν_{11} (2)	711	ν_{12} (2)	650
ν_{13} (1)	600	ν_{14} (2)	555	ν_{15} (3)	542
ν_{16} (1)	518	ν_{17} (2)	390	ν_{18} (2)	337
ν_{19} (1)	322	ν_{20} (2)	307	ν_{21} (1)	295
ν_{22} (3)	180	ν_{23} (2)	174	ν_{24} (3)	66
HCCF					
ν_1 (1)	3499.722	ν_2 (1)	2283.781	ν_3 (1)	1076.266
ν_4 (2)	596.836	ν_5 (2)	375.411	X'_{11}	-52.000
X'_{12}	-11.165	X'_{13}	-3.869	X'_{14}	-22.261
X'_{15}	-8.981	X'_{22}	-7.790	X'_{23}	-0.118
X'_{24}	-6.727	X'_{25}	-16.630	X'_{33}	-6.850
X'_{34}	-2.380	X'_{35}	3.253	X'_{44}	-1.010
X'_{45}	0.684	X'_{55}	0.281	g_{44}	4.898
g_{45}	0.177	g_{55}	0.879		

$$\begin{aligned}
& \sum_{\{n_s\}_s} \left[\sum_{r,s} X_{rs} n_r e^{-\beta \nu_r n_r} \prod_{t \neq r} e^{-\beta \nu_t n_t} \right. \\
& + \sum_{r,s \neq r} X_{rs} n_r n_s e^{-\beta \nu_r n_r} e^{-\beta \nu_s n_s} \prod_{t \neq r,s} e^{-\beta \nu_t n_t} \\
& \left. + \sum_s X_{ss} n_s^2 e^{-\beta \nu_s n_s} \prod_{t \neq s} e^{-\beta \nu_t n_t} \right] \\
& = \left[\sum_{r,s} X_{rs} D_r + \sum_{r,s \neq r} X_{rs} D_r D_s + \sum_s X_{ss} D_s (2D_s + 1) \right] \\
& \quad \times \prod_t S_t^{(0)} \\
& = \prod_t S_t^{(0)} \times \sum_{r,s} X_{rs} (\delta_{rs} + 1) D_r (D_s + 1) \\
& = Q_v(\beta) \times C_X^{(1)}(\beta), \tag{10}
\end{aligned}$$

where Q_v is the zero-order harmonic partition function as defined in Eq. (1), and $S_r^{(k)}$ and D_r are defined by

$$S_r^{(k)} = \sum_n n^k e^{-\beta \nu_r n} \quad S_r^{(k)} = -\frac{\partial S_r^{(k-1)}}{\partial \beta \nu_r}$$

so that

$$\begin{aligned}
D_r &= e^{-\beta \nu_r} (1 - e^{-\beta \nu_r})^{-1} \\
S_r^{(0)} &= D_r e^{\beta \nu_r}, \\
S_r^{(1)} &= D_r S_r^{(0)}, \\
S_r^{(2)} &= D_r (2D_r + 1) S_r^{(0)}. \tag{11}
\end{aligned}$$

Looking back at Eq. (9), it is clear that the first-order anharmonic partition function can be finally written as

$$Q_{v,a}^{(1)}(\beta) = Q_v(\beta) \times [1 - \beta C_X^{(1)}(\beta)]. \tag{12}$$

In Table IV, results obtained for the molecule HCCF by using this approximation are compared with exact direct count results. All anharmonic constants for HCCF are given¹¹ as listed in Table III. The obvious trend is that the approximation underestimates the exact values at high energies. This is only partially the effect of having neglected the higher orders in the anharmonic constants. In fact, we were able to analytically simplify the second order term in the partition function and include it in the numerical integration. The improvement was not impressive, for example, the relative difference of the DOS from the exact count value for HCCF at 20 000 cm^{-1} decreased from 6.4% to 4.0%. This did not compensate the increase in the calculation time (roughly twofold).

The problem is that the cubic potential approximation is not physically meaningful at large interatomic distances, and the corresponding anharmonic partition function is not well defined; the energy levels summation diverges unless it is truncated below the dissociation threshold. On the other hand, the "exact" DOS from the direct count is not affected by the nonphysical portion of the anharmonic potential if the energy at which it is evaluated is below the dissociation threshold, so that the corresponding partition function is really the anharmonic one truncated at the dissociation energy. At first sight, it would seem unlikely that the series expansion of the untruncated anharmonic partition function could give a good approximation for the truncated one, even if the expansion is finite at all orders, since

TABLE IV. Direct count (DC) DOS and sum of states (SUM) for the anharmonic model of HCCF, which parameters are listed in Table III. Normalized to these exact values, are listed the results of the SR algorithm (Ref. 8) in which the off-diagonal anharmonic couplings cannot be included, the results of the BS algorithm, in which all anharmonic couplings are neglected, and the results of our numerical method (RL), where the partition function was expanded at the first order in the anharmonic constants. For the RL DOS, we used $\delta=200\text{ cm}^{-1}$ and we smoothed the DC, BS, and SR DOS data with a Gaussian of the same $1/e$ half-width. For the SUM data δ was 10 cm^{-1} , while the DC, BS, and SR data were evaluated without smoothing on 10, 1, and 1 cm^{-1} energy partitions, respectively.

