Title
A NEW LOOK AT AN OLD PROBLEM: INVERSION IN MX3(C3v) MOLECULES

Author
Bernstein, Lawrence S.

Publication Date
1974-11-01

Submitted to Journal of Chemical Physics

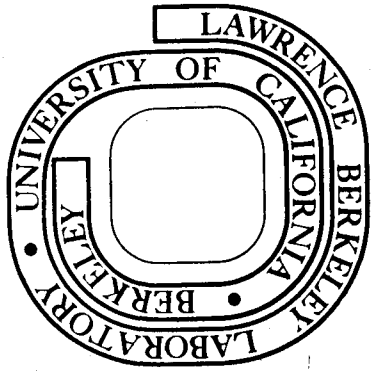
LBL-3514
Preprint

A NEW LOOK AT AN OLD PROBLEM: INVERSION IN $MX_3(C_{3v})$ MOLECULES

Lawrence S. Bernstein

November, 1974

Prepared for the U. S. Atomic Energy Commission
under Contract W-7405-ENG-48



DISCLAIMER

A NEW LOOK AT AN OLD PROBLEM: INVERSION IN $MX_3(C_{3v})$ MOLECULES

Lawrence S. Bernstein

Inorganic Materials Research Division, Lawrence Berkeley Laboratory
and Department of Chemistry; University of California,
Berkeley, California 94720

ABSTRACT

A pseudo Jahn-Teller formalism has been used to construct a potential function for the inversion of MX_3 (C_{3v}) molecules. This potential has the form

$$V(S_2) = \frac{1}{2}\,\Delta\varepsilon_o[1-(1+4\alpha^2 S_2^2)^{\frac{1}{2}}] + \frac{1}{2}\,C_2\,S_2^2$$

where S_2 is the inversion coordinate, $\Delta\varepsilon_o$ is the $^1A_1' \rightarrow {}^1A_2''$ electronic transition, and both α and C_2 are fixed by the values of $\Delta\varepsilon_o$, the curvature of the potential at the equilibrium geometry, and the value of S_2 at the equilibrium geometry. The actual curvature of the potential at the equilibrium geometry, which is chosen to fit the average $\nu_{0\rightarrow 1}(A_2'')$ transition (i.e., averaging inversion splittings), is the only adjustable parameter of the potential. This approach yields a fit to the first eight A_2'' vibrational levels in NH_3 comparable to that obtained with a freely adjustable five parameter model. With this potential the barriers to planarity have been determined in NH_3 (2179 cm^{-1}), PH_3 (16452 cm^{-1}), AsH_3 (14798 cm^{-1}), and SbH_3 (17514 cm^{-1}).

I. INTRODUCTION

This article will develop a general treatment of large amplitude motion with application to the familiar problem of inversion in MX_3 ammonia-like molecules of C_{3v} symmetry. The MX_3 system was chosen as a test for this theory because it is well studied both experimentally and theoretically. In later papers the theory presented here will be applied to equatorial-axial interchange in bipyramidal molecules MX_5 (D_{3h}), (PF_5, AsF_5, NbF_5, TaF_5, VF_5) molecules, two dimensional pseudorotation in MX_7 (distorted D_{5h}), (IF_7, ReF_7) molecules, and three dimensional pseudorotation in MX_6 (distorted O_h, XeF_6) molecules.

By large amplitude motion we mean any internal motion which carries the molecule along a path or surface in coordinate space far away from the potential minimum. In MX_3 molecules two equivalent permutations of the X-atoms are separated by a relatively long one dimensional path along the $S_2(A_2'')$ symmetry coordinate in Fig. 1. The two equivalent C_{3v} forms at $-S_o$, and S_o are at potential minima, while the D_{3h} form at $S = 0$, represents a potential maximum. The molecular properties computed from a double minimum potential are sensitive to more than just the symmetry of the potential. For instance, a Gaussian barrier might yield a better fit to the experimental energy levels than a quadratic barrier even though both types of potentials are symmetrically equivalent.[1]

