A Frequency Rule for Non-Isotopic Molecules

SVEND BRODERSEN and A. LANGSETH

Chemical Laboratory of the University of Copenhagen, Denmark

Recently the present authors have pointed out that there exists a simple relation between the vibrational frequencies of certain isotopic molecules. A complete isotopic rule was formulated which allows the calculation of all vibrational frequencies of one isotopic molecule from those of two others.

In the present paper it is shown that this rule may even be applied to chemically different (non-isotopic) molecules with reasonable success. For a few molecules, taken as examples, all the vibrational frequencies are calculated, in each case from the known frequencies of two related molecules. In spite of the apparently rough approximations, introduced when the isotopic rule is applied to non-isotopic molecules, the results obtained are sufficiently accurate to be a valuable help in the interpretation of complex vibrational spectra.

One of the objectives of molecular spectroscopy is — through measurement and interpretation of the spectra — to determine the potential function of the molecule under investigation. As the potential function may be regarded as a quantitative representation of the valence forces within the molecule, it is of evident chemical interest and of fundamental importance for the further development of the quantum-mechanical valence theory.

The interpretation of the observed bands in a spectrum in terms of fundamentals, combination frequencies, and overtones is often a rather difficult task. Except for di-atomic and certain high-symmetrical tri-atomic molecules it will always be necessary to include an investigation of certain istopic molecules as well, in order to make an unambiguous interpretation of the spectrum possible, and — at the same time — to get sufficient experimental data for the evaluation of the potential constants.

As the potential function is unaltered by isotopic substitution there exist certain relations between the fundamental frequencies of isotopic molecules. Such relations (so-called "isotopic rules") represent one or more single relations between the vibrational frequencies and the geometrical parameters of the isotopic molecules, but the potential constants ("force constants") do not occur. Therefore, the fulfilment of the requirements of these isotopic rules is a very useful check on the correctness of a given interpretation.

Recently the present authors have reported on a new isotopic rule [1]. This rule we have called "the complete isotopic rule" because it allows the calculation of all the vibrational frequencies of certain molecules from the frequencies of other definite isotopic molecules.

The proof of this rule is based on the assumption of a harmonic (quadratic) potential function. The agreement between observed and calculated frequencies achieved by use of the complete isotopic rule is, however, much better than that obtained by the ordinary calculation of vibrational frequencies based on a definite harmonic potential function. This is due to the fact that the application of the complete rule actually amounts to a sort of interpolation between the frequencies of two "extreme" molecules to give the frequencies of the "intermediate" molecule in question. This means that we need not assume one definite harmonic potential function — which would be an approximation, the real potential function always being more or less anharmonic — but implicitely uses three slightly different harmonic functions for the three isotopic molecules involved in the calculation. If these functions are "linearly" related a significantly better approximation to the real anharmonic potential function of the "intermediate" molecule is to be expected. This has been verified in an extensive study and calculation of the fundamental frequencies of all the different deuterated species of benzene [2].

This situation suggests that the complete isotopic rule may even be applied to chemically different molecules with tolerable success. Derivatives of a definite compound formed by substitution of one or more atoms for equivalent atoms of other elements will have materially different potential functions

Table 1. Vibrational frequencies (in cm^{-1}) of CO_2, OCS, and CS_2.

	Sym. Class	Obs.	Calc.	Calc. — Obs.
CO_2	Σ_g^+	1 337 [a]		
	Σ_u^+	2 349		
	Π_u	667		
OCS	Σ^+	858	880	+ 22
		2 062	2 068	+6
	Π	522	549	+27
CS_2	Σ_g^+	660 [a]		
	Σ_u^+	1 536		
	Π_u	397		

[a] Assumed unperturbed value.

even if the geometry of these derivatives is approximately the same. It may, however, be expected that the potential function of an "intermediate" derivative with a fair approximation can be obtained by "linear" interpolation between the potential functions of two "extreme" molecules, as for instance that of $O=C=S$ from those of $O=C=O$ and $S=C=S$. If this is the case the complete frequency rule may be applied with reasonable success.

As discussed in detail in our previous paper [1] the complete isotopic rule is strictly valid for all fundamental frequencies of linear molecules and for the out-of-plane fundamentals of plane molecules (as for instance ethylene and aromatic hydrocarbons). As examples for the application of the complete frequency rule to non-isotopic molecules we have therefore chosen $O=C=S$ and some fluoro and chloro derivatives of ethylene: $CF_2=CFCl$, $CF_2=CCl_2$, trans-$CFCl=CFCl$, and $CFCl=CCl_2$. The fundamentals of $O=C=S$ are cal-

Table 2. Out-of-plane frequencies (in cm⁻¹) of ethylene derivatives.