E/cm^{-1}	DC DOS	DC SUM	SR DOS	SR SUM	BS DOS	BS SUM	RL DOS	RL SUM
			DC	DC	DC	DC	DC	DC
1 000	$2.873\,46 \times 10^{-2}$	1.200×10^1	0.926	1.000	0.947	1.000	1.008	1.000
2 000	$1.132\,55 \times 10^{-1}$	7.100×10^1	0.913	1.000	0.934	1.000	0.996	1.000
3 000	$3.381\,77 \times 10^{-1}$	2.860×10^2	0.914	0.906	0.945	0.942	0.996	1.004
4 000	$8.348\,67 \times 10^{-1}$	8.460×10^2	0.886	0.877	0.936	0.936	1.001	1.026
5 000	$1.799\,90 \times 10^0$	2.093×10^3	0.871	0.887	0.917	0.931	0.991	0.984
6 000	$3.524\,63 \times 10^0$	4.653×10^3	0.857	0.878	0.911	0.926	0.990	0.982
7 000	$6.419\,73 \times 10^0$	9.500×10^3	0.845	0.864	0.907	0.919	0.990	0.996
8 000	$1.107\,57 \times 10^1$	1.809×10^4	0.832	0.850	0.898	0.910	0.988	0.980
9 000	$1.826\,54 \times 10^1$	3.243×10^4	0.817	0.840	0.888	0.902	0.988	0.984
10 000	$2.898\,57 \times 10^1$	5.568×10^4	0.803	0.827	0.879	0.896	0.980	0.993
15 000	$1.932\,92 \times 10^2$	5.080×10^5	0.738	0.768	0.833	0.854	0.964	0.971
20 000	$8.328\,13 \times 10^2$	2.753×10^6	0.676	0.712	0.784	0.812	0.936	0.953

the only summations involved are of the kind $S^{(k)}$ [defined in Eq. (11)], which are bound and analytic for any value of k . However, the low orders of this expansion do appear to work quite well, and we believe that this is a consequence of the fact that the summations $S^{(k)}$ always involve only the “unperturbed” harmonic potential energy levels. The rapidly decreasing Boltzmann factors for these harmonic levels give an effective truncation of the summations at each perturbative level. At temperatures much lower than the dissociation energy, the fact that the anharmonic partition function is suddenly truncated is actually not relevant, since the Boltzmann factor smoothly terminates the summation much before the truncation point. Indeed, in our numerical recipe the integration path is always such that the temperature (a complex quantity, here) is smaller, in absolute value, than the energy at which the DOS is evaluated. In the Appendix is shown that in the high-energy limit $1/x_0 \simeq E/N$, where N is the number of modes, so that at all points of the integration path the approximation holds. In conclusion, it should be noticed that going to higher orders in the perturbative expansion, the Boltzmann factors in the $S^{(k)}$ summations are multiplied by n^k , where k can be as large as the perturbative order. Therefore the truncation effect of the Boltzmann factors becomes effective at higher and higher energies, until it starts including unperturbed harmonic energy levels which are above the dissociation energy. The effect is that higher perturbative orders cannot give physically correct corrections and convergence to the correct result.

To quantify the magnitude of the anharmonic contribution to the DOS, we also list in Table IV the results obtained by setting all anharmonic constants to zero and using the BS algorithm with 1 cm^{-1} energy partitions. We also compared these BS values with an harmonic direct count and found agreement in $\sim 1\%$, which is the effect of rounding the HCCF normal frequencies to the closest integer values. As shown in the same table, the SR algorithm results obtained by neglecting only the off-diagonal anhar-

monic couplings are even worse than the harmonic values. This is due to the fact that in HCCF the lower energy bending modes, which are responsible for most of the DOS, have positive diagonal anharmonic corrections. On the other hand, when also the negative off-diagonal anharmonic corrections are included, these low energy modes have an overall negative anharmonic correction.

A last warning about using the anharmonic expansion with values of δ smaller than the average level spacing. The problem is that the fine details of the DOS cannot be described in a perturbative expansion. Due to the anharmonic interactions all energy levels shift or split and the distribution and ordering of eigenstates changes completely. Only for a sufficiently coarsely smoothed DOS the changes are small enough to be described by a perturbative expansion.