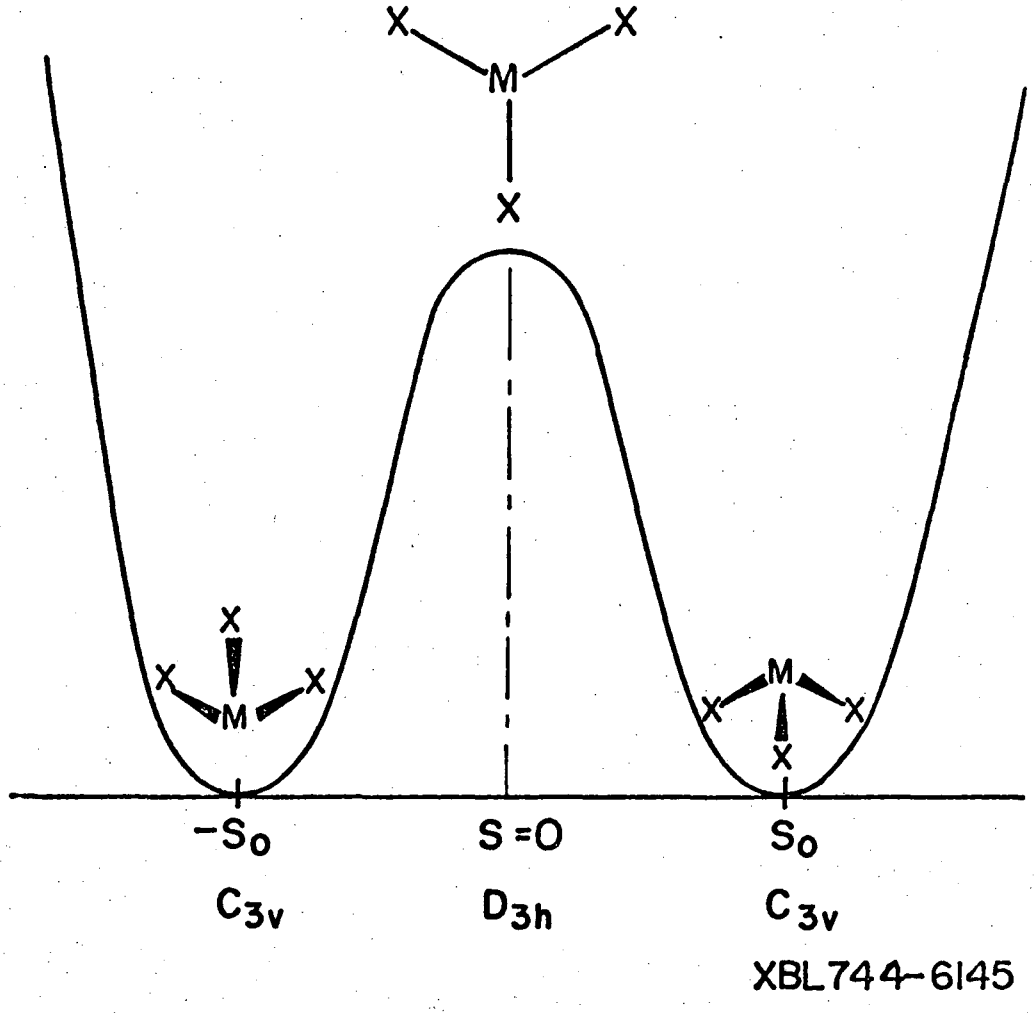
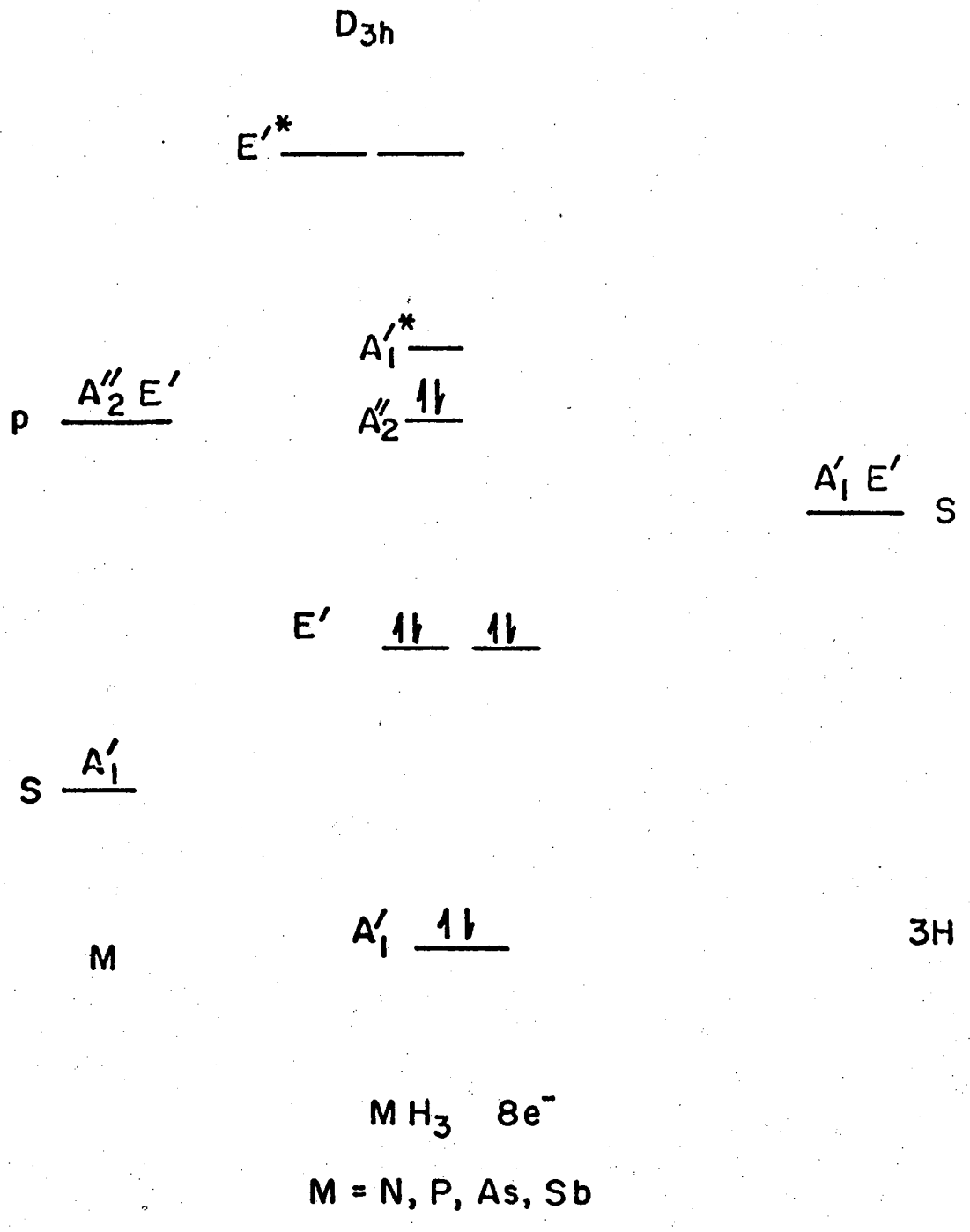


Figure 1. Double minimum potential along the $S_2(A_2'')$ path.

While many empirical potentials of the double minimum variety have been employed in the past, we will show here that it is possible to deduce a "preferred" form for the inversion potential.

The theoretical formalism used to construct the inversion potential is an application of the pseudo Jahn-Teller effect.[2-3] The Jahn-Teller[4-8] theorem states that a molecule in an orbitally degenerate electronic state will distort itself in order to lift the orbital degeneracy. The basis of the pseudo Jahn-Teller effect is that a molecule in a nondegenerate electronic state which is relatively close to other electronic states of proper symmetry may distort itself to increase the relative distance between these states.

The pseudo Jahn-Teller effect can be used as an explanation of why NH_3 prefers a C_{3v} configuration rather than the more symmetrical D_{3h} form. From the molecular orbital diagram of a hypothetical $MH_3(D_{3h})$ molecule in Fig. 2., we see that the ground electronic state is relatively close to the first excited state formed by promotion of an electron from the A_2'' orbital to the $A_1'^*$ orbital. As we will see in more detail shortly these two states can interact via a distortion of the proper symmetry. As the symmetry of the molecule is lowered from D_{3h} to C_{3v}, the A_2'' and $A_1'^*$ representations both decompose to the A_1 representation under the C_{3v} point group. It is well-known that two states of the same symmetry will tend to repulse each other with one state lowering in energy and the other gaining energy (non-crossing rule). The



XBL744-6143

Figure 2. Molecular orbital diagram for MH_3 molecules.

end result for NH_3 is that it can lower its ground electronic state energy by distorting to a C_{3v} symmetry. The final C_{3v} geometry will be determined by the increasing nonbonded repulsive interactions of the H atoms which approach each other as the symmetry is lowered from D_{3h}, and opposes the decrease in the ground electronic state energy.

