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## Simplifying the MIME: A Formula Relating Normal Mode Distortions and Frequencies to the MIME Frequency

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Received November 7, 1986

A simple formula is derived for the missing mode effect (MIME) frequency. The formula relates the distortions and frequencies of the individual modes, together with the overall damping factor, to the MIME frequency. The formula provides a quick and accurate method for calculating the MIME frequency without having to calculate the full Fourier transform of the overlaps to obtain the spectrum. Example calculations are presented for a variety of distortions, frequencies, and damping factors and are compared to the full calculation. Proper application of the formula and unusual cases are discussed.

The missing mode effect (MIME) is a regularly spaced vibronic progression in a luminescence spectrum that does not correspond to any ground-state normal mode of vibration.<sup>2</sup> Two or more modes conspire to give the appearance of a single progression in poorly resolved spectra. The same factors which cause a MIME in emission also apply to absorption spectra, but a MIME in the absorption spectra is more difficult to distinguish because the exact excited-state frequencies are usually not available. The MIME exists in the spectrum of many metal complexes,<sup>3-6</sup> but detailed analyses of the contributing modes have only been carried out for a small number of molecules. The analysis requires the calculation of the time dependence of the overlaps of each contributing mode and the Fourier transform of the product of all of the overlaps to obtain the spectrum in the frequency domain.<sup>5,6</sup> Whereas this calculation is straightforward (see eq 1), it is very desirable to have a quick and accurate formula for predicting the MIME frequency for a given set of frequencies and displacements. This paper provides such a formula.

The unabridged method for calculating the MIME spectrum (and thus the MIME frequency by inspection) also requires the frequencies and displacements of all of the participating modes, which are assumed to be harmonic. Given this information, a time dependent formula is computed (eq 1), which physically is the overlap between an "initial" wave packet  $|\phi\rangle$  (the ground vibrational level of an excited electronic state) and that wave packet propagated on the lower electronic energy surface. The latter, moving wave packet  $|\phi(t)\rangle$  is not a stationary state of the lower electronic energy surface and so moves according to the time-dependent Schrodinger equation. The quantity of interest is the overlap of the initial wave packet with the time-dependent wave packet,  $\langle\phi|\phi(t)\rangle$ . For the case of a multiple-mode harmonic potential surface with equal vibrational frequencies in the initial and final states the overlap is<sup>7</sup>

$$\langle\phi|\phi(\tau)\rangle = \exp\left\{-\sum_k \left[ \frac{1}{2} \Delta_k^2 (1 - e^{-i\omega_k \tau}) - i\omega_k \tau / 2 \right] - E_0 \tau / \hbar - \Gamma^2 \tau^2 \right\} \quad (1)$$

where  $\omega_k$  and  $\Delta_k$  are the frequency and displacement of the  $k$ th normal mode,  $\Gamma$  is the damping factor (vide infra), and  $E_0$  is the origin of the spectrum. This expression for the complete overlap is Fourier transformed to give the electronic absorption or emission spectrum in the frequency domain. The emission spectrum is given by

$$I(\omega) = \omega^3 \int_{-\infty}^{\infty} e^{-i\omega \tau} \langle\phi|\phi(\tau)\rangle d\tau \quad (2)$$

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We remark that eq 2 is quite general; it does not rely upon particular assumptions about the potential energy surface. If we knew  $|\phi(t)\rangle$  for a complicated potential surface, eq 2 would give the luminescence spectrum. The available data for metal complex luminescence spectra do not support the choice of complicated forms for potential surfaces and are in any case fairly consistently treated by harmonic oscillators. Equation 1 is based on the simplifying harmonic oscillator model. The ground- and excited-state modes are assumed to be the same to further simplify things.

The overriding advantage of the Fourier transform method is the ability to calculate incompletely resolved spectra when many modes are involved. This can easily be done in circumstances where the direct Franck-Condon approach is inconvenient or impossible due to the large density of states. The MIME is a further distillation of the time-dependent approach, and it reveals why so many incompletely resolved spectra appear to be dominated by a single displaced mode. But such behavior is often just mimicry!

