9 August 1996

ELSEVIER

Chemical Physics Letters 258 (1996) 25–29

CHEMICAL
PHYSICS
LETTERS

Density of vibrational states of a given symmetry type for octahedral AB_6 molecules

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Received 20 March 1996; in final form 4 June 1996

Abstract

Crude estimations of the densities of states of different symmetry types are made on the basis of the ratio of fundamental frequencies. The theoretical calculation is based on the generating function approach developed recently for this kind of problem. The behavior of the regular and oscillatory parts of the density of states in the limit of high vibrational excitations is compared with the simplest estimate based on the proportionality between density of states of a given symmetry type and the dimension of corresponding irreducible representations. SF_6 and UF_6 molecules are studied as examples.

1. Introduction

The density of vibrational states is a characteristic important for the description of chemical reactions and many intramolecular processes related to the energy redistribution [1–14]. For highly symmetric molecules the decomposition of the total density into partial densities of different symmetry species is needed for both concrete applications (due to various symmetry selection rules) and abstract theoretical analysis [15]. In particular, partial densities give important information about the fraction of the available phase space associated with each symmetry type of the vibrational motion.

Effective numerical algorithms were proposed long ago [8–13] for density-of-state calculations. Recently, considerable efforts were devoted to constructing simple models allowing the reproduction of vibrational densities for the whole range of energies under (and even above) the dissociation limit [1–3]. Alternatively, an algebraic approach has been proposed [16] which enables one to find explicit analytical formulae for partial numbers of states of a given symmetry type. This approach is based on the old group-combinatorial idea [17], the generating function method, which has recently found various applications in physics, in general, and in molecular physics, in particular [16,18–21].

This Letter presents an application of the generating function approach developed recently by Sadovskii and Zhilinskii [16] to the estimation of the vibrational densities of states of AB_6 type octahedral molecules. Details of the method are given in Ref. [16]. Here we analyze the dependence of partial vibrational densities (for each symmetry species) on the ratio of fundamental frequencies and the decomposition of the total density into regular and oscillatory parts as described in Ref. [16]. Thus, we only discuss briefly the assumptions and algorithm and present the results of the direct theoretical model.

PII S0009-2614(96)00618-5

Straightforward generalization of our calculations to any molecule with symmetry group O_h is possible without any modification in the group theoretical part of the present work.

2. Assumptions

We consider the vibrational structure of the ground electronic state, supposing that this electronic state can be regarded as isolated, and neglect the rotational structure.

To predict the densities (differential or integral) of vibrational states it is necessary to use some model for the potential. The absolute values of the total vibrational density (counting all vibrational states irrespective of their symmetry) depends strongly on the anharmonicity and dissociation energy. At the same time it was found earlier by direct numerical calculations and formulated as a general conjecture by Quack [5–8] that the partial numbers (densities) of vibrational states of different symmetry types are proportional among themselves. The ratio of the numbers of states of any two symmetry types $n_{\Gamma_1}/n_{\Gamma_2}$ approaches in the limit of high excitation the ratio of squares of dimensions of corresponding representations $[\Gamma_1]^2/[\Gamma_2]^2$. Nevertheless, for some molecules at reasonable energies this limit may not be achieved. In Ref. [16] an explicit algebraic formula was obtained for the partial number of states of a given symmetry type in the harmonic approximation. It was equally shown for the example of H_3^+ that the convergence to the asymptotic limit for the integral number of states of given symmetry type can be rather slow. The anharmonicity correction, which strongly modifies the absolute densities of each symmetry type, does not influence considerably the ratio of densities of states of different symmetry types. This is why it is interesting to perform calculations of the relative densities of states of different symmetry types for a molecule with high symmetry even in the simplest harmonic approximation, i.e. neglecting the anharmonicity. In this way, the sensitivity of the partial numbers of states of different symmetry to the ratio of fundamental frequencies can be studied directly. Molecules with high symmetry group are especially interesting because in this case the group itself has many different irreducible representations. At the same time only some of these irreducible representations are present as symmetry types of fundamental vibrations. Some symmetry species arise for the first time only at the second or third overtone, or a combination band. To demonstrate the behavior of the vibrational densities of states of a high symmetry molecule we have chosen the AB_6 molecule with symmetry O_h. The only initial molecular data for such a calculation are the symmetry types of the fundamental vibrations and the ratio of their fundamental frequencies. We are not interested in the fine structure of the densities of states. Therefore, a crude rational approximation of the ratio of frequencies is sufficient for our purposes.

