Estimation of Vibrational Frequencies and Vibrational Densities of States in Isotopically Substituted Nonlinear Triatomic Molecules[†]

B. C. Hathorn[‡] and R. A. Marcus*[,§]

Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, and Noyes Laboratories of Chemical Physics, California Institute of Technology, Pasadena, California 91125

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For use in unimolecular reactions, a simple method is introduced for obtaining the unknown vibration frequencies of the many asymmetric isotopomers of a molecule from those of the symmetric ones. The method is illustrated for a triatomic molecule XYZ, ozone. It is based on the neglect of a single **G** matrix element in the **GF** expression for XYZ, yielding for it a block-factored expression of the XYX type for the frequencies of all the isotopomers XYZ. It agrees with available data to the accuracy needed, a few cm^{-1}. The first-order perturbation vanishes. (The zeroth-order case is not a symmetric molecule since it contains all three masses.) A simple second-order perturbation result for the **GF** matrix using data for one asymmetric isotopomer then provides agreement to about 1 cm^{-1}. The virtues of the method are its simplicity, transparency, and novelty, though normally one would use much more general methods such as ASYM 20 or 40. The method itself is not restricted to triatomic molecules.

Introduction

In a number of recent calculations, we have required the vibrational densities of states of isotopically substituted ozone molecules to perform Rice−Ramsperger−Kassel−Marcus (RRKM) calculations of the microcanonical rate constants.[1] Typically, the vibrational densities of states are obtained either by a direct enumeration over the vibrational energies[2]

$$E_{\mathrm{vib}} = \sum_i \left(n_i + \frac{1}{2}\right) h\nu_i \tag{1}$$

or by the Whitten−Rabinovitch formula or by a classical approximation,[3,4]

$$\rho_{\mathrm{vib}}(E) = \frac{E^{n-1}}{(n-1)!\Pi_i h\nu_i} \tag{2}$$

where ρ_{vib} is the density of states, E is the total energy available to the system, excluding zero-point energy, n is the total number of harmonic vibrations, h is Planck's constant and the ν_i are the individual vibrational frequencies. In some cases, anharmonicity effects are introduced,[4,5] the harmonic expression then serving as a very useful starting point.

In eq 2, it is clear that the classical density of states is inversely proportional to the product of the vibrational frequencies, $\Pi_i h\nu_i$, which can be estimated from the Teller−Redlich product rule,[6]

$$\left(\frac{A'B'C'}{ABC}\right)^{1/2} = \left(\frac{M'}{M}\right)^{3/2} \prod_i \left(\frac{\nu_i}{\nu_i'}\right) \prod_k \left(\frac{m_k}{m_k'}\right)^{3/2} \tag{3}$$

where A, B, and C are the rotational constants of the molecule, M is the total molecular mass, the m_k are the individual atomic masses, the ν_i are the vibrational frequencies, and the primes represent the isotopically substituted species.

Equation 3 provides an estimate of the product of the vibrational frequencies. However, the relationship fails to provide an estimate of the zero-point energy of the system, which is related to the sum of the vibrational frequencies,

$$E_z = \sum_i \left(\frac{h\nu_i}{2}\right) \tag{4}$$

When all three isotopes, ^{16}O, ^{17}O, and ^{18}O are accounted for in all possible combinations, there are 18 different ozone isotopomers possible with three vibrational frequencies each, leading to 54 different vibrational frequencies. Of these, only 26 have been measured, leaving 28 of the vibrational frequencies experimentally unknown.

Our interest is in devising a simple method to determine these many unknown frequencies of the ozone isotopomers, using the known frequencies of a number of symmetric ones, and, for a minor correction, if desired, data on one asymmetric isotopomer. For our present purpose for unimolecular reaction rate calculations, only a relatively low accuracy of the order of a few cm^{-1} is needed. If the primary interest were, instead, the accurate determination of frequencies or force constants, the procedure would be quite different,[7] e.g., the known frequencies would be corrected to their harmonic values using overtone energy level differences (anharmonicities),[8b] a correction which can be quite large, e.g., ≈17 cm^{-1} for SO_2,[8c] and both the symmetric isotopomers and an asymmetric one would be used to avoid ambiguity that can arise in solving a quadratic equation for the force constants.[8d] However, one could introduce, instead, the actual frequencies into the publicly available program (ASYM 20 or 40) as though they were the harmonic ones, together with the isotopic frequency shifts as input data, and obtain the shifts in frequencies for the other isotopomers.[7b] The isotopic shifts

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[‡] Oak Ridge National Laboratory.