The main purpose of this paper is to derive a formula that is simpler than the full overlap equation (eq 1) for calculating the MIME frequency. The results of using the simple formula are compared to those obtained by using the more rigorous calculation for many test cases. The importance of the various input quantities and illustrative examples are discussed.

### Simple Formula for the MIME Frequency

The main idea of the MIME is that a partial recurrence at  $t \approx \tau_M$  is responsible for the appearance of a regularly spaced progression at a frequency  $\omega_M = 2\pi/\tau_M$ . Our strategy is to find the maxima of  $|\langle\phi|\phi(t)\rangle|$  corresponding to the first large recurrence time  $\tau_M$ . This will correspond to

$$\frac{d}{dt} |\langle\phi|\phi(\tau)\rangle| = 0 \\ = -\sum_k \frac{1}{2} \Delta_k^2 \omega_k \sin(\omega_k \tau_M) - 2\Gamma^2 \tau_M \quad (3)$$

The condition on  $\tau_M$  is thus

$$\sum_k \frac{1}{2} \Delta_k^2 \omega_k \sin(\omega_k \tau_M) + 2\Gamma^2 \tau_M = 0 \quad (4)$$

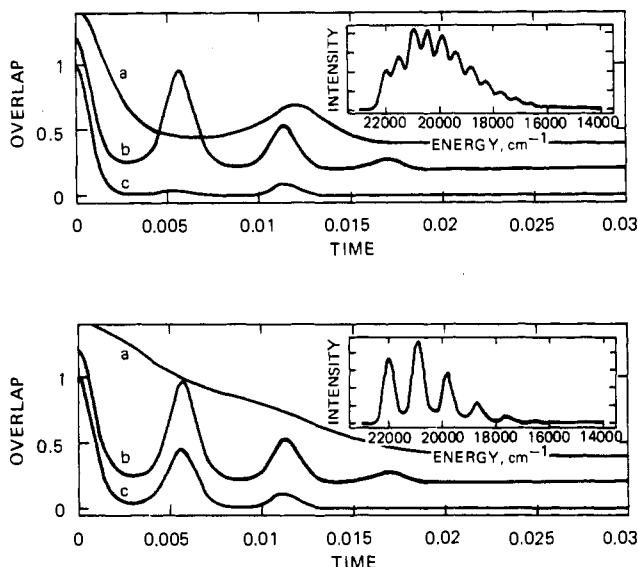
although solutions to this equation will include minima in  $|\langle\phi|\phi(t)\rangle|$  as well as local maxima that may be very much smaller than the main recurrence at time  $\tau_M$ . Thus one strategy to find  $\omega_M$  is to solve eq 4 for the various times  $t'$  for which it has a solution and then to examine  $|\langle\phi|\phi(t')\rangle|$  to find the  $t' = \tau_M$  corresponding to the large recurrence. To arrive at a simpler formula, we notice that the arguments of  $\sin(\omega_k \tau_M)$  should all be near some multiple of  $2\pi$  at  $\tau_M$ , especially in the large  $\Delta$  modes. This is necessary for a healthy recurrence to happen at  $\tau_M$ . Assuming that the  $k$ th mode is experiencing its  $n_k$ th return visit (i.e. recurrence) near  $\tau_M$ , that is  $\omega_k \tau_M \approx 2\pi n_k$ , we have

