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Theory of the Renner effect in the NH₂ radical

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The observations of Dressler and Ramsay on the vibronic absorption spectrum of the NH₂ radical are interpreted quantitatively in terms of the Renner effect. The use of a perturbation method leads to frequency predictions which are in good accord with experiment and confirm the view of these authors that the absorption band is associated with transitions between the components of an electronic II state which are widely separated by electronic–vibrational interaction.

1. INTRODUCTION

Dressler and Ramsay [1] have recently investigated the lowest electronic transition of the NH₂ radical and its deuterated isotope in absorption, and find that the spectra have an unusual type of vibrational structure. Their measurements strongly suggest that the radical is linear in the upper state, but that in this state the vibronic energy depends markedly on the total angular momentum about the molecular axis. They have interpreted this as a case of the 'Renner effect', that is, a strong coupling between the electronic and vibrational motions leading to a breakdown of a Born–Oppenheimer (fixed-nucleus) approximation. Renner [2] showed that an electronic II state of a linear molecule splits into two real components when the molecule is bent; one of these is symmetric and the other antisymmetric about the plane of the deformed molecule. The electronic energies of the two states (evaluated in fixed nuclear configurations) diverge from one another as the angle of bending increases, and may behave in any one of the three ways illustrated in figure 1 where the abscissa denotes the extent of deformation. Renner considered only the case depicted in figure 1 (a), where both curves are parabolas of positive curvature; it is quite possible, however, for either or both curves to have negative curvature at the origin as indicated in figures 1 (b) and 1 (c).

The theoretical work of Walsh [5] and the experiments of Dressler and Ramsay, taken together, strongly suggest that the NH₂ radical is a case of the
Walsh pointed out that according to molecular orbital theory the 
ground state of NH$_2$ should differ from that of OH$_2$, which is bent, 
only in the absence of one of the 2p electrons of the central atom, but 
that this would not affect the valency angle very much. As to the first excited state of NH$_2$, Walsh's prediction was less definite, 
but the alternation of symmetry type for successive bands in the 
progression indicates, as Dressler and Ramsay point out, a change 
from a bent to a linear structure. In the absence of a theory of the Renner 
effect for case 1 (b), however, this argument is suggestive rather than conclusive, 
so we have undertaken a theoretical investigation of the type of spectrum to be 
expected in this case. We have found indeed that an effect of the type postulated 
by Dressler and Ramsay accounts very adequately for certain observed features 
of the NH$_2$ absorption spectrum.

2. Theoretical model

We shall adopt a simplified theoretical model in order to set up the mathem-
atical equations for the relevant vibronic levels. As will appear, this model 
incorporates the essential features of the situation in, for example, the NH$_2$ 
radical; that is to say, the resulting equations of motion are mathematically 
equivalent to those obtained by Renner from more sophisticated premisses.

We restrict consideration to three degrees of freedom of the radical. The 
first two of these are the two components of the doubly degenerate bending 
mode, with which may be associated two coordinates: the amplitude $r$ of the 
distortion and the angle $\phi$ between the plane of bending and a fixed plane $P$ 
through the axis of the unbent radical. The other degree of freedom may be 
described as the angular distance of the odd electron round the molecular axis, 
as measured from the plane $P$. This angle, to be denoted as $\theta$, is more properly 
regarded as the coordinate conjugate to the axial angular momentum of all the 
electrons, but the simpler interpretation is physically more illuminating. Our 
notation is illustrated in figure 2. The coordinate $r$ is positive or zero; $\phi$ and $\theta$ lie 
in the range 0 to 2$\pi$.

Our procedure is now as follows: first to determine the nature of the vibronic 
states when there is no coupling between $\theta$ and $\phi$; secondly, to discover how
these states are modified when such a coupling is introduced into the Hamiltonian; and thirdly, to see how far, in the case of NH₂, it is possible to calculate the actual energies of the vibronic levels without introducing unknown parameters into the calculation.

In the absence of any coupling between \( \theta \) and \( \phi \), each vibronic wave function may be separated into an electronic and a vibrational factor. The electronic factor is \( \exp(iA\theta) \) where \( A = \pm 1 \) for an electronic \( \Pi \) state. The vibrational factor is determined by a potential which depends on \( r \) only and therefore takes the form

\[
|n, l\rangle = \rho_{ji} \exp(i\phi), \tag{2.1}
\]

where \( l \) is the vibrational angular momentum quantum number. The quantum number \( n \) (often denoted by \( v_2 + 1 \)) is assigned the values

\[
n = |l| + 1, \quad |l| + 3, \ldots \tag{2.2}
\]

If the vibrational potential is harmonic, the wave functions (2.1) reduce to the well-known form for the two-dimensional harmonic oscillator.