[§] California Institute of Technology.

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so obtained would be presumed not to be sensitive to the anharmonicities.

In the present article, the problem is reduced instead to one of lower dimensions by omitting any **G** matrix elements which prevent the **GF** matrix for the asymmetric isotopomers from having the same block factor form as that for the symmetric isotopomers. The first-order correction, at least for the present case of ozone, vanishes by symmetry as discussed later, and the second-order correction is easily estimated from data for an asymmetric isotopomer. (It should be emphasized that this zeroth-order **GF** expression used here is not that of a symmetric molecule XYX. It contains the masses of all three atoms in a molecule XYZ.) The correction is small and is immediately obtained. The present procedure might be applied to molecules with more atoms. (We have not, for example, examined its application to tetratomic C_{3v} molecules whose **GF** matrix block factors into three 2 × 2 matrices.) It provides a simple way of obtaining the missing frequencies at a level quite adequate for kinetic purposes, such as those in ref 1, and requires no elaborate input of data. The accuracy, judging from the fits, is estimated to be about 1 cm^{-1}.

Theory

The procedure we introduce is based on the following: We consider as a simple example of a bent triatomic molecule XYZ. For isotopomers the **F**-matrix for force constants of XYZ has the symmetry of XYX, when expressed in terms of symmetry coordinates of the latter.

However, the **G**-matrix (momentum coefficients) is no longer block diagonal. Nevertheless, if a single off-diagonal element for XYZ with Z ≠ X is neglected, the **G**-matrix for XYZ has the same block form as that for XYX and expressions based on that form can then immediately be used to obtain, in this approximation, the frequencies of all isotopomers. We note in passing that for a molecule that has the potential energy symmetry of the ozone isotopomers there are four independent force constants in the most general force field,[8f] and so we have at our disposal four parameters.

On the basis of this general force field, we note, upon expressing the **GF** matrix in symmetry coordinates for XYX, that the various frequencies and sums and products of frequencies arising from the secular equation $|\mathbf{GF} - \lambda\mathbf{I}| = 0$ can be written. For XYX, using results in refs 8e and 8g, we have

$$\nu_3^2 = \mathrm{A}_3\left(\mu_1 + 2\mu_3 \sin^2\frac{\alpha}{2}\right) \tag{5}$$

$$(\nu_1\nu_2)^2 = A_{12}^2[(\mu_1 + \mu_3)^2 - {\mu_3}^2] \tag{6}$$

$$\nu_1^2 + \nu_2^2 = A'_{12}\,(\mu_1 + d\mu_3) \tag{7}$$

where $\mu_i = 1/m_i$ and, for $i = 1$, is the reciprocal mass of an end atom X in XYX, while for $i = 3$ it is that of the central atom Y. There are seen to be four unknown constants in eqs 5−7. The α in eq 5 is the bond angle, 116.8° in the present case.[9] The constants in eqs 5−7 could be expressed in terms of the various force constants in the potential energy expression in eq 8,[8a,10] and we give those expressions for completeness in terms of eqs 9−12 below. However, as stated earlier, for our purpose there is no need to extract these various force constants, *f*'s, and we do not do so.

$$2V = f_r[(\Delta r_1)^2 + (\Delta r_2)^2] + f_\alpha(r\Delta\alpha)^2 + 2f_{rr}(\Delta r_1)(\Delta r_2) + 2f_{r\alpha}(\Delta r_1 + \Delta r_2)r\Delta\alpha \tag{8}$$

where r is the O−O bond length. We have[10]

$$A_3 = f_r - f_{rr} \tag{9}$$

$$A_{12}^2 = 2f_\alpha(f_r + f_{rr}) - 4f_{r\alpha}^2 \tag{10}$$

$$A'_{12} = f_r + f_{rr} + 2f_\alpha \tag{11}$$

$$A'_{12}d = 2(f_r + f_{rr})\cos^2\frac{\alpha}{2} + 4f_\alpha\sin^2\frac{\alpha}{2} - 4f_{r\alpha}\sin^2\alpha \tag{12}$$

Using eqs 5 and 6, the parameters A_3 and A_{12} are obtained from a fit to their average values for four symmetric isotopomers where the vibrational frequencies are known, $^{16}\mathrm{O}^{16}\mathrm{O}^{16}\mathrm{O}$, $^{18}\mathrm{O}^{18}\mathrm{O}^{18}\mathrm{O}$, $^{16}\mathrm{O}^{18}\mathrm{O}^{16}\mathrm{O}$, and $^{18}\mathrm{O}^{16}\mathrm{O}^{18}\mathrm{O}$. The parameters A'_{12} and d are obtained by rearranging eq 7, so as to plot $({\nu_1}^2 + {\nu_2}^2)/\mu_1$ *vs* μ_3/μ_1, the slope and intercept providing the desired values.