3. AB_6 type molecules

Among the octahedral AB_6 type molecules reasonably well characterized by vibrational frequencies we have chosen the group of hexafluorides. For XF_6 molecules with a heavy central atom there is an obvious tendency to show the splitting of fundamental frequencies in two groups of "stretching" and "bending" vibrations. This suggests simple models with degenerate stretching and bending frequencies. We remark that the ratio between the stretching and bending modes may vary from 2.5 to 3.5 depending on the molecule. This ratio is significantly higher than the ratio between stretching and bending vibra-

Table 1
Vibrational frequencies of XF_6 molecules (O_h symmetry)

Molecule	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_{av}
	A_{1g}	E_g	F_{1u}	F_{1u}	F_{2g}	F_{2u}	
SF_6	770	640	940	614	522	344	620.7
UF_6	666	535	626	189	200	144	347.5

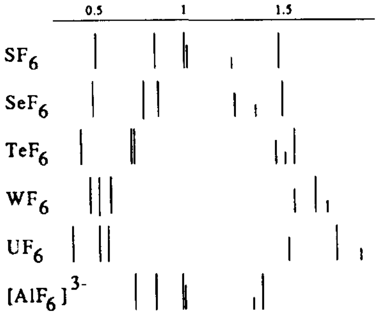

Fig. 1. Distribution of normalized fundamental frequencies ν_i/ν_{av} for XF_6 molecules. ν_{av} is the average frequency defined in Eq. (1).

tions in light tetrahedral molecules which is normally accepted to be around 2 (this example was treated in Ref. [16]).

The AB_6 molecule which has O_h equilibrium structure possesses six vibrational modes listed in Table 1 along with their symmetry labels and numerical values of frequencies for the SF_6 and UF_6 molecules as examples.

It is clear that the simultaneous scaling of all vibrational frequencies makes no effect on the partial densities while variation of the ratio of fundamental frequencies does. To compare the fundamental frequencies of different molecules from the point of view of the frequency ratio we normalize all frequencies by calculating the average fundamental frequency

$$\nu_{av} = [\nu_1 + 2\nu_2 + 3(\nu_3 + \nu_4 + \nu_5 + \nu_6)]/15 \quad (1)$$

and by setting it to 1. The resulting normalized frequencies ν_i/ν_{av} for various XF_6 molecules are shown in Fig. 1. (Numerical values are taken from Ref. [22]). This figure is useful for choosing approximate models of the ratio of fundamental frequencies listed in Table 2.

We performed an analysis of three different models. (i) The model with the ratio 7:6:9:6:5:3 corresponding to the SF_6 molecule. (ii) The model with the ratio 7:7:7:2:2:2 appropriate for UF_6 and similar molecules. (iii) The theoretical model with the ratio 1:1:1:1:1:1 which does not really correspond to any particular molecule but is interesting as a reference model. When we compare the convergence of the density as a function of energy we use the average energy of fundamental states as the unit of energy. This average frequency is $88/15 \approx 6$, 4, and 1 for models (i), (ii) and (iii) cited above.

4. Algorithm

Initial formulae for the density of state calculation (using the generating function approach) are given by generating functions for invariants and covariants constructed for every irreducible representation. (For the O_h group all these functions can be found in Refs. [18–20].)

The next step is the construction of multi-parameter generating functions counting all (symmetric) tensors of certain symmetry type constructed from the initial reducible representation span by vibrational symmetry coordinates. One parameter always corresponds to one vibrational mode [18–20].

Finally, taking into account the resonance conditions between different vibrational modes the six-

Table 2
Simple models for the ratio of the fundamental frequencies of XF_6 molecules (O_h symmetry)

$[\nu_1]$ A_{1g}	$[\nu_2]$ E_g	$[\nu_3]$ F_{1u}	$[\nu_4]$ F_{1u}	$[\nu_5]$ F_{2g}	$[\nu_6]$ F_{2u}	The most relevant XF_6 molecules
3	3	3	1	1	1	X = Re, Pt
7	7	7	2	2	2	X = U, Np, Pu
5	5	5	2	2	2	X = Te, W
3	2	3	2	2	2	X = Al
5	5	6	3	3	2	X = Se
7	6	9	6	5	3	X = S
4	3	5	3	3	2	X = S
7	6	8	5	4	3	X = S

parameter generating functions are transformed into one-parameter generating functions which give numbers of states of different symmetry types formed by excitations of any vibration [16].

Realization of the analytical calculations for molecules with high symmetry group and large number of vibrational degrees of freedom is done using Maple [23].

5. Results and discussion

Let us start with the simplest model corresponding to the complete degeneracy of all frequencies (1 : 1 : 1 : 1 : 1 : 1). For each representation Γ the regular part of the partial number ω^{Γ} of the vibrational states of type Γ is given by the asymptotic expansion

$$\frac{1}{[\Gamma]^2}\omega^{\Gamma} = \frac{1}{48} \pm \frac{45045}{64E^5} \mp \frac{675675}{32E^6} + \dots, \qquad (2)$$

where $[\Gamma]$ means the dimension of the representation Γ and the upper sign refers to $\Gamma = A_{1g}$, A_{2g}, E_g, F_{1u}, F_{2u}. We assume that $E = 1$ corresponds to the energy of a fundamental excitation. Higher order terms in Eq. (2) differ for different Γ.