II. THEORY

The vibronic Hamiltonian, H_v, for an arbitrary MX_3 molecule can be expanded about a D_{3h} reference configuration in a complete set of symmetry coordinates (Fig. 3).

$$H_v = H_N + H_v(S_o) + \sum_K \left(\frac{\partial H_v}{\partial S_K}\right)_{S_o} S_K + \frac{1}{2} \sum_K \sum_L \left(\frac{\partial^2 H_v}{\partial S_K \partial S_L}\right)_{S_o} S_K S_L + \ldots \qquad (1)$$

The first term, H_N, is the nuclear kinetic energy. The second term, $H_v(S_o)$, is the nonrelativistic Hamiltonian for the electrons moving in the D_{3h} potential due to the fixed nuclear framework, S_o. The remaining terms couple the motion of the electrons to the motion of the nuclei, and also describe nuclear-nuclear repulsion. A purely vibrational Hamiltonian can be obtained if a suitable average over the electronic coordinates can be performed in those terms which couple the electronic and nuclear motions. The most convenient electronic basis in which to perform this average is defined by the eigenfunctions of the electronic Hamiltonian, $H_v(S_o)$.

$$H_v(S_o)|\psi_n\rangle = \xi_n|\psi_n\rangle \quad n = 0,1,2,\ldots \qquad (2)$$

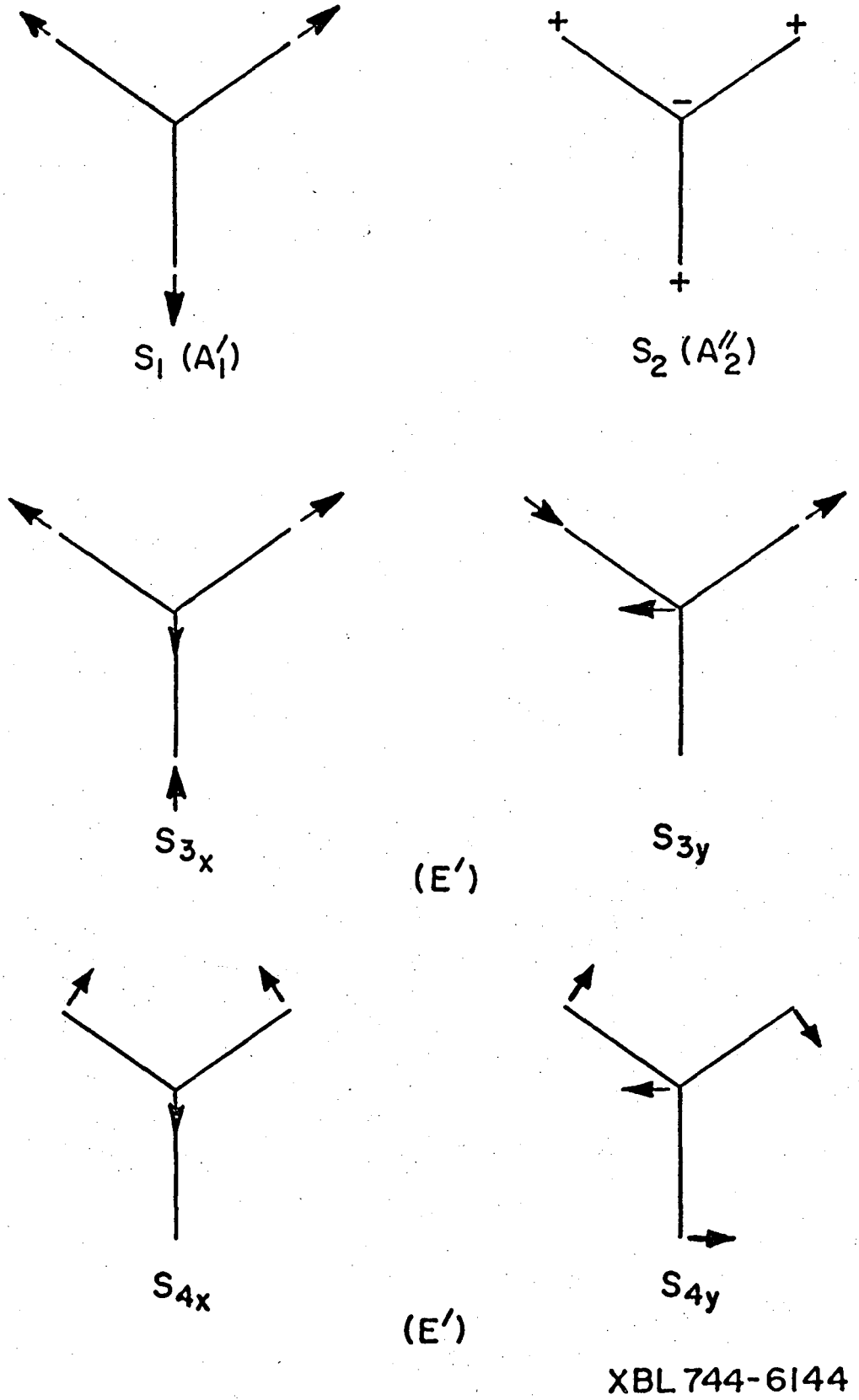


Figure 3. Symmetry coordinates for $MX_3(D_{3h})$ molecules.

The lowest order approximation to the ground state vibrational potential can be obtained by using just the electronic ground state, $|\psi_o\rangle$, in the averaging process.

$$V_o(S) = \langle\psi_o|H_v - H_N|\psi_o\rangle = \xi_o + \sum_K \langle\psi_o| \left(\frac{\partial H_v}{\partial S_K}\right)_{S_o} |\psi_o\rangle S_K + \frac{1}{2}\sum_K \sum_L \langle\psi_o| \left(\frac{\partial^2 H_v}{\partial S_K \partial S_L}\right)_{S_o} |\psi_o\rangle S_K S_L + \ldots \quad (3)$$

Group theoretical considerations can be used to determine whether some of the matrix elements in Eq. (3) vanish. It will be assumed that the ground electronic state is non-degenerate in its spatial dependence. For non-degenerate electronic states it is well-known that the linear term in S_K vanishes.[7,8]

In general the matrix elements associated with the quadratic terms, $S_K S_L$, will be nonzero. The original approximation to the vibrational potential in Eq. (3) simplifies to,

$$V_o(S) = \xi_o + \frac{1}{2}\sum_K \sum_L C_{KL} S_K S_L \quad (4)$$

$$C_{KL} = \langle\psi_o| \left(\frac{\partial^2 H_v}{\partial S_K \partial S_L}\right)_{S_o} |\psi_o\rangle .$$

The potential in Eq. (4) is the usual quadratic approximation used as the starting point for a normal coordinate analysis. This approximation to the vibrational potential of an arbitrary MX_3 molecule does not have the flexibility to express a

double minimum potential. An improved approximation to the ground state vibrational potential is to include the effect of higher electronic states on the linear term. We are interested in terms of the form

$$\langle\psi_o| \left(\frac{\partial H_v}{\partial S_K}\right)_{S_o} |\psi_n\rangle \qquad n>0. \tag{5}$$