The parameters so obtained using known data of the six symmetric isotopomers are $A_3 = 7105957$, $A_{12} = 715358$, $d = 0.660716$, and $A'_{12} = 7193874$, not all of these figures being significant, as noted later. Given these values, the unknown ν_3's are calculated from eq 5. The unknown ν_1's and ν_2's are calculated from the solution of an equation quadratic in ν^2, $\nu^4 - b\nu^2 + c = 0$ with $b = A'_{12}\,(\mu_1 + d\mu_3)$ and $c = {A_{12}}^2[(\mu_1 + \mu_3)^2 - {\mu_3}^2]$. The two positive roots of this equation are ν_1 and ν_2, $\nu_\pm = [b/2 \pm 1/2(b^2 - 4c)^{1/2}]^{1/2}$, where ν_1 corresponds to the positive sign.

To obtain approximate but simple expressions for asymmetric isotopomers, we proceed as follows:

We use expressions[8e] for the **G** and **F** matrices for XYZ given in terms of the XYX symmetry coordinates, but neglecting for XYZ a single off-diagonal element G_{31} (= G_{13}), one which is zero for XYX. As we have noted earlier, examination of the relevant matrices provides immediately the extension.

The product of the eigenvalues of the secular determinant in the block diagonal **GF** matrix is, for ${\nu_3}^2$ in eq 5, $\mathrm{G}_{33}\mathrm{F}_{33}$. Using the known G_{33},[8e] eq 5 is seen to be replaced by eq 13 below. For $\nu_1\nu_2$ the relevant term in the **GF** matrix is[8g] $(\mathrm{G}_{11}\mathrm{G}_{22} - {\mathrm{G}_{12}}^2)(\mathrm{F}_{11}\mathrm{F}_{22} - {\mathrm{F}_{12}}^2)$. The $\mathrm{G}_{11}\mathrm{G}_{22} - {\mathrm{G}_{12}}^2$ for XYX is $2[(\mu_1 + \mu_3)^2 - {\mu_3}^2]$, while for XYZ it is[8e] $2[(1/2(\mu_1 + \mu_2) + \mu_3)^2 - {\mu_3}^2]$, leading to eq 14 below. For ${\nu_1}^2 + {\nu_2}^2$ the relevant **GF** element is[8g] $\mathrm{G}_{11}\mathrm{F}_{11} + 2\mathrm{G}_{12}\mathrm{F}_{12} + \mathrm{G}_{22}\mathrm{F}_{22}$. This quantity is seen from the expressions in ref 8e to be a linear combination of μ_1 and μ_3 in eq 7. For XYZ, it is seen to be the same linear combination, but of $1/2(\mu_1 + \mu_2)$ and μ_3, leading to eq 15 below.

$$\nu_3^2 = A_3^2\left(\frac{\mu_1 + \mu_2}{2} + 2\mu_3\sin^2\frac{\alpha}{2}\right) \tag{13}$$

$$(\nu_1\nu_2)^2 = A_{12}^2\left[\left(\frac{\mu_1 + \mu_2}{2} + \mu_3\right)^2 - {\mu_3}^2\right] \tag{14}$$

$$\nu_1^2 + \nu_2^2 = A'_{12}\left(\frac{\mu_1 + \mu_2}{2} + d\mu_3\right) \tag{15}$$

That is, in each case the μ_1 in eqs 5−7 is becomes $(\mu_1 + \mu_2)/2$.