	Sym. Class	Obs.[3]	Calc.		Calc. — Obs.	
			This Invest.	Mann et al.[3]	This Invest.	Mann et al.[3]
$F_2C=CF_2$	A_{1u}	190				
	B_{1u}	406				
	B_{2g}	508				
$F_2C=CFCl$	A''	166	171	169	+5	+3
		369	382	377	+13	+8
		538	509	516	−29	−22
trans- FClC=CFCl	A_u	ca. 140	139	140	ca. −1	ca. 0
		333	359	358	+26	+25
	B_g	529	510	514	−19	−15
$F_2C=CCl_2$	A_2	ca. 167	155	157	ca. −12	ca. −10
	B_2	323	353	337	+30	+14
		564	509	523	−53	−41
$FClC=CCl_2$	A''	ca. 130	129	129	ca. −1	ca. −1
		313	324	318	+11	+5
		537	511	517	−26	−20
$Cl_2C=CCl_2$	A_{1u}	110				
	B_{1u}	288				
	B_{2g}	512				

Table 3. In-plane frequencies (in cm⁻¹) of ethylene derivatives.

	Sym. Class	Obs.[3]	Calc.		Calc. − Obs.	
			This Invest.	Mann et al.[3]	This Invest.	Mann et al.[3]
$F_2C = CF_2$	A_{1g}	394 778 1 872				
	B_{1g}	551 1 340				
	B_{2u}	218 1 337				
	B_{3u}	558 1 186				
trans- FClC = CFCl	A_g	288 425 632 1 186 1 707	299 420 648 1 157 1 755	302 414 645 1 207 1 734	+11 −5 +16 −29 +48	+14 −11 +13 +21 +27
	B_u	175 426 892 1 190	184 467 818 1 278	186 437 880 1 234	+9 +41 −74 +88	+11 +11 −12 +44
$F_2C = CCl_2$	A_1	258 434 622 1 032 1 749	271 420 622 1 003 1 749	260 433 611 1 065 1 731	+13 −14 0 −29 0	+2 −1 −11 +33 −18
	B_1	192 459 993 1 327	189 453 960 1 339	192 443 957 1 327	−3 −6 −33 +12	0 −16 −36 0
$Cl_2C = CCl_2$	A_{1g}	235 447 1 517				
	B_{1g}	347 1 000				
	B_{2u}	176 908				
	$B_{3\,1}$	310 777				

culated from those of CO_2 and CS_2, and all the out-of-plane fundamentals of the ethylene derivatives from those of $CF_2=CF_2$ and $CCl_2=CCl_2$. The procedure used in the calculations is exactly the same as that described for isotopic molecules [1]. The results are given in Tables 1 and 2 together with the observed frequencies. The agreement obtained is quite satisfactory in consideration of the material differences between the potential functions of the various molecules. An accuracy like that obtained in these examples will in most cases be sufficient for assignment purposes.

Recently Mann et al.[3] have calculated the vibrational frequencies of the fluoro and chloro derivatives of ethylene using a method of calculation which in principle has much in common with the one proposed here. According to these authors the frequencies are calculated from a definite potential function for each molecule. Every separate one of these functions has been derived from those of $CF_2=CF_2$ and $CCl_2=CCl_2$ by interpolation for each potential constant separately. The results obtained by Mann et al. are for the sake of comparison included in Table 2. It is seen that they are slightly better than ours.

As we have shown in our previous papers [1,2] the field of application of the complete isotopic rule may be extended considerably for hydrocarbons by introducing a splitting of the rule into separate rules comprising either the low frequencies or the high hydrogen (or deuterium) stretching frequencies. Because of the great difference in frequency the interaction between these groups of fundamentals is small enough to make the separation permissible. This approximation extends the applicability of the complete isotopic rule also to the planar vibrational frequencies of a great number of plane molecules.

For the halogen derivatives, which we are considering here, a corresponding separation should from a theoretical point of wiew not be permissible because the C—F and the C—Cl stretching frequencies are much lower, being actually of the same order of magnitude as several of the other fundamental frequencies. On the basis of this consideration one should therefore not expect the frequency rule to hold to a sufficient aproximation when applied to the planar frequencies of the substituted ethylenes. If we, nevertheless, use the frequency rule as if the separation were permissible we get the results shown in Table 3. It is seen that the results are almost as good as those obtained from the "valid" rule given in Tables 1 and 2. The results of Mann et al., included in Table 3, are again slightly, but not essentially, better than ours. However, considering the enormous simplification of the calculations achieved by use of the frequency rule rather than the extremely elaborate procedure used by Mann et al., the small gain in quality of the results seems insignificant.

The unexpected success of applying the complete isotopic rule to these cases seems to indicate that the potential functions to a fairly good approximation allow the separation of stretching frequencies from other vibrational frequencies even if they all are of the same order of magnitude. A definite establishment of this interesting feature will, however, require a much larger material than that presented here. If it actually can be shown that the separation is generally permissible the frequency rule will be a most valuable instrument for the interpretation of a great many vibrational spectra. We hope to be able to give a more detailed discussion of this problem in a later paper.

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