The nonvanishing terms of this type are defined by

$$\Gamma_{\psi_o} \times \Gamma_{S_K} \times \Gamma_{\psi_n} = A_1' \tag{6}$$

where Γ is an irreducible representation of the D_{3h} point group. If we consider the NH_3 series (NH_3, PH_3, AsH_3, SbH_3) then $\Gamma_{\psi_o} = {}^1A_1'$ (Fig. 2), and Eq. (6) simplifies to

$$\Gamma_{S_K} \times \Gamma_{\psi_n} = A_1'. \tag{6a}$$

This condition will be satisfied in those cases in which $\Gamma_{\psi_n} = \Gamma_{S_K}$. From the molecular orbital diagram (Fig. 2) it is clear that the lowest excited electronic states for the NH_3 series are ${}^3A_2''$ and ${}^1A_2''$. The triplet excited state, ${}^3A_2''$, will not mix with the ground electronic state, ${}^1A_1'$, even if condition (6a) is satisfied because of orthogonality of the triplet and singlet spin functions. The ${}^1A_1'$ and ${}^1A_2''$ states can be coupled by any symmetry coordinate transforming as A_2''. The symmetry coordinates for a D_{3h} configuration of an MX_3 molecule are displayed in Fig. 3 where it is seen that there is a mode of A_2'' symmetry. Furthermore, this is the motion involved in the inversion of $MX_3(C_{3v})$ molecules.

The contribution of the $^1A_2''$ excited electronic state to the ground state vibrational potential can be determined by finding the lowest root of the determinant of the matrix element of the linear term in the $|\psi_{1A_1'}>$, $|\psi_{1A_2''}>$ electronic basis.

$$\begin{array}{c} \\ |\psi_{1A_1'}> \\ |\psi_{1A_2''}> \end{array} \begin{array}{c} \begin{array}{cc} |\psi_{1A_1'}> & |\psi_{1A_2''}> \end{array} \\ \begin{vmatrix} -\xi & a\,S_2 \\ a\,S_2 & bS_1 + \Delta\varepsilon_o - \xi \end{vmatrix} \end{array} = 0 \qquad (7)$$

where a, b, and $\Delta\varepsilon_o$ are defined by

$$a = <\psi_{1A_1'}| \left(\frac{\partial H_v}{\partial S_2}\right)_{S_o} |\psi_{1A_2''}> \qquad (8a)$$

$$b = <\psi_{1A_2''}| \left(\frac{\partial H_v}{\partial S_1}\right)_{S_o} |\psi_{1A_2''}> \qquad (8b)$$

$$\Delta\varepsilon_o = \xi_{1A_2''} - \xi_{1A_1'} = \xi_{1A_2''} \qquad (8c)$$

where we can define $\xi_{1A_1'} = 0$.

The eigenvalues of Eq. (7) are

$$\xi = \frac{1}{2}\left[(\Delta\varepsilon_o + bS_1) \pm (\Delta\varepsilon_o + bS_1)(1 + 4a^2S_2^2/(\Delta\varepsilon_o + bS_1)^2)^{\frac{1}{2}}\right]. \qquad (9)$$

The presence of the symmetrical stretching coordinate S_1 in addition to the inversion mode S_2 allows an analytic description of the change in bond length (M-X) in going from the planar to the pyramidal form. Only a small change in bond length is expected since the symmetry and nature of the bonding do not change much during the inversion. This assumption is quantitatively justified by SCF calculations on NH_3[9] and PH_3.[10] If we now ignore the coupling of S_1 to S_2 by setting b equal to zero the eigenvalue simplifies to,

$$\xi_L = \frac{1}{2}\Delta\varepsilon_o[1-(1+4\alpha^2S_2^2)^{\frac{1}{2}}] \qquad \alpha = \frac{a}{\Delta\varepsilon_o} \tag{10}$$

where ξ_L represents the lower root of Eq. (9) because we are interested in the ground state vibrational potential. The potential contributed by the ξ_L term is added to the previous approximation to the ground state vibrational potential, $V_o(s)$ (Eq. (4)). Because ξ_L involves only the inversion coordinate, S_2, the other coordinates in $V_o(s)$ can be ignored which leaves just the inversion potential.

$$V(S_2) = \frac{1}{2}\Delta\varepsilon_o[1-(1+4\alpha^2S_2^2)^{\frac{1}{2}}] + \frac{1}{2}C_2(D_{3h})\,S_2^2. \tag{11}$$

Expansion of the first term in Eq. (11) yields

$$\xi_L \approx -\alpha^2\Delta\varepsilon_o S_2^2 + \alpha^4\Delta\varepsilon_o S_2^4 + \ldots. \tag{12}$$

We can define a truncated form of the potential in Eq. (11) by

$$V_{Trunc}(S_2) = (-\alpha^2\Delta\varepsilon_o + \tfrac{1}{2}C_2(D_{3h}))\,S_2^2 + \alpha^4\Delta\varepsilon_o\,S_2^4. \tag{13}$$

From a physical point of view the quantity $C_2(D_{3h})$ chiefly represents the nonbonded repulsive forces between the X atoms and should be a positive quantity. If the following situation occurs

$$\alpha^2 \Delta\varepsilon_o > C_2(D_{3h})/2 \tag{14}$$

then the quadratic term in S_2 will have a negative coefficient and the molecule will have a nonplanar equilibrium configuration. In this instance the truncated potential becomes

$$V_{Trunc}(S_2) = -aS_2^2 + bS_2^4 \qquad a,b>0. \tag{15}$$

The improved version of the potential in Eq. (11) is seen to have the flexibility to describe a double minimum vibration. Furthermore, in the limit of $1 >> 4\,\alpha^2 S_2^2$ over the range of S_2 of interest the expansion of the potential is reasonable and the potential takes a very simple form (15).

There are other contributions to the ground state vibrational potential which were ignored in our derivation. First there are terms which arise from coupling of the ground electronic state to higher electronic states of symmetry other than the first excited state, $^1A_2''$. These will give contributions of the same form as found in Eq. (10) for ξ_L, however, the relevant symmetry coordinate would be other than S_2, which is the coordinate of primary interest in the inversion process. These other contributions will be less significant than that for S_2 because the relevant $\Delta\varepsilon$ associated with the other electronic transitions are much larger than for the

