INVERSION OSCILLATIONS IN MOLECULAR SYSTEMS

Yu. V. OVCHINNIKOV and S. P. IONOV

Institute of Theoretical Physics, Academy of Sciences, U.S.S.R.

Submitted February 2, 1967

Zh. Eksp. Teor. Fiz. 53, 598–604 (August, 1967)

A classification of inversion-vibrational levels in weakly distorted molecular systems of tetrahedral or octahedral symmetry is presented. The magnitude of the vibrational level splitting is determined in the quasiclassical approximation. Numerical estimates of the splitting are given for manganese and cobalt complexes.

1. Much progress has been made recently in the study of the geometric structure of molecules. Resonance methods (EPR, NMR, NQR, NGR), capable of resolving process times from 10^{-6} to 10^{-10} sec, have been successfully employed, as well as classical methods (electron, neutron, or x-ray diffraction and spectrometric methods). The resolution time of the latter is from 10^{-10} to 10^{-20} sec. Naturally, some distortions of the geometric structure of the molecules are observed in some methods and not in others. One of the main causes of the "increase" of the symmetry of the geometric configuration of molecules in resonance methods is the inversion effect. The inversion effect was first observed in the ammonium molecule NH_3.[1] An experimental investigation of even NH_3-like molecules entails considerable difficulties. There are definite indications, however, that the effect is present also in complex molecular systems.

The frequencies of the inversion oscillations were calculated for the NH_3 molecule by Hund[2] and also by Dennison and Uhlenbeck[3]. In this case, the problem of the spectrum of the inversion oscillation reduces to a one-dimensional Schrödinger equation.

We determine in this paper the classification and the spectrum of the inversion oscillations for more general cases that can be observed in practice.

2. If the nuclei are symmetrically arranged, the electronic term of the molecule may turn out to be degenerate, and in this case the lowering of the molecule symmetry leads to a decrease in the energy. However, this gives rise to several equivalent positions of the system. This means that the Hamiltonian is invariant with respect to a certain point symmetry group. Neglecting the possibility of transition from one equivalent state to the other, each level turns out to be degenerate. Allowance for such transitions (inversion oscillations) lifts the degeneracy. The character of the splitting, that is, the number of sublevels and their degeneracy multiplicity, is determined by the point group of the system.

To find the distance between the levels we shall use the following consideration. Let x_i be the normal vibrational coordinates, motion along which can let the system go into all stable states. Let us assume that it is precisely these normal coordinates which are significant in the level-splitting problem. Then the determination of the spectrum reduces to a solution of the Schrödinger equation

$$\left[-\frac{1}{2\mu^*}\frac{\partial^2}{\partial x_i{}^2} + V(x_i) - E\right]\psi = 0, \qquad (1)$$

when μ^* is the effective mass.

We now consider molecular systems with coordination numbers 4 and 6.

The maximum symmetries in this case are T_d and O_h. In real systems, however, such high symmetries may not be realized, owing to distortion of individual valence angles or the nonequivalence of equilibrium internuclear distances. Lowering of the symmetry can occur, for example, when the ground state of the high-symmetry system is degenerate and the system tends to go over into an energetically more favored state (Jahn-Teller effect). For the most frequently encountered cases of lowering of the symmetry of the groups T_d and O_h, the table lists a classification of the inversion vibrational levels of the "ground" state.

Let us consider the case of lowering of the symmetry from T_d to C_{3v}. Three vibrational coordinates are significant, ϑ_1, ϑ_2, and ϑ_3; they form a representation T_2 of group T_d. Therefore the index i in (1) runs through the values 1, 2, and 3. The potential V has four wells, located at the vertices of a tetrahedron with distance d from the center to the vertex (see the appendix).

Let ψ_0 be a scalar on the group T_d, and ψ_1 the Y_1^0 component of a vector;

$$[p^2/2\mu^* + V]\psi_i = E_i\psi_i \qquad (i = 0,1). \qquad (2)$$

Multiplying the first equation by ψ_1 and the second by ψ_0, subtracting one from the other, and integrating over a certain domain D, we get

$$(E_1 - E_0)\int_D \psi_0\psi_1 d\tau = \frac{1}{2\mu^*}\int_S (\psi_1\nabla\psi_0 - \psi_0\nabla\psi_1)\,dS. \qquad (3)$$

It is convenient to choose as the domain D that part of space which is bounded by three planes passing through the center of the tetrahedron perpendicular to the three edges in Fig. 1.