$$\sin \omega_k t \approx \omega_k t - n_k \quad (5)$$

Table I

$\omega_1$	$\Delta_1^a$	$\omega_2$	$\Delta_2^a$	full calcn MIME, <sup>b</sup> $\text{cm}^{-1}$	transcendental expression (eq 4), $\text{cm}^{-1}$	short expression (eq 6), $\text{cm}^{-1}$	$\Gamma$ , $\text{cm}^{-1}$	$n_1$	$n_2$
500	1.7	1100	1.7	550	550	549	130	1	2
500	1.7	1100	1.7	550	550	927	130	1	1 <sup>c</sup>
500	0.5	1100	1.7	1125	1124	1098	130	1	1
525	1.8	700	1.68	637	638	630 <sup>d</sup>	100	1	1
600	1.8	750	0.45	629	628	630 <sup>d</sup>	100	1	1
203	2.5	302	2.5	277	276	274	48	1	1
203	2.5	302	2.5	101	101	100	30	2	3

<sup>a</sup> For convenience we transform to dimensionless normal coordinates, whence, e.g.  $\Delta_k = (m_k \omega_k / \hbar)^{1/2} \delta_k$ . <sup>b</sup> The complete spectrum was generated by calculating the wave packet dynamics on the multidimensional potential surface. The vibronic spacings were determined by removing the broad envelope with an FT high pass filter and then measuring the spacing between the remaining peaks. <sup>c</sup> The erroneous choice of  $n_2 = 1$  is used here to illustrate the importance of the value of  $n$ . <sup>d</sup> Note the two different sets of distortions yielding the same MIME frequency.



**Figure 1.** Top: overlaps in the time domain for two modes with  $\omega_1 = 500 \text{ cm}^{-1}$  and  $\Delta_1 = 1.7$  (curve a),  $\omega_2 = 1100 \text{ cm}^{-1}$  and  $\Delta_2 = 1.7$  (curve b), and  $\Gamma = 130 \text{ cm}^{-1}$ . The maximum recurrence in the product occurs when  $n_{1100} = 2$  and  $n_{500} = 1$  (curve c). Bottom: overlaps in the time domain under the same conditions as above except that  $\Delta_2 = 0.5$  (curve a) and  $\Delta_1 = 2.0$  (curve b). Note that the sharp recurrences of  $\omega_1$  dominate the overlaps giving  $\omega_M \approx \omega_1$  (curve c). The units of time are  $c/2\pi s$ , and  $E_0 = 22000 \text{ cm}^{-1}$ .

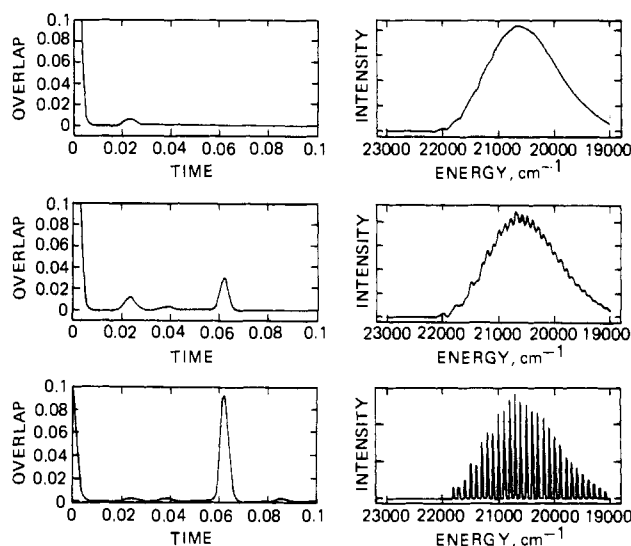
near  $t \approx \tau_M$ . (Usually,  $n_k$  is 1; sometimes it is 0, 2, or 3.) Equations 4 and 5 give ( $\omega_M = 2\pi/\tau_M$ )

$$\omega_M = \left\{ \sum_k \omega_k^2 \Delta_k^2 + 4\Gamma^2 \right\} / \sum_k \omega_k \Delta_k^2 n_k \quad (6)$$

## Results and Discussion

Examples of calculations of the MIME frequency by using eq 6 are given in the Table I and are compared to the MIME frequencies calculated by using the complete time-dependent overlap (eq 1) and the transcendental eq 4. Three quantities in eq 6 that are crucial not only to the calculation but also to the understanding of the MIME are  $n_k$ ,  $\Gamma$ , and  $\Delta$ . Misapplication of any of these quantities, but especially  $n_k$ , will lead to significant errors in the calculation of the MIME frequency. In the following sections, the meanings of these quantities and their effects on the MIME frequency are examined in detail for the simplest case of only two modes.