$^1A_1' \rightarrow {}^1A_2''$ transition. A larger $\Delta\varepsilon$ implies a smaller ξ_L because the leading term in the expansion of ξ_L is proportional to $1/\Delta\varepsilon$ and the n'th order terms in ξ_L are proportional to $(1/\Delta\varepsilon)^{n-1}$. There are also terms which were ignored due to truncation of the expansion of the vibronic Hamiltonian to second order in Eq. (1). What we are asserting in this theory is that for the mode in which the large amplitude motion occurs the higher order terms which result from the linear term (Eq. (12)) are more important than the corresponding terms which were ignored in the expansion of H_v. More precisely we are implying that

$$\left| \frac{2^{n-1} \cdot 1 \cdot 1 \cdot 3 \cdot 5 \cdots |2n-3| \left| \langle \psi_{1A'_1} \left| \left(\frac{\partial H_v}{\partial S_2} \right)_{S_o} \right| \psi_{1A''_2} \rangle \right|^{2n}}{n!\ \Delta\varepsilon_o^{2n-1}} \right| >>$$

$$\left| \frac{\langle \psi_{1A'_1} \left| \left(\frac{\partial^{2n} H_v}{\partial S_2^{2n}} \right)_{S_o} \right| \psi_{1A'_1} \rangle}{(2n)!} \right| \qquad (16)$$

$$n = 1, 2, 3 \ldots$$

where there are no odd terms because the molecule contains a plane of symmetry with respect to motion along the S_2 coordinate. The quantity to the left of the above inequality may be much more slowly convergent for large n then the quantity to its right. In fact, for values of the ratio of the linear matrix element to $\Delta\varepsilon_o$ on the order of unity the quantity on the left diverges for large n. The quantity on the right has a coefficient, $\frac{1}{(2n)!}$, which drops of rapidly for large n. We already know that this inequality must exist for the quadratic terms in S_2 or the molecule would not have a C_{3v} geometry (see Eq. (14)). It is reasonable to expect that the same inequality will also be valid for the higher order terms in S_2.

Now that the form of the inversion potential has been established in Eqs. (11 and 15) it remains to give the various parameters a quantitative meaning. Working first with Eq. (11), values are needed for $\Delta\varepsilon_o$, α, and $C_2(D_{3h})$. $\Delta\varepsilon_o$ can be found from the ultraviolet absorption spectrum of the MH_3 molecules[11-13] and is just the $^1A'_1 \rightarrow {}^1A''_2$ transition. Strictly speaking

$\Delta\varepsilon_o$ is the excitation with respect to the planar form, which we will label $\Delta\varepsilon_o(D_{3h})$ from now on to distinguish it from the experimentally observed quantity $\Delta\varepsilon_o(C_{3v})$. The correction of $\Delta\varepsilon_o(C_{3v})$ to $\Delta\varepsilon_o(D_{3h})$ will be discussed later. Values for $C_2(D_{3h})$, the force constant for the A_2'' motion in the (hypothetical) D_{3h} configuration, and α, the linear matrix element, can be established by the following procedure. Take the first derivative of the potential (11) and set it equal to zero at the potential minimum (C_{3v}) and potential maximum (D_{3h}) (Fig. 1).

$$\frac{\partial V}{\partial S_2} = -2\Delta\varepsilon_o\alpha^2(1+4\alpha^2S_2^2)^{-1/2}\ S_2 + C_2(D_{3h})\ S_2 = 0 \qquad (17)$$

This yields

$$S_2 = 0 \qquad D_{3h} \text{ maximum} \qquad (17a)$$

$$-2\Delta\varepsilon_o\alpha^2(1+4\alpha^2S_2^2)^{-1/2} + C_2(D_{3h}) = 0 \text{ at the } C_{3v} \text{ minimum } (S_2=S_0). \qquad (17b)$$

The second derivative must equal the curvature (k_o) at the C_{3v} configuration (S_o).

$$\frac{\partial^2 V}{\partial S_2^2} = -2\Delta\varepsilon_o\alpha^2(1+4\alpha^2S_2^2)^{-1/2} + 8\Delta\varepsilon_o\alpha^4(1+4\alpha^2S_2^2)^{-3/2}\ S_2^2 + C_2(D_{3h}) = k_o \qquad (18)$$

$$\text{at } S_2 = S_o.$$

Initially, k_o can be approximated by the A_2'' force constant in the actual C_{3v} conformation. To obtain the true k_o, the force constant, which is based on a normal coordinate analysis,

must be corrected for anharmonicity effects. This correction will be discussed later. Equations (17b) and (18) can be solved simultaneously to yield α and $C_2(D_{3h})$.

$$\frac{\alpha^4}{(1+4\alpha^2 S_o^2)^{3/2}} = \frac{k_o}{8\Delta\varepsilon_o S_o^2} \quad . \tag{19a}$$

Solve Eq. (19a) iteratively for α, then $C_2(D_{3h})$ is

$$C_2(D_{3h}) = 2\Delta\varepsilon_o \alpha^2 (1+4\alpha^2 S_o^2)^{-1/2}. \tag{19b}$$

The same analysis can be applied to the truncated potential (15) to define the constants a, and b.

$$a = \frac{k_o}{4} \qquad b = \frac{k_o}{8S_o^2}. \tag{20}$$

We return now to the correction of $\Delta\varepsilon_o(D_{3h})$ and k_o. The relationship between $\Delta\varepsilon_o(D_{3h})$ and $\Delta\varepsilon_o(C_{3v})$ can be visualized as in Fig. 4. NH_3 is definitely known to have a planar excited state ($^1A_2''$) while the remaining MH_3 molecules are also thought to have a planar first excited state.[11] Then the correction for the MH_3 molecules is

$$\Delta\varepsilon_o(D_{3h}) = \Delta\varepsilon_o(C_{3v}) - \delta_1 - \delta_2 \tag{21}$$

where δ_1 is just the barrier height and δ_2 is the energy required to bend the excited state from the ground state pyramidal geometry to the planar form. δ_2 is known for NH_3[11] from spectroscopic measurements and has a value of 5400 cm^{-1}. For PD_3,[11] δ_2 is known spectroscopically to be $\delta_2 \approx 5000$ cm^{-1}.

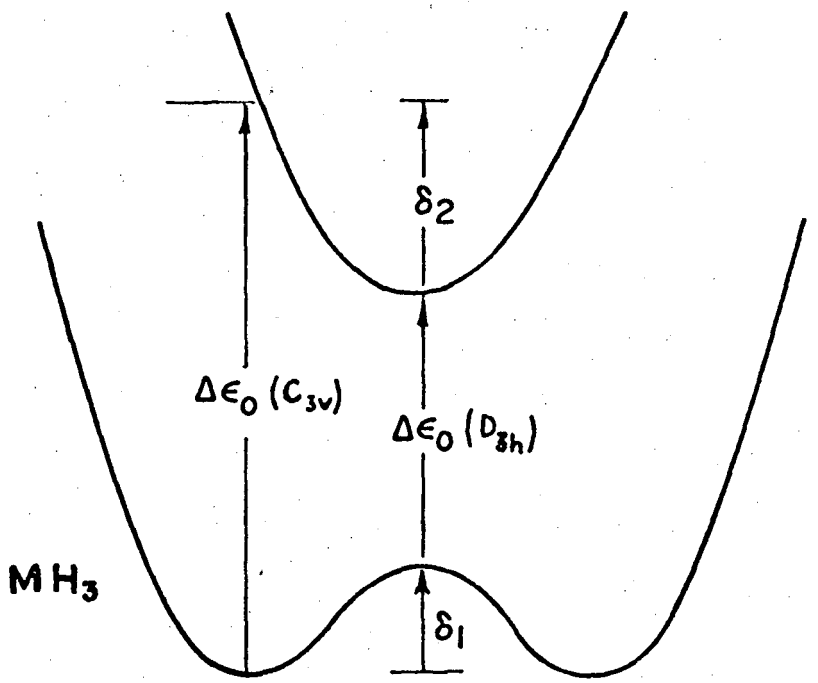


Figure 4. Relationship of $\Delta\varepsilon_o(C_{3V})$ to $\Delta\varepsilon_o(D_{3h})$ in MH_3 molecules.