Recognizing that ψ_0 is a scalar on a group, and ψ_1 transforms like a Y_1^0 component of a vector, we get
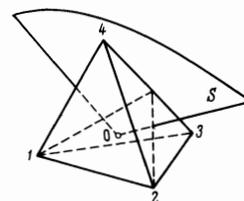
FIG. 1.

$$\int_S (\psi_1 \nabla \psi_0 - \psi_0 \nabla \psi_1) dS = -3 \int_{S'} \psi_0 \nabla \psi_1 dS. \qquad (4)$$

If the transparency of the barrier is small, we get in the zeroth approximation

$$\psi_0 = 1/2(a_1 + a_2 + a_3 + a_4), \qquad \psi_1 = \frac{1}{2\sqrt{3}}(a_1 + a_2 + a_3 - 3a_4). \qquad (5)$$

Here a_4 is the solution of (2) for $V(r)$ with one well, and the functions a_i (i = 1, 2, 3) are naturally defined as

$$a_i = T_{C_2^i} a_4. \qquad (6)$$

Here $T_{C_2^i}$ is the operator of rotation about a twofold axis, whereby the point 4 goes over into the point i.

From (4)–(6), neglecting the overlap integrals, we get

$$\int_D \psi_0 \psi_1 d\tau = -\sqrt{3}/4, \qquad E_1 - E_0 = \frac{2\sqrt{3}}{\mu^*} \int_{S'} \psi_0 \nabla \psi_1 dS. \qquad (7)$$

Inasmuch as the potential V is unknown, certain assumptions on the relation V = V(r) must be made in order to calculate the splitting with the aid of formula (7). In particular, if each well can be regarded as spherically symmetrical, then the main contribution is made by a narrow region on a plane near the point of its intersection with the line (3–4), and in this case

$$E_1 - E_0 = \frac{4\pi l}{\mu^*} a_4^2(l), \qquad l = \frac{d\sqrt{2}}{\sqrt{3}}, \qquad (8)$$

where d is given by formula (21) of the Appendix.
In the oscillator approximation

$$E_1 - E_0 = \frac{4\pi l}{\mu^*} \left(\frac{\mu^*\omega}{\pi}\right)^{1/2} \exp(-\mu^*\omega l^2). \qquad (9)$$

we note that the parameters ω and l can be determined experimentally.

We can consider analogously the lowering of the symmetry from O_h to D_{2h}^* (a rectangle with the angle α_0 between diagonals is located in the equatorial plane). Such distortions are obtained in motion along three normal coordinates which give the representation T_2^g of the group O_h. If we put $x_1 = d(\pi/2) - \alpha)$ (d—distance between the central atom and the ligand), then $\mu^* = m_{lig}$, and the potential V has six minima located at the vertices of an octahedron, with distances from the center

$$\rho = d(\pi/2 - \alpha_0).$$

We now draw planes through the center and the four edges of the cube (14, 43, 32, 21). The region D lies above these planes (Fig. 2). Let φ_6 be the solution of (1) if only one well is retained in V. We put $\varphi_1 = T_{C_4^{(1)}} \varphi_6$ and analogously for the remaining φ_i (i = 2, 3, 4, 5). The wave functions $\varphi_1 - \varphi_6$ form a representation of the group O_h, which is expanded into A_1, E, and T_1. By way of the basis of these representations we can choose the following:

Classification of inversion vibrations

T_d			O_h			
C_{3v}	S_4	C_{2v}	D_{2h}^*	D_{4d}	D_{2h}^{**}	C_s
A_1, T_2	A_1, E	A_1, E, T_2	A_1, E, T_2	A_1, E	$A_1, A_2, 2E$	$A_1^g, A_2^u, T_2^g, T_1^u$

Note: A rectangle (*) or a rhombus (**) lies in the equatorial plane of the distorted octahedron.

$$A_1: \qquad \psi_0 = \frac{1}{\sqrt{6}} \sum_{i=1}^6 \varphi_i,$$

$$E: \quad \begin{cases} \psi_1 = \frac{1}{2\sqrt{3}}[(\varphi_1 + \varphi_2 + \varphi_3 + \varphi_4) - 2(\varphi_5 + \varphi_6)], \\ \psi_2 = 1/2[(\varphi_1 + \varphi_3) - (\varphi_2 + \varphi_4)], \end{cases} \qquad (10)$$

$$T_1: \quad \tilde\psi_1 = \frac{1}{\sqrt{2}}(\varphi_5 - \varphi_6), \quad \tilde\psi_2 = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_3), \quad \tilde\psi_3 = \frac{1}{\sqrt{2}}(\varphi_2 - \varphi_4).$$