The variable  $n_k$  is an integer for each mode with nonzero displacement. It corresponds to the number of the mode's return visit when all of the other distorted modes are closest to having returned. As an example, for two modes at 1100 and 500  $\text{cm}^{-1}$  with comparable distortions, the 500- $\text{cm}^{-1}$  mode will have returned only once when the 1100- $\text{cm}^{-1}$  mode will have just finished its second return, giving  $n_{500} = 1$  and  $n_{1100} = 2$ . The plots of the overlaps in the time domain and the resulting spectrum in the frequency domain are shown in Figure 1 (top). From this plot it can be seen that the largest product of the overlaps is found when the second recurrence of the high-frequency mode overlaps



**Figure 2.** Left: overlaps in the time domain for two modes with  $\omega_1 = 203 \text{ cm}^{-1}$ ,  $\omega_2 = 302 \text{ cm}^{-1}$ ,  $\Delta_1 = 2.5$ , and  $\Delta_2 = 2.5$ . Top:  $\Gamma = 48 \text{ cm}^{-1}$ . Note that  $\omega_M = 277 \text{ cm}^{-1}$ . Middle:  $\Gamma = 30 \text{ cm}^{-1}$ . Note that  $\omega_M = 101 \text{ cm}^{-1}$ . Bottom:  $\Gamma = 4 \text{ cm}^{-1}$ . Note that even here not all vibronic bands are resolved (eg. the 609  $\{3 \times 203\}$  and 604  $\{2 \times 302\}$   $\text{cm}^{-1}$  Franck-Condon factors are still together). Right: Fourier transform of the overlaps (left) to the frequency domain.  $E_0 = 22000 \text{ cm}^{-1}$ .

the first recurrence of the low-frequency mode. The MIME frequency of 549  $\text{cm}^{-1}$  calculated by using the simple formula (eq 6) is in excellent agreement with the value of 550  $\text{cm}^{-1}$  calculated by using the complete expression (eq 1). Note from the sample calculations in Table I that if the values of  $n$  had both erroneously been chosen to be 1, the MIME frequency calculated by using eq 6 would have been 927  $\text{cm}^{-1}$ , drastically in error.

A second example of the importance of  $n$  is illustrated by the calculation of  $\omega_M$  for  $\text{W}(\text{CO})_5(\text{py})$ . The observed MIME frequency is 550 + 10  $\text{cm}^{-1}$ . In this 18-mode problem, the simple formula would be expected to lose accuracy due to the breakdown in the assumption of  $\omega_k \tau_M \approx 2\pi n_k$  or  $\omega_k / \omega_M \approx n_k$ . The determination of  $n$  is very critical in the calculation for a large number of modes. The correct value for  $n_k$  is obtained by dividing each frequency by an initially assumed value for  $\omega_M$ , choosing  $n_k$  as the nearest integer, calculating  $\omega_M$ , using the new  $\omega_M$  to determine a new value for  $n_k$ , and iterating until self-consistency is achieved. The best assumption for  $\omega_M$  is the most highly distorted mode in a group of highly distorted modes. For the  $\text{W}(\text{CO})_5(\text{py})$  molecule this is the 434- $\text{cm}^{-1}$  mode, giving in only three iterations  $\omega_M = 525 \text{ cm}^{-1}$ . The distortions and frequency used are given and explained in ref 5 and the self-consistent  $n_k$  values are given in footnote 8. Any initial value for  $\omega_M$  could have been chosen between 420 and 850  $\text{cm}^{-1}$  and still iterate to 525  $\text{cm}^{-1}$ . This