Application of the parameters A_{12}, A'_{12}, A_3, and d and the results corresponding to eqs 13−15 lead to approximate vibrational frequencies for ozone isotopomers listed in Table 2. The fit is seen there to be about 1 per mil, so that the figures given earlier for the parameters are significant only to that extent. Although the simplified model does not give exact results, it does give values that are close to the experimentally observed values, where available, given in Table 1. In particular,

TABLE 1: Experimental Vibrational Frequencies (cm^{-1}) of Ozone Isotopomers[a]

isotopomer	ν_1	ν_2	ν_3
$^{16}\mathrm{O}^{16}\mathrm{O}^{16}\mathrm{O}$	1103.1373	700.9311	1042.0840
$^{17}\mathrm{O}^{17}\mathrm{O}^{17}\mathrm{O}$	1070.946		1012.163
$^{18}\mathrm{O}^{18}\mathrm{O}^{18}\mathrm{O}$	1041.5556	661.4925	984.816
$^{16}\mathrm{O}^{16}\mathrm{O}^{17}\mathrm{O}$	1095.693	692.435	1035.693
$^{16}\mathrm{O}^{17}\mathrm{O}^{16}\mathrm{O}$	1087.829	697.079	1024.395
$^{16}\mathrm{O}^{16}\mathrm{O}^{18}\mathrm{O}$	1090.3541	684.6134	1028.1120
$^{16}\mathrm{O}^{18}\mathrm{O}^{16}\mathrm{O}$	1074.3076	693.3057	1008.4528
$^{18}\mathrm{O}^{18}\mathrm{O}^{16}\mathrm{O}$	1060.709	677.5038	993.927
$^{18}\mathrm{O}^{16}\mathrm{O}^{18}\mathrm{O}$	1072.2172	668.0850	1019.350

[a] From ref 9.

TABLE 2: Calculated Molecular Constants for Ozone Isotopomers Calculated Vibrational Frequencies[a] **and Differences from Experimental Values (cm^{-1}) for Ozone Isotopomers**

isotopomer	ν_1	ν_2	ν_3	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$
$^{16}\mathrm{O}^{16}\mathrm{O}^{16}\mathrm{O}$	1103.9	701.3	1043.3	0.8	0.4	0.9
$^{17}\mathrm{O}^{17}\mathrm{O}^{17}\mathrm{O}$	1071.0	680.3	1012.2	0.1		0.0
$^{18}\mathrm{O}^{18}\mathrm{O}^{18}\mathrm{O}$	1040.8	661.2	983.7	−0.8	−0.3	−1.1
$^{16}\mathrm{O}^{16}\mathrm{O}^{17}\mathrm{O}$	1095.6	692.7	1037.0	−0.1	0.3	1.3
$^{16}\mathrm{O}^{17}\mathrm{O}^{16}\mathrm{O}$	1088.2	697.3	1025.0	0.1	0.3	0.6
$^{16}\mathrm{O}^{16}\mathrm{O}^{18}\mathrm{O}$	1088.1	685.0	1031.4	−2.2	0.4	3.3
$^{16}\mathrm{O}^{18}\mathrm{O}^{16}\mathrm{O}$	1074.2	693.5	1008.4	−0.1	0.2	−0.1
$^{17}\mathrm{O}^{17}\mathrm{O}^{16}\mathrm{O}$	1079.6	688.9	1018.6			
$^{17}\mathrm{O}^{16}\mathrm{O}^{17}\mathrm{O}$	1087.2	684.0	1030.7			
$^{17}\mathrm{O}^{17}\mathrm{O}^{18}\mathrm{O}$	1063.3	672.5	1006.4			
$^{17}\mathrm{O}^{18}\mathrm{O}^{17}\mathrm{O}$	1056.5	676.7	995.4			
$^{18}\mathrm{O}^{18}\mathrm{O}^{16}\mathrm{O}$	1057.5	677.7	996.1	−3.2	0.2	2.2
$^{18}\mathrm{O}^{16}\mathrm{O}^{18}\mathrm{O}$	1072.3	667.9	1019.4	−0.1	−0.2	0.0
$^{18}\mathrm{O}^{18}\mathrm{O}^{17}\mathrm{O}$	1048.7	669.0	989.5			
$^{18}\mathrm{O}^{17}\mathrm{O}^{18}\mathrm{O}$	1055.6	664.5	1000.6			
$^{16}\mathrm{O}^{17}\mathrm{O}^{18}\mathrm{O}$	1071.9	681.3	1012.9			
$^{16}\mathrm{O}^{18}\mathrm{O}^{17}\mathrm{O}$	1065.4	685.2	1001.9			
$^{17}\mathrm{O}^{16}\mathrm{O}^{18}\mathrm{O}$	1079.8	676.1	1025.1			

[a] The small differences (less than cm^{-1}) in these calculated frequencies to those in the first table of ref 1(b) are due to a slightly different calculational procedure.

we note that the values for the asymmetric isotopomers are well reproduced, although eqs 13−15 were derived with the neglect of an off-diagonal element G_{13}. We have also applied the formula to ozone isotopomers, *ijk*, where *i*, *j*, and *k* are all different and where no experimental vibrational frequencies are available.