We will assume this same value for PH_3, and due to a lack of published spectra this same value for δ_2 will be assumed for AsH_3 and SbH_3. $\Delta\varepsilon_o(D_{3h})$ can now be corrected in an iterative manner. Using the initial guess of the potential, where it was assumed $\Delta\varepsilon_o(D_{3h}) = \Delta\varepsilon_o(C_{3v})$, calculate the barrier height and apply Eq. (21). This can be repeated until the correction becomes negligible. The justification for this procedure is that $\Delta\varepsilon_o(C_{3v})(\sim 10^4\ cm^{-1})$ is roughly an order of magnitude larger than the barrier height $(\sim 10^3\ cm^{-1})$ in MH_3 molecules.

The correction of k_o for anharmonicity is also an iterative procedure. The initial approximation is that

$$k_o = C_2(C_{3v}) \tag{22}$$

where $C_2(C_{3v})$ is the A_2'' force constant in the actual C_{3v} configuration. The usual method of calculating $C_2(C_{3v})$ assumes that the $0\rightarrow 1(A_2'')$ transition is harmonic. In any real potential, terms of order three or greater in the displacement coordinate will also contribute somewhat to the $0\rightarrow 1$ transition. Thus in cases where these higher order contributions are non-negligible the curvature (second derivative) of the actual potential will be different from the harmonically approximated force constant. The first step in the correction of k_o for these effects is to apply the above approximation (22) and use the resulting potential (11) to calculate the average $\nu_{0\rightarrow 1}(A_2'')$ transition energy (i.e., averaging the inversion splittings).

The difference between the calculated and observed transition energy can then be compensated by appropriately adjusting k_o. This adjustment of k_o is then repeated until the calculated and observed transitions are sufficiently close. Each time k_o is changed one must re-evaluate the potential parameters [Eqs. 19 and 20]. In addition, a change in these potential parameters will cause a change in the calculated barrier height which means $\Delta\varepsilon_o(D_{3h})$ must be readjusted according to Eq. (21). This parametric dependence of the quantities $\Delta\varepsilon_o(D_{3h})$, $C_2(D_{3h})$, and α on k_o establishes the earlier claim that this is a one parameter model for the inversion potential.

III. CALCULATIONS

The inversion coordinate S_2 is defined by

$$S_2^{\beta} = \sqrt{3}\, r(\beta - \beta_{D_{3h}}) = \sqrt{3}\, r\Delta\beta \qquad (23)$$

where r is the M-X bond length and β is the angle of an M-X bond with respect to a planar configuration (Fig. 5). Because the literature values of the C_{3v} force constant[14] $C_2(C_{3v})$ are based on the coordinate

$$S_2^{\alpha} = \sqrt{3}\, r(\alpha - \alpha_{C_{3v}}) = \sqrt{3}\, r\Delta\alpha \quad \text{(Fig. 4)} \qquad (24)$$

we must adjust $C_2(C_{3v})$ to our inversion coordinate S_2^{β}. The reason for changing coordinates from S_2^{α} to S_2^{β} is the anomalous

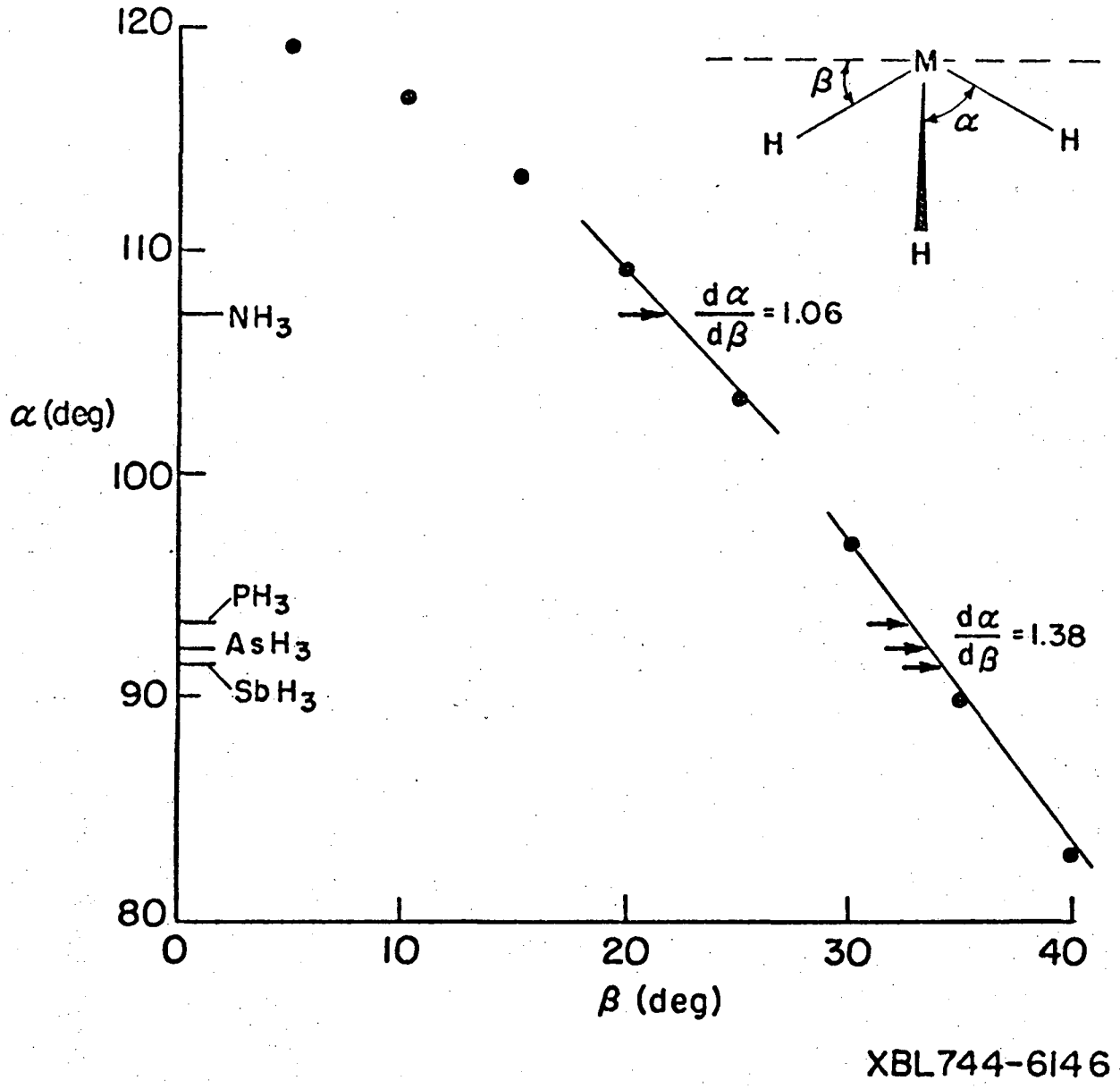


Figure 5. Plot of α versus β for MX_3 molecules.