(8) Self-consistent  $\omega_k(\text{cm}^{-1})$ ,  $\Delta_k$ , and  $n_k$  values at  $\Gamma = 72 \text{ cm}^{-1}$ : 195, 1.42, 0; 427, 1.01, 1; 434, 1.08, 1; 462, 0.87, 1; 470, 0.56, 1; 602, 0.64, 1; 636, 0.68, 1; 1012, 0.81, 2; 1073, 0.37, 2; 1223, 0.43, 2; 1489, 0.10, 3; 1607, 0.39, 3; 1651, 0.18, 3; 1890, 0.27, 4; 1934, 0.14, 4; 1953, 0.15, 4; 1973, 0.24, 4; 2075, 0.28, 4.

example demonstrates that, even in a complex molecule, the formula works quite well.

The Gaussian damping factor  $\Gamma$  causes a quenching of the magnitude of the recurrence overlaps in the time domain. It physically represents relaxation into other modes, the bath, etc. In the calculations discussed here it can be considered to be a phenomenological line width factor.  $\Gamma$  is usually in the range of 50–200  $\text{cm}^{-1}$  for metal complexes in condensed media.

An example of conditions where  $\Gamma$  can have a major effect is given in the table. If  $\omega_1 = 203 \text{ cm}^{-1}$  and  $\omega_2 = 302 \text{ cm}^{-1}$ , the maximum of the product of the overlaps occurs when  $n_1 = 2$  and  $n_2 = 3$ . These conditions give  $\omega_M = 101 \text{ cm}^{-1}$  (Figure 2, middle). However,  $\Gamma$  must be small enough for the overlap at these values of  $n$  to be significant. If  $\Gamma$  is larger, these higher recurrences will be damped out and only the first recurrence of each mode will have significant magnitude. In this case, only the product at  $n_1 = 1$  and  $n_2 = 1$  is important and  $\omega_M = 277 \text{ cm}^{-1}$  (Figure 2, top).

It is also important to recognize that  $\Gamma$  cannot be too small. If it is small enough to allow a large number of recurrences to have significant amplitude, no MIME will be observed, but instead a highly resolved spectrum consisting of progressions in all of the displaced modes will be seen (Figure 2, bottom).

The effect of the displacements  $\Delta_k$  on the MIME frequency is apparent from eq 6. The displacements act as a type of weighting factor on the contributions of the normal modes to the MIME. In some situations, the value of  $\Delta$  for one mode will be much larger than those for other displaced modes. In this case the MIME frequency will be very close to the frequency of the most highly displaced mode and may be indistinguishable from it in an experimental spectrum. This situation commonly arises in metal complexes where a metal–ligand bond is highly displaced while bond lengths within the ligand itself are only slightly changed. The origin of this effect is readily seen from eq 6. If  $\Delta_k$  for one mode is much larger than the other  $\Delta$ 's, it will dominate the sums in both the numerator and the denominator and  $\omega_M \approx \omega_k$ .

The effect of having  $\Delta$  for one mode much larger than the  $\Delta$ 's for the other modes on the overlaps in the time domain is shown in Figure 1 (bottom). In this example,  $\Delta_{500} = 0.5$  while  $\Delta_{1100} = 1.7$ . The overlap recurrences for the highly displaced high-frequency mode are sharp while those for the low-frequency mode with a small displacement are broad. The total product overlap

is thus dominated by the sharp recurrences of the low-frequency mode, and the spectrum in the frequency domain shows a spacing of  $1125 \text{ cm}^{-1}$ .