The vibronic wave functions can now be written

\[
|A, n, l\rangle = \exp(iA\theta)\rho_{ji} \exp(i\phi), \tag{2.3}
\]

it being implied that they are eigenfunctions of both the electronic and the vibrational angular momentum about the molecular axis. Figure 3 shows the resulting scheme of energy levels when the bending vibration is harmonic; the energy is then proportional to \( n \) and independent of \( l \) and \( A \). At the bottom of the figure are printed the symbols conventionally used for classifying the vibronic states according to the value of \( |K| \), where \( K = A + l \) and is proportional to the total angular momentum in the direction of the axis.

\[
\begin{array}{ccccccc}
| -1, 4, -3 \rangle & |1, 4, -3 \rangle & |1, 4, -1 \rangle & |1, 4, 1 \rangle & |1, 4, 3 \rangle & | -1, 4, -1 \rangle & | -1, 4, 1 \rangle & | -1, 4, 3 \rangle \\
| -1, 3, -2 \rangle & |1, 3, -2 \rangle & |1, 3, 0 \rangle & |1, 3, 2 \rangle & |1, 3, 4 \rangle & | -1, 3, 0 \rangle & | -1, 3, 2 \rangle & | -1, 3, 4 \rangle \\
| -1, 2, -1 \rangle & |1, 2, -1 \rangle & |1, 2, 1 \rangle & |1, 2, 3 \rangle & |1, 2, 5 \rangle & | -1, 2, 1 \rangle & | -1, 2, 3 \rangle & | -1, 2, 5 \rangle \\
| -1, 1, 0 \rangle & |1, 1, 0 \rangle & |1, 1, 2 \rangle & |1, 1, 4 \rangle & |1, 1, 6 \rangle & | -1, 1, 2 \rangle & | -1, 1, 4 \rangle & | -1, 1, 6 \rangle \\
\end{array}
\]

\[
\begin{array}{ccccccc}
\Gamma_{(K=-4)} & \Phi_{(K=-3)} & \Delta_{(K=-2)} & \Pi_{(K=-1)} & \Sigma_{(K=0)} & \Pi_{(K=1)} & \Delta_{(K=2)} & \Phi_{(K=3)} & \Gamma_{(K=4)}
\end{array}
\]

Figure 3.

We now have to consider how this scheme will be modified by introducing into the Hamiltonian additional terms \( H' \) representing an angular coupling between the odd electron and the nuclear framework. In the first place we note that such coupling terms can only depend on the relative angle \( \alpha = \theta - \phi \).
The Renner effect in NH$_2$

and the amplitude $r$. Secondly, $H'$ must be a symmetrical function of $x$ and consequently can be expanded in the form

$$H' = V_0(r) + V_1(r)\left[\exp(iz) + \exp(-iz)\right] + V_2(r)\left[\exp(2iz) + \exp(-2iz)\right] + \ldots,$$

(2.4)

where $V_m(r)$ is of order $r^m$ at $r=0$. Further, reference to (2.3) shows that $H'$, depending only on $\theta - \phi$, can only mix together functions with the same value of the quantum number

$$K = A + l.$$

(2.5)

Thus $K$ remains a good quantum number, as would be expected since it represents the total angular momentum about the axis. Hence within the electronic system $A = \pm 1$ (that is, within the components of the II electronic state) the only non-vanishing matrix elements of $H'$ are those of the form

\begin{align*}
\langle 1, n, K-1 | H' | 1, n', K-1 \rangle &= \langle n, K-1 | V_0 | n', K-1 \rangle, \\
\langle -1, n, K+1 | H' | -1, n', K+1 \rangle &= \langle n, K+1 | V_0 | n', K+1 \rangle, \\
\langle 1, n, K-1 | H' | -1, n', K+1 \rangle &= \langle n, K-1 | V_2 \exp(-2i\phi) | n', K+1 \rangle,
\end{align*}

and

\begin{align*}
\langle -1, n, K+1 | H' | 1, n', K-1 \rangle &= \langle n, K+1 | V_2 \exp(2i\phi) | n', K-1 \rangle.
\end{align*}

(2.6)

where on the right-hand side only the vibrational degrees of freedom enter into consideration. Since $V_1$, $V_3$ ... do not appear in (2.6), one may, provided mixing with other electronic states is unimportant, take $H'$ in the simpler form

$$H' = V_0 + V_2[\exp(2iz) + \exp(-2iz)]$$

(2.7)

without making any difference at all to the results.