From (3) and (10) we get

$$E_1 - E_0 = \frac{3}{\sqrt{2}\mu^*} \int_S \psi_0 \nabla \psi_1 dS, \qquad \tilde E_1 - E_0 = \frac{\sqrt{3}}{\mu^*} \int_S \psi_0 \nabla \tilde\psi_1 dS. \qquad (11)$$

In the oscillator approximation

$$E_1 - E_0 = \frac{3}{2}(\tilde E_1 - E_0) = \frac{6\pi l}{\mu^*}\left(\frac{\mu^*\omega}{\pi}\right)^{3/2} \exp(-\mu^*\omega l^2), \qquad (12)$$

where

$$l = \frac{d}{\sqrt{2}}\left(\frac{\pi}{2} - \alpha_0\right).$$

We can regard analogously the lowering symmetry from O_h to D_{4d}.[4] In this case there are two essential normal coordinates, ϑ_1 and ϑ_2, giving the representation E_g of the O_h group. The potential V has three wells located at the vertices of a regular triangle (Fig. 3).

We shall reckon the distance along the normal coordinates in real atomic displacements. Then $\mu^* = 12m$ (m—mass of ligand), and the distance of the vertex to the center of the regular triangle is

$$d = (b - a)/3,$$

where a and b—the half-diagonals in the distorted molecule.

For the "ground" state we obtain by the method described above

$$A_1: \qquad \psi_0 = \frac{1}{\sqrt{3}}(\varphi_1 + \varphi_2 + \varphi_3),$$

$$E: \quad \begin{cases} \psi_1 = \frac{1}{\sqrt{3}}(\varphi_1 + e^{2\pi i/3}\varphi_2 + e^{-2\pi i/3}\varphi_3), \\ \psi_2 = \frac{1}{\sqrt{3}}(\varphi_1 + e^{-2\pi i/3}\varphi_2 + e^{2\pi i/3}\varphi_3), \end{cases} \qquad (13)$$

where φ_1 is the solution of (1) for the case of one well at the point 1, and $\varphi_2 = T_{2\pi/3}\varphi_1$, $\varphi_3 = T_{2\pi/3}^{-1}\varphi_2$.

Choosing the domain D in a manner shown in Fig. 3, and using the customary reasoning, we obtain

$$E_1 - E_0 = -\frac{3}{2\mu^*} \int_L \psi_0 \frac{\partial \psi_1}{\partial n} dl, \qquad (14)$$

where $\partial/\partial n$ is the derivative along the normal to the line L.

In the oscillator approximation we have

$$E_1 - E_0 = 3l\omega(\mu^*\omega/\pi)^{1/2} \exp(-\mu^*\omega l^2), \qquad (15)$$

where $l = (b - a)/2\sqrt{3}$.

For the first excited state (the potential has one well
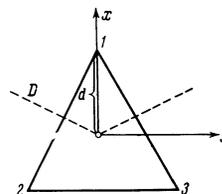
FIG. 2.
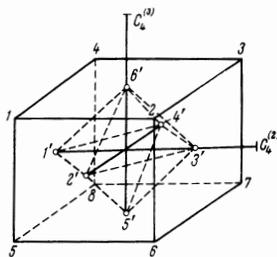
FIG. 3.

at the point 1), two modes of oscillations are possible. The wave function of one of them $\{\varphi_1\}$ is multiplied by $+1$ upon reflection about the x axis, and the other $\{\widetilde{\varphi}_1\}$ by -1. Just as in the case of the ground state, we find that the functions φ_1, $T_{2\pi/3}\varphi_1$, and $T_{2\pi/3}^{-1}\varphi_1$ form a representation of the group C_{3V} which breaks up into A_1 and E. The distance between levels is given by formulas (13) and (14). On the other hand, in the case of the function $\widetilde{\varphi}_1$, there arise the representations A_2 and E, and the distance between the levels is given by the formula

$$\bar{E}_1 - \bar{E}_0 = \frac{3}{2\mu^*} \int_L \widetilde{\psi}_1 \frac{\partial \widetilde{\psi}_0}{\partial n} \, dl, \qquad (16)$$

where the functions $\widetilde{\psi}$ are determined by formula (13), except that φ_1 is replaced by $\widetilde{\varphi}_1$.