Five qualitative features of the simple formula (eq 6) are worth discussing. First, if all of the  $n_k = 1$ , then the MIME frequency must fall between the highest and the lowest real frequencies. Second, it can happen that  $\omega_M$  is lower than any of the individual frequencies. (This situation was illustrated above for  $\omega_1 = 302$  and  $\omega_2 = 203$  where  $\omega_M = 101$ .) Third, it is not possible for  $\omega_M$  to be larger than the highest frequency  $\omega_k$  except for a minor shift due to  $\Gamma$ . Fourth,  $\omega_M$  may correspond fortuitously to one of the  $\omega_k$  values, but mode  $k$  may not even be displaced! Fifth, it is clear from eq 6 that many combinations of  $\Delta$ 's and  $\omega$ 's can give the same  $\omega_M$ . Thus,  $\omega_M$  can not be used to provide a unique determination of the contributing modes nor their displacements.

In several recently reported spectra,<sup>9</sup> clusters of sharp phonon mode features are superimposed on the broader scale MIME frequency bands. These types of features should not be confused with the clusters of intramolecular bands, which, by virtue of the large  $\Gamma$ , are unresolved and form the MIME spacing. The frequencies of the phonon bands will either change or the bands will disappear when the condensed medium is changed from a single crystal to different types of glasses or matrices. The MIME features should not change (or only slightly change if the vibrational frequencies of the molecule are sensitive to the medium.)

In summary, equally spaced vibronic peaks in poorly resolved luminescence spectra of large molecules in condensed media will usually be MIME peaks. They may be indistinguishable from a progression in one mode of the displacement if that mode is much larger than all other displacements. When  $\Gamma$  is small, a highly resolved spectrum containing bands from progressions in all of the displaced modes will be obtained and no MIME will be observed. When the MIME is present, the simple formula for the MIME frequency that was derived above gives a result that is very close to the result from the exact calculation but does not require calculations of overlaps or Fourier transforms.

**Acknowledgment.** E.J.H. and J.I.Z. gratefully acknowledge the NSF (Grants CHE-85-07138 and CHE-85-09329, respectively) for support of this work.

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## Synthesis, Reactivity, and Variable-Temperature NMR Studies of Transition-Metal Complexes Containing the 2,3-Dihydrothiophene Ligand

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Received December 9, 1986

The transition-metal complexes  $\text{W}(\text{CO})_5(2,3\text{-DHT})$  (**1**),  $[\text{Re}(\text{CO})_5(2,3\text{-DHT})]\text{SO}_3\text{CF}_3$  (**3**),  $\text{PdCl}_2(2,3\text{-DHT})_2$  (**4**), and  $\text{Ru}(\text{C}-\text{O})_3\text{Cl}_2(2,3\text{-DHT})$  (**5**) containing S-bound 2,3-dihydrothiophene (2,3-DHT), a proposed intermediate in thiophene hydrodesulfurization, have been prepared and characterized. Variable-temperature  $^1\text{H}$  NMR studies of complexes **1**, **3**, and **5** establish that the barrier to inversion of the coordinated sulfur increases with the oxidation state of the metal:  $\text{W}(\text{0}) < \text{Re}(\text{I}) < \text{Ru}(\text{II})$ . In the series of  $\text{W}(\text{CO})_5(\text{L})$  complexes, where  $\text{L} = 2,3\text{-DHT}$ ,  $2,5\text{-DHT}$ , and tetrahydrothiophene (THT), the inversion barriers decrease in the order  $2,3\text{-DHT}$  (48.5 kJ/mol)  $>$   $2,5\text{-DHT}$  (45.6)  $>$  THT (43.9), which is also the order of decreasing ring strain in the sulfur ligands. Thus, the less strained the ligand, the more easily it achieves the planar transition state required for inversion.

### Introduction

Hydrogenation of thiophene to 2,3-dihydrothiophene (2,3-DHT) has been proposed as the initial step in the hydrodesulfurization (HDS) of thiophene.<sup>2–4</sup> In order to understand how 2,3-DHT



2,3-DHT

might coordinate to metal ion sites on the HDS catalyst, we have prepared several of its transition-metal complexes. Little is known

(1) Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division.

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