behavior of $\Delta\alpha$ in the neighborhood of the planar conformation. $\Delta\alpha$ does not change sign in passing through the planar form, which means it does not have the proper symmetry to express the inversion process. However, if the equilibrium structure is not too close to D_{3h}, $\Delta\alpha$ is suitable for expressing small equilibrium displacements. The relationship between $C_2^{\alpha}(C_{3v})$ and $C_2^{\beta}(C_{3v})$ in the region of the equilibrium structure (C_{3v}) is

$$C_2^{\beta}(C_{3v}) = C_2^{\alpha}(C_{3v}) \left(\frac{d\Delta\alpha}{d\Delta\beta}\right)^2_{C_{3v}} . \tag{25}$$

A similar relationship exists between the reduced mass based on the two coordinates.

$$m_2^{\beta} = m_2^{\alpha} \left(\frac{d\Delta\alpha}{d\Delta\beta}\right)^2_{C_{3v}} . \tag{26}$$

The value of $(d\Delta\alpha/d\Delta\beta)_{C_{3v}}$ for a specific molecule can be determined from the slope of a plot of α versus β (Fig. 5). The reduced masses used in the calculations were based on Wilson's[15] high frequency approximation. In this case the high frequency was taken as the A_1 stretch and the low frequency as the A_1 bend, relative to the C_{3v} form (App. 1). The initial value of the force constants $C_2^{\beta}(C_{3v})$ used in the calculations were based on the derived masses (26).

$$C_2^{\beta}(C_{3v}) = (5.90 \times 10^{-7})(\nu_{0\to1}^{exp})^2 \, m_2^{\beta} \tag{27}$$

$\nu_{0\to1}$ is entered in (cm^{-1}), and m_2^{β} in (amu) then $C_2^{\beta}(C_{3v})$ will be in (mdyn/Å). Formula (27) is just a rearrangement of

$\nu_o = \frac{1}{2\pi} (K/m)^{\frac{1}{2}}$, which shows how the frequency of a harmonic oscillator is determined by its force constant (K) and mass (m). The appropriate experimental[11-13,16] information used as input to the potential function can be found in Table 1.

The energy levels calculated from the potential were obtained by computer diagonalization of the vibrational Hamiltonian in a 40-member harmonic oscillator basis set. The final results can be found in Tables 2 and 3. In Table 2 we see that it took 3 iterations to converge on the final NH_3 potential, while for all the other molecules almost exact agreement between $\nu_{0\rightarrow1}^{calc}$ and $\nu_{0\rightarrow1}^{exp}$ was obtained on the first iteration. Because of the relatively small barrier in NH_3 compared to $\nu_{0\rightarrow1}^{exp}$ we would expect a large anharmonicity correction while for the other molecules the well is so deep that it is very nearly harmonic about the potential minima. A small correction (3 cm^{-1}) to $\nu_{0\rightarrow1}^{calc}$ in PH_3 could be made, however, it would not significantly alter the indicated parameters.

IV. DISCUSSION

For the MH_3 series we have found that the parameters α, and S_o^β are very close to unity (Table 2). Therefore the condition for using the truncated potential ($1 >> 4\alpha^2 S_2^2$) is not met. This is why only the full potential (Eq (28A)) was used in the calculations.

It is interesting to compare the various potentials used to describe NH_3 inversion[17-19] with the one derived in this work.

$$V(S) = \frac{1}{2}\Delta\epsilon_o(D_{3h})[1-(1+4\alpha^2S^2)^{\frac{1}{2}}] + \frac{1}{2}C_2(D_{3h})\,S^2 \quad \text{(This work)} \tag{28a}$$

$$V(S) = -C\,\mathrm{sech}^2\left(\frac{S}{2p}\right) + D\,\mathrm{sech}^4\left(\frac{S}{2p}\right) \quad \text{(Manning)}^{17} \tag{28b}$$

$$V(S) = K(a + bS^2)^2/(1 + S^2)^2 \quad \text{(Newton)}^{18} \tag{28c}$$

$$V(S) = \frac{1}{2}aS^2 + \frac{1}{2}bS^4 + v\exp(-cS^2) \quad \text{(Swalen)}^{19} \tag{28d}$$

where S is the inversion coordinate. In Manning's potential C, p and D are arbitrary constants which were adjusted to obtain the best fit to the available experimental energy levels. The arbitrary constants K, a, and b in Newton's potential were fit to the first four levels of NH_3 with extra weighting given to the $0_S \rightarrow 0_A$ splitting. This accounts for Newton's success at fitting $0_S \rightarrow 0_A$ while not managing as well with the $1_S \rightarrow 1_A$ transition (Table 3). In Swalen's potential the constants a, b, the reduced mass ratio of NH_3 to ND_3, and the pyramid height were least squares fit to the first fourteen (seven each) levels of NH_3 and ND_3.

The potential used here (28a) differs greatly in form and concept from its predecessors (28b, c, d). Both Manning and Newton picked their particular form to obtain a reasonably easy to solve form for the Schrödinger equation. Swalen chose his very flexible five parameter potential in order to get a very exact fit to the energy levels (Table 3), and hence closely approximate the true potential. In this work the parameters of the potential have a direct physical interpretation and more importantly the form of the potential is not arbitrary but

derived, with various approximations, from the exact non-relativistic Hamiltonian. It should be stressed that in the fit for our potential listed in table 3 only two constraints were placed on the potential constants: (1) that the average $\nu_{0\to1}^{exp}$ transition was fit and, (2) that the experimental equilibrium geometry was a potential minimum. If one least squares adjusted the constants m_2^{β}, α, $\Delta\varepsilon_o(D_{3h})$, and $C_2(D_{3h})$ to the first fourteen levels in NH_3 and ND_3 one could probably obtain a considerably improved fit to the spectra.

We have focused our discussion primarily on NH_3 simply because a comparable amount of experimental and theoretical information is not available for the other MH_3 (PH_3, AsH_3, SbH_3) molecules. The absence of an observable inversion splitting in the lower levels of these molecules makes it impossible to fit an arbitrary double minimum potential to the splitting in order to obtain an estimate of the barrier height. In this work detailed experimental information (inversion splittings) is not needed and we have calculated the inversion potentials for the entire MH_3 series (Table 2).