In the oscillator approximation we have

$$E_1 - E_0 = \frac{3l}{2\mu^*} \left(\frac{\mu^*\omega}{\pi}\right)^{3/2} \exp(-\mu^*\omega l^2) \left[3\mu^*\omega l^2 - \frac{5}{2}\right],$$

$$\bar{E}_1 - \bar{E}_0 = -\frac{3l}{2\mu^*} \left(\frac{\mu^*\omega}{\pi}\right)^{3/2} \exp(-\mu^*\omega l^2) \left[\mu^*\omega l^2 + \frac{1}{2}\right]. \qquad (17)$$

We note that the inversion oscillations go over into ordinary oscillations when the barrier between "wells" is lowered, and the distance between levels become exponentially small when it is raised. The quasiclassical approximation is valid if the splitting $\Delta\nu$ satisfies the condition $\Delta\nu/\nu \ll 1$. On the other hand, for an experimental observation it is usually necessary to satisfy the condition $\Delta\nu/\nu \gtrsim \exp(-10)$. Using formulas (12) and (15) we can estimate the region $1 \ll \mu^*\omega l^2 \lesssim 10$ of molecule distortion, in which it is simplest to observe the inversion oscillations.

Formulas (12) and (15) make it easy to obtain an estimate of the frequency of the inversion oscillations. For example, in the case of the octahedral complexes $Mn(H_2O)_6^{3+}$ and $Co(H_2O)_6^{3+}$, using the well known values of the frequencies of the valence oscillations ($\nu \approx 250$ cm^{-1}) and values $a - b = 0.325$ and 0.068 Å respectively[4], we get $\Delta\nu/\nu \approx 10^{-7}$ for the manganese complex and $\Delta\nu/\nu \approx 0.1$ for the cobalt complex.

We note that even the harmonic-oscillator approximation (formulas (12) and (15)) yields a satisfactory expression for the frequency of the inversion oscillations. For example, in the case of the NH_3 molecule we get for the splitting[3]

$$\Delta E = \frac{2}{\mu^*} \psi(a) \psi'(a). \qquad (18)$$

Formula (18) is similar to expressions (11) and (16). Using for ψ the wave function of the harmonic oscillator, we get

$$\Delta E = 2\omega a \left(\frac{\mu^*\omega}{\pi}\right)^{1/2} \exp(-\mu^*\omega a^2), \quad \mu^* = \frac{3mM}{3m+M}. \qquad (19)$$

Here M is the mass of the nitrogen atom, m the mass of the hydrogen atom, a the height of the pyramid of the NH_3 molecule. Substituting in (19) the known values $\omega = 1.75 \times 10^{14}$ sec^{-1} and a = 3.46×10^{-9} cm, we obtain the magnitude of the splitting in the "ground" state $\Delta E = 0.44$ cm^{-1} ($\Delta E_{exp} = 0.79$ cm^{-1}). Such a difference is connected with the fact that in the case of the NH_3 molecule the distance between wells is not small ($2a/r_0 \sim 1$).

The possibility of inversion in complex molecules (SF_3, ClF_3) was first pointed out by Muetterties and Phillips[5] and also by Liehr[6].

Recently, Atkins and Symons[7] investigated the EPR spectrum of the radical $\cdot PF_4$. In analogy with the molecules SF_4 and PF_4^-, this radical should have a distorted tetrahedral configuration with symmetry C_{2V}. In this case (see the table) there exist six equivalent positions, and a one-dimensional approach[8] is evidently not correct. The presence of six equivalent positions explains the temperature variation of the EPR spectrum.

At low temperatures ($\omega_{inv.\,eff} \ll \omega_{EPR}$) the spectrum is anisotropic. A rise in temperature leads to an increase of $\omega_{inv.\,eff}$, and when $\omega_{inv.\,eff} \gg \omega_{EPR}$ the spectrum becomes isotropic.

Distortion of the tetrahedral symmetry was observed also in compounds of the AO_4 type. According to Morton's data[9], the radicals ClO_4 and SO_4^- have low symmetry (C_{3V} or C_S).

The inversion vibrations are possible also in compounds with higher coordination numbers. Berry[10] considered the regrouping of atoms in PF_5 compounds ($\vartheta \approx 10^5$ sec^{-1}) and PCl_5 ($\vartheta \approx 10^{-4}$ sec^{-1}).

Electron diffraction methods have demonstrated the presence of distortions in the XeF_6[11] molecule.

The distortion of the molecule (one of the FXeF valence angles increases) is the result of an unshared pair located on the shell 5s of the Xe atom[12]. In this case there arise eight equivalent positions (see the table), and the spectrum of the inversion vibrations for the "ground" state consists of two triplets and two single lines. However, no such distortion is observed in the NMR spectrum[13]. This apparently means that $\omega_{inv} \gg \omega_{NMR}$.