A similar expression for the "UF_6" model (7:7:7:2:2:2) is

$$\frac{1}{[\Gamma]^2}\omega^{\Gamma} = \frac{1}{48} \pm \frac{7}{64}\,\frac{45045}{64E^2} + \dots. \qquad (3)$$

Higher order terms are omitted from the expansion (3) because they now depend on the type of representation.

Finally, for the "SF_6" model (7:6:9:6:5:3) only the constant term of the asymptotic expansion is the same for all representations. Thus we give two different formulae, one for one- and two-dimensional representations:

$$\frac{1}{[\Gamma]^2}\omega^{\Gamma} = \frac{1}{48} \pm \frac{15^5}{88^5}\,\frac{91216125}{32E^5} + \dots \qquad (4)$$

and another for triply degenerate representations:

$$\frac{1}{[\Gamma]^2}\omega^{\Gamma} = \frac{1}{48} \pm \frac{15^5}{88^5}\,\frac{30405375}{32E^5} + \dots. \qquad (5)$$

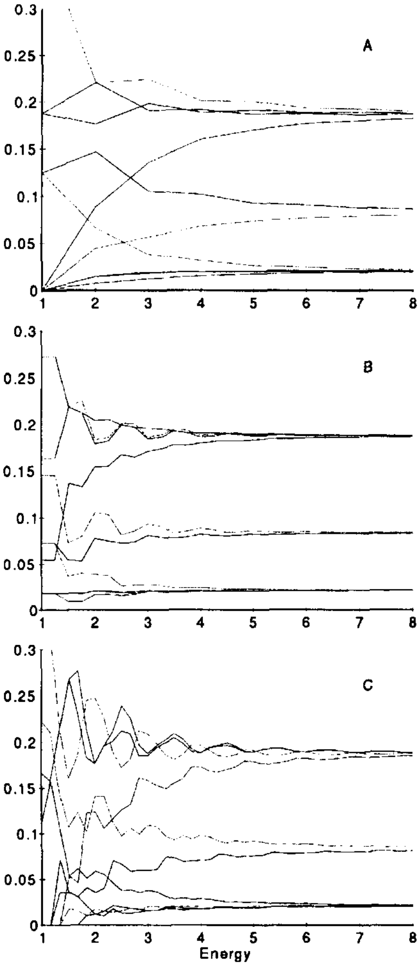

Fig. 2. Partial integral densities of vibrational states of different symmetry types for three harmonic models of the force field for the octahedral AB_6 molecule. The ratio of fundamental frequencies $\nu_1 : \nu_2 : \nu_3 : \nu_4 : \nu_5 : \nu_6$ is (A) 1 : 1 : 1 : 1 : 1 : 1; (B) 7:7:7:2:2:2; (C) 7:6:9:6:5:3. The energy is given in units of average frequency for each model.

Comparison of the formula given above shows that the the regular part of the partial densities goes to the asymptotic limit as $\propto E^{-5}$. The coefficient at E^{-5} becomes smaller with the increasing dispersion of fundamental frequencies.

At the same time the oscillatory part becomes more pronounced for models with a resonance relation expressed by higher natural numbers. This is clearly seen in Figs. 2a–2c, which show the complete density as a function of normalized energy.

6. Conclusions

We have calculated partial numbers of vibrational states of different symmetry as a function of energy for the octahedral molecules XF_6. The main conclusion of this Letter is the fact that the regular part of the partial vibrational density of state converges rapidly to its asymptotic value defined completely by the dimensions of corresponding irreducible representations. The asymptotic values are almost achieved at energies of the order of $(5-8)\hbar\nu_{av}$.

The modification of the distribution of fundamental frequencies influences mainly the oscillatory part of the density (which is important at low excitations) rather than the convergence properties of the regular part at high excitations. From the point of view of analytical calculations explicit formulae for the regular part are rather simple and can be written explicitly for any model ratio of fundamental frequencies. At the same time the description of the oscillatory part is much more complicated and its extrapolation to higher rational approximations is not straightforward. This question should be analyzed in more detail on simpler examples.

Aknowledgement

The authors thank Dr. D. Sadovskii for help with the Maple program and for a critical reading of the manuscript. The Laboratoire de Physico-Chimie d'Atmosphère participates in the Centre d'Etudes et de Recherches Lasers et Applications, supported by the Ministère chargé de la Recherche, the Région Nord/Pas de Calais and the Fonds Européen de Développement Economique des Régions. One of the authors (PS) was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. A4040501).

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