From the energy level computations we have estimated the $O_S \to O_A$ inversion splittings to be $\sim10^{-5}$ cm^{-1} for AsH_3, $\sim10^{-8}$ cm^{-1} for PH_3 and $\sim10^{-9}$ cm^{-1} for SbH_3. The best available data on the inversion potential in the molecules other than NH_3 is an SCF calculation on PH_3[10] in which the barrier height was calculated to be 13,012 cm^{-1}. We calculate the PH_3 barrier to be 16,452 cm^{-1} (Table 2). A recent SCF

calculation on NH_3[9] placed the barrier at 2,589 cm^{-1} compared to the average experimental determination (table 3) of 2,123 cm^{-1}. This is a difference of about 25%. In view of the NH_3 case it is not unreasonable that the two calculated barriers for PH_3 differ by approximately 25%.

Table 1. Experimental Data for MH_3 Molecules

	$\Delta\beta_{C_{3v}}$ (DEG)	r_{M-H}(Å)	S_o^β(Å)	$\nu_{0\to1}^{exp}$(cm^{-1})	m_2^β (amu)	$C_2^\beta(C_{3v})$ ($\frac{mdyn}{Å}$)	$\Delta\varepsilon_o(C_{3v})$ (mdyn-Å)
NH_3	21.8	1.011	.669	950	.832	.443	1.024
PH_3	32.4	1.419	1.390	991	.951	.551	1.103
AsH_3	33.6	1.523	1.549	906	.951	.412	1.085
SbH_3	34.0	1.712	1.764	782	.951	.343	1.008

Table 2. Refined Parameters for MH_3 Potential Function

	$\alpha(\text{Å}^{-1})$	$\Delta\varepsilon_o(D_{3h})$ (mdyn-Å)	$k_o(\frac{\text{mdyn}}{\text{Å}})$	$C_2(D_{3h})$ $(\frac{\text{mdyn}}{\text{Å}})$	$E_{Barrier}(cm^{-1})$	$\nu_{0\to1}^{calc}(cm^{-1})$	$\nu_{0\to1}^{exp}(cm^{-1})$
	.826	.881	.443	.806	1,787	859.5	950
NH_3[a]	.897	.873	.531	.890	2,226	961.6	950
	.890	.873	.522	.890	2,179	951.4	950
PH_3	1.273	.675	.551	.595	16,452	988	991
AsH_3	1.056	.691	.412	.450	14,798	904	906
SbH_3	1.176	.560	.343	.363	17,514	782	782

[a] The three lines give the results of successive iterations - see text.

Table 3. Comparison of Observed and Computed Properties of NH_3

	Obs.	This Work	Manning	Swalen	Newton
Barrier (cm^{-1})		2179	2072	2018	2225
0_S	0.00	0.00	0.00	0.00	0.00
0_A	0.79	0.78	0.83	0.83	0.79
1_S	932.5	938	935	930	933
1_A	968.3	965	961	966	956
2_S	1597.6	1660	1610	1596	
2_A	1910	1892	1870	1882	
3_S	2383.5	2410	2360	2385	
3_A	2895.5	2891	2840	2897	

APPENDIX 1.

High Frequency Approximation in Calculating the Mass for the Inversion Motion in $MX_3(C_{3v})$ Molecules

The G-matrix element for the symmetrical stretch (A_1) is

$$G_{11} = \frac{1}{m_x} + \frac{(1+2\cos\alpha)}{m_M} \tag{1}$$

where m_x, m_M are the masses of atoms x, and M respectively, and α is defined in Fig. 4. The G-matrix element for the symmetric bend (A_1) is

$$G_{22} = 2\left(\frac{1+2\cos\alpha}{1+\cos\alpha}\right)\left(\frac{1}{m_x} + \frac{2(1-\cos\alpha)}{m_M}\right) \tag{2}$$

The cross term is

$$G_{12} = -\frac{2(1+2\cos\alpha)(1-\cos\alpha)}{m_M \sin\alpha} \tag{3}$$

The high frequency approximation becomes

$$G_{22}^{o} = G_{22} - \frac{G_{12}^2}{G_{11}} \tag{4}$$

The inversion mass can now be defined as

$$m_2^{\alpha} = (G_{22}^{o})^{-1} \tag{5}$$

ACKNOWLEDGEMENTS

I wish to thank Professor Kenneth S. Pitzer for many helpful discussions and suggestions. Professor W. D. Gwinn and members of his group have been very generous in supplying me with various computer programs and assisting me with their use. I thank Professor Herbert L. Strauss for clarifying some troublesome points. This work was sponsored by the U. S. Atomic Energy Commission and a Proctor and Gamble Research Fellowship (Oct., 1973 - Nov., 1974).

REFERENCES

1. D. O. Harris, H. W. Harrington, A. C. Luntz, and W. D. Gwinn, J. Chem. Phys. 44, 3467 (1966).
2. L. S. Bartell, J. Chem. Ed. 45, 754 (1968).
3. A. D. Liehr, J. Phys. Chem. 67, 389 (1963).
4. H. A. Jahn and E. Teller, Proc. Roy. Soc. 161, 220 (1937).
5. U. Öpik, M.H.L. Pryce, Proc. Roy. Soc. A., 238, 425 (1957).
6. H. C. Longuet-Higgins, U. Öpik, and M. H. L. Pryce, Proc. Roy. Soc. A., 244, 1 (1958).
7. J. H. Van Vleck, J. Chem. Phys. 7, 72 (1939).
8. W. L. Clinton and B. Rice, J. Chem. Phys. 30, 542 (1959).
9. R. G. Body, D. S. McClure, and E. Clementi J. Chem. Phys. 49, 4916 (1968).
10. J. M. Lehn and B. Munsch, Chem. Comm. 1327 (1969).
11. C. M. Humphries, A. D. Walsh and P. A. Warsop, Disc. Faraday Soc. 35, 148 (1963).
12. A. E. Douglas, Disc. Faraday Soc. 35, 158 (1963).
13. M. Halmann, J. Chem. Soc. 2853 (1963).
14. T. Shimanouchi, I. Nakagawa, J. Hiraishi and M. Ishi, J. Mol. Spectry., 19, 78 (1966).
15. E. B. Wilson, Jr., J. Chem. Phys. 9, 76 (1941).
16. G. DeAlti, G. Costa, V. Galasso, Spectrochim. Acta 20, 965 (1964).
17. M. F. Manning, J. Chem. Phys. 3, 136 (1935).
18. R. R. Newton, L. H. Thomas, J. Chem. Phys. 16, 310 (1948).
19. J. D. Swalen, J. A. Ibers, J. Chem. Phys. 36, 1914 (1962).

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720