When considering the partial failure of the first order approximation in HCCF at very high energies (the dissociation for HCCF is $\sim 40\,000\text{ cm}^{-1}$), it should be noticed that this molecule is a particularly challenging case, possessing large anharmonic coefficients of different signs.

With respect to the optimal value of x_0 , the anharmonic correction for it is expected to be negligible. In fact, the reported results were obtained with x_0 optimized for the harmonic partition function alone, and the integrand function always appeared to be well-behaved.

ACKNOWLEDGMENTS

We thank the referee for the useful comments. This work was supported by the Donors of the Petroleum Research Fund, administered by the American Chemical Society.

APPENDIX

It seems plausible that the position of the first recurrence in the integrand function $\exp(\beta E)Q(\beta)$ is in general related to the mean spacing of the energy levels at the

energy E where the DOS is being evaluated. In this Appendix we show that at least in the high-energy limit the average position of the first recurrence $\langle y_1 \rangle$ should be of the same order of magnitude as the DOS. This is the same as saying that $\langle y_1 \rangle^{-1}$ is of the order of the mean energy-level spacing.

We start by showing that the real-axis saddle-point coordinate x_0 corresponds to the temperature for which the thermal-average energy is equal to the energy E where the DOS is being evaluated. The saddle point is a minimum along the real axis

$$\beta = x_0 \rightarrow 0 = \frac{\partial}{\partial \beta} [e^{\beta E} Q(\beta)] \rightarrow E = - \frac{\partial \ln Q}{\partial \beta} \Big|_{\beta=x_0} \quad (\text{A1})$$

which is the formula for the average energy in a canonical ensemble. The high-energy limit is given by

$$E \simeq NKT \rightarrow x_0 \simeq N/E. \quad (\text{A2})$$

Let us now consider one of the factors appearing in the partition function

$$\frac{1}{1 - e^{-\beta \nu_s}} = \frac{1}{1 - \epsilon_s (\cos y \nu_s - i \sin y \nu_s)}, \quad (\text{A3})$$

where $\beta = x_0 + iy$ and $\epsilon_s = \exp(-x_0 \nu_s)$. Its absolute value is

$$\left| \frac{1}{1 - e^{-\beta \nu_s}} \right| = (1 + \epsilon_s^2 - 2\epsilon_s \cos y \nu_s)^{-1/2}. \quad (\text{A4})$$

This is identical, except for a constant factor, to the field transmittivity function of an étalon with mirrors of field reflectivity $R = \epsilon_s$. The width at half-maximum of the peaks of this function is approximately $\Delta y_s = 2\sqrt{3}(1 - \epsilon_s)/\nu_s \sqrt{\epsilon_s}$. Since the distance between two peaks is $2\pi/\nu_s$, an estimate for the average probability that a peak will occur for a given value of y is

$$P_s = \frac{\nu_s}{2\pi} \Delta y_s = \frac{\sqrt{3}}{\pi} \frac{1 - \epsilon_s}{\sqrt{\epsilon_s}} \simeq \frac{\sqrt{3}}{\pi} \frac{N \nu_s}{E}, \quad (\text{A5})$$

where the last step is true in the high-energy limit, where $x_0 \simeq N/E \ll \nu_s^{-1}$. Therefore, when $y = 2\pi/\nu_s$ the probability

that all other factors are at a peak (producing a "recurrence"), is $\prod_{r \neq s} P_r$ if we make the assumption that peaks due to different factors are statistically independent. Since the average number of peaks of the factor s needed for the first recurrence is the inverse of this probability, then the average position for the first recurrence is

$$\langle y_1 \rangle = \frac{2\pi}{\nu_s} \prod_{r \neq s} P_r^{-1} \simeq \frac{2\sqrt{3}}{N^{N-1}} \left(\frac{\pi}{\sqrt{3}} \right)^N \frac{E^{N-1}}{\prod_r \nu_r} \quad (\text{A6})$$

which is very close to the semiclassical DOS

$$\rho_{\text{class.}} = \frac{1}{(N-1)!} \frac{E^{N-1}}{\prod_r \nu_r}. \quad (\text{A7})$$

By using Stirling's approximation, it can be seen that the coefficient $1/(N-1)!$ is close to $e^N/N^{N-1} \sqrt{2\pi N}$. The fact that the coefficients do not match may depend from the relatively arbitrary choice of the width Δy_s as the "width at half-maximum," to which the coefficient we obtain is very sensitive. Besides this, the assumption of independent probabilities in general will not hold, especially in case of degeneracy or if some of the normal frequencies have a ratio close to that of some small integers.

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