We note that the approximate result presented here gives absolute values for the calculated vibrational frequencies, which are close to their experimental counterparts, leading also to a close estimation of the zero-point energy in eq 4. In addition, the product of the calculated vibrational frequencies is close to the experimental one, leading to the correct scaling in the classical approximation, eq 2. In the case of ozone, we find that the calculated frequencies are both internally consistent with each other and suitable for either a classical evaluation or direct count of the vibrational density of states.

One expects, of course, that the agreement between calculated and experimental frequencies will be best when the masses of the end atoms differ by less than two mass units. This expectation is borne out by the available data in Table 2. Of the remaining isotopomers for which the frequencies have not been measured, the masses of the end atoms differ by two in only one of the nine cases.

The error in Table 2 for XYZ can be reduced to about 1 cm^{-1} by an application of second-order perturbation theory. We note that the first- and second-order corrections to the eigenvalue λ_i ($= 4\pi\nu_i^2$) of the **GF** matrix are[12]

$$\lambda_i^{(1)} = (\mathbf{L}_0^{-1}\Delta\mathbf{G}\mathbf{L}_0^{-1T}\mathbf{\Lambda}_0)_{ii} \tag{16}$$

$$\lambda_i^{(2)} = \sum_{j\neq i} \frac{(\mathbf{L}_0^{-1}\Delta\mathbf{G}\mathbf{L}_0^{-1T}\mathbf{\Lambda}_0)_{ij}(\mathbf{L}_0^{-1}\Delta\mathbf{G}\mathbf{L}_0^{-1T}\mathbf{\Lambda}_0)_{ji}}{\lambda_j^{(0)} - \lambda_i^{(0)}} \tag{17}$$

where T denotes transpose, Λ_0 is a diagonal matrix whose eigenvalues $\lambda_i^{(0)}$ are those of the $\mathbf{G}_0\mathbf{F}_0$ matrix, and $\mathbf{L}_0$ is a right eigenvector of $\mathbf{F}_0\mathbf{G}_0$. We note, that $\mathbf{F}_0 = \mathbf{F}$ in the present case.

When eq 16 is applied to the ozone system, one notes that the only nonzero element in $\Delta\mathbf{G}$ is $\mathbf{G}_{13}$, which is proportional to $\mu_1 - \mu_2$. By symmetry with respect to exchange of atoms 1 and 3,[8e] it can be shown that $\lambda_i^{(0)}$ vanishes for all three frequencies and that the off-diagonal elements in eq 17 are proportional to $\mu_1 - \mu_2$, and so $\lambda_i^{(2)}$ is proportional to $(\mu_1 - \mu_2)^2$. The coefficient of proportionality varies with i, $i = 1$ to 3. Because $\Delta\lambda_i = 8\pi^2\nu_i\Delta\nu_i$, it is seen from eq 17 that $\Delta\nu_i$, the correction to ν_i, varies as $(\mu_1 - \mu_2)^2$.

Using these corrections for $^{16}\mathrm{O}^{16}\mathrm{O}^{18}\mathrm{O}$ or $^{18}\mathrm{O}^{18}\mathrm{O}^{16}\mathrm{O}$, seen in Table 2, or averaging them for each i, they are ca. −2.7, 0.3, and 2.7 cm^{-1}, for $\Delta\nu_1$, $\Delta\nu_2$, and $\Delta\nu_3$, respectively. This same mean correction can then be used for the missing $^{16}\mathrm{O}^{17}\mathrm{O}^{18}\mathrm{O}$ isotopomer. For the case where the end atoms differ by only 1 mass unit, the correction on this basis would be about −0.6, 0.1, 0.6, which is within the present "noise level," but could be introduced before round off. In summary, the use of data for one asymmetric isotopomer, preferably with the maximum difference in $(\mu_1 - \mu_2)$, suffices to provide an immediately applied correction to the data in Table 2, and obtain values correct to about 1 cm^{-1}.

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p 242. (g) For example, Califano, S. Vibrational States; John Wiley: New York, 1976; p 222 for the present $\nu_1^2 + \nu_2^2$ and $\nu_1^2\nu_2^2$ (ν_i^2 is proportional to λ_i there). For ν_2 it is clearly $G_{33}F_{33}$ from the expression for the secular determinant.

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