Inversion vibrations can also occur in an octahedron as a result of nonequivalent bond lengths[4,14].

The experimental data point to the presence of distortions in the molecular systems with coordination numbers larger than 6[15]:

$$Mo(CN)_8^{4-}, \; JF_7, \; Re\,Hg^{2-}, \; PF_4N(CH_3)_2, \; B_2Cl_4.$$
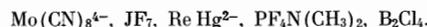
Inverse regrouping is of great interest in biochemical objects (DNA, RNA), in which collective proton transitions, such as occur in dimers of carboxylic acids[16], can occur.

In conclusion, the authors are sincerely grateful to A. I. Larkin for continuous interest in the work and valuable remarks.

APPENDIX

The effective mass μ^* can be represented in the form

$$\mu^* = M + 2m(l_1^2 + l_2^2)/l_M^2, \qquad (20)$$

where M is the mass of the central atom, m the mass of the ligand, and l_i the real displacement of the atom when the molecule goes from one equivalent state to the other.

The displacements l_i can be readily related to the structural parameters of the molecule:

$$l_M^2 = \frac{8}{3} d^2 = \frac{8}{3} \frac{m^2 (b - 3a \cos \alpha)^2}{(M + 4m)^2}, \tag{21}$$

$$l_1^2 = \{[M(3b - a \cos \alpha - 2\sqrt{2}\,a \sin \alpha) + m(10a \cos \alpha + 10b$$

$$+ 8\sqrt{2}\,a \sin \alpha)]^2 + [Ma(\sin \alpha - 2\sqrt{2}\cos \alpha)$$

$$+ m(4a \sin \alpha - 2\sqrt{2}\cos \alpha - 2\sqrt{2}\,b)]^2\}[9(M + 4m)^2]^{-1}, \tag{22}$$

$$l_2^2 = \frac{\{Ma(\sin \alpha - 2\sqrt{2}\cos \alpha) + m[4a \sin \alpha - 2\sqrt{2}(a \cos \alpha + b)]\}^2}{3(M + 4m)^2}. \tag{23}$$

Here b is the distance to the "singled-out" ligand from the central atom, a—distance to the remaining three ligands, cos α—modulus of the cosine of the angle between the directions to the singled-out ligand and the direction to one of the remaining three ligands.

[1] C. E. Clecton and N. H. Williams, Phys. Rev. 45, 234 (1934).

[2] F. Hund, Z. Physik 43, 805 (1927).

[3] D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. 41, 313 (1932).

[4] V. I. Avvakumov, Zh. Eksp. Teor. Fiz. 37, 1017 (1959) [Sov. Phys.-JETP 10, 723 (1960)]; I. B. Bersuker, Zh. Strukturn. khimii 2, 734 (1961).

[5] E. Muetterties and W. Philips, J. Amer. Chem. Soc. 79, 322 (1957); W. Mahler and E. Muetterties, Inorg. Chem. 2, 613 (1963); 3, 1298 (1964); 4, 1520 (1965).

[6] A. D. Liehr, J. Phys. Chem. 67, 471 (1963).

[7] P. W. Atkins and M. Symons, J. Chem. Soc. NT-11, 4363 (1964).

[8] G. W. Chantry and V. C. Ewing, Mol. Phys. 5, 210 (1962).

[9] J. R. Morton, J. Chem. Phys. 45, 1800 (1966).

[10] R. S. Berry, J. Chem. Phys. 32, 933 (1960).

[11] L. S. Bartell, R. M. Gavin, Jr., H. Bradeford, Thompson, and C. L. Chernick, J. Chem. Phys. 43, 2547 (1965).

[12] R. J. Gillespie, J. Chem. Soc. NT-10, 4672 (1963); S. P. Ionov and G. V. Ionova, TEKh UkrSSR 6, (1967).

[13] R. Blinc, E. Prikmajer, J. Slivnik, and I. Zupaneie, J. Chem. Phys. 45, 1488 (1966); Soedineniya blagorodnykh gazov (Inert Gas Compounds), Atomizdat, 1965, p. 411.

[14] I. B. Bersuker, Zh. Eksp. Teor. Fiz. 44, 1577 and 1239 (1963), and 43, 1315 (1962) [Sov. Phys.-JETP 17, 1060 and 836 (1963) and 18, 933 (1962)].

[15] E. L. Muetterties, Inorg. Chem. 4, 770 (1965).

[16] I. V. Aleksandrov, Teoriya yadernogo magnitnogo rezonansa (Theory of Nuclear Magnetic Resonance), Nauka, 1964, p. 122.

Translated by J. G. Adashko
69