In order to understand the separation of the pairs of curves in figure 1 it is necessary to investigate the effect of the perturbation (2.7) on the electronic potential function, which in the unperturbed situation we may take to be $U^0(r)$. If the nuclei are held in a non-linear configuration the perturbation $H'$ causes the electronic sub-levels $\exp(\pm i\theta)$ to interact and resolves their degeneracy in the first order. For given $r$ and $\phi$ the matrix of $H'$ between the functions $\exp(i\theta)$ and $\exp(-i\theta)$ is immediately seen to be

$$\begin{pmatrix}
V_0 & V_2 \exp(-2i\phi) \\
V_2 \exp(2i\phi) & V_0
\end{pmatrix}$$

(2.8)

and diagonalization of this matrix leads at once to the zeroth-order wave functions $\cos(\theta - \phi)$ and $\sin(\theta - \phi)$, with which are associated the first-order energies $V_0 + V_2$ and $V_0 - V_2$ respectively. Hence, as remarked earlier, the Born-Oppenheimer electronic wave function is split into two real components by the distortion, the associated bending potentials being

$$U^+ = U^0 + V_0 + V_2,$$

$$U^- = U^0 + V_0 - V_2,$$

(2.9)

according as the electronic wave function is symmetric or antisymmetric about the plane of the distortion. In the next section we shall assume that $V_2$ is positive, so that $U^+$ is the potential for the upper surface. If $V_2$ is negative a corresponding theory is easily developed with some change of notation.
3. The Upper Vibronic Levels

Since we are primarily interested in the upper vibronic levels of NH$_2$, we shall begin by taking the unperturbed situation to be one in which $U^0(r)$ is identical with $U^+(r)$, the potential for the upper curve in figure 1 (b). From this point of view the lower curve is regarded as diverging from the upper curve as a consequence of the perturbation

$$H' = V_0[1 - \exp(2i\alpha) - \exp(-2i\alpha)]$$  \hspace{1cm} (3.1)

in which $V_2$ has been set equal to $-V_0$, so that by (2.9) the upper curve is not affected in any way. Our reason for adopting this standpoint, rather than setting $U^0 = \frac{1}{2}(U^+ + U^-)$ as Renner did, is that we may hope, by sacrificing accuracy in our treatment of the lower levels, to gain accuracy in our quantitative calculations on the upper ones. There is also a point of convenience, namely that the upper curve is more nearly parabolic than the lower, so that we can make full use of the specially simple properties of the harmonic oscillator.

Before discussing arbitrary values of $K$ we must, however, draw attention to an important property, first pointed out by Renner, of the levels for which $RT = 0$. Considerations of symmetry alone show that these levels, the $\Sigma$ levels, must fall into two classes, $\Sigma^+$ and $\Sigma^-$, according as the vibronic wave function is unchanged or changes sign when the signs of $\theta$ and $\phi$ are simultaneously reversed. Now the functions $|1, n, -1\rangle$ and $|-1, n, 1\rangle$ taken separately do not have this property, but their sum is a $\Sigma^+$ function and their difference a $\Sigma^-$ function. It is obvious on grounds of symmetry that the matrix elements between $\Sigma^+$ and $\Sigma^-$ functions of any perturbation must vanish; it is also true, as will immediately be shown, that the perturbation (3.1) has vanishing matrix elements between all pairs of $\Sigma^+$ functions. For by (2.6)

$$\langle 1, n, -1 | H' | 1, n', -1 \rangle = 2\pi \int_0^\infty \rho_{n1} V_0 \rho_{n'1} r dr = \langle -1, n, 1 | H' | -1, n', 1 \rangle,$$

(3.2)

$$\langle 1, n, -1 | H' | -1, n', 1 \rangle = 2\pi \int_0^\infty \rho_{n1} V_2 \rho_{n'1} r dr = \langle -1, n, 1 | H' | 1, n', -1 \rangle.$$

(3.3)

Hence the matrix element of $H'$ between the combinations

$[|1, n, -1\rangle + |-1, n, 1\rangle]/\sqrt{2}$ and $[|1, n', -1\rangle + |-1, n', 1\rangle]/\sqrt{2}$

reduces to

$$2\pi \int_0^\infty \rho_{n1}(V_0 + V_2) \rho_{n'1} r dr;$$

(3.4)

and if $V_0 + V_2 = 0$ this vanishes. Therefore the $\Sigma^+$ functions are unaffected either in form or in energy by any perturbation of the type (3.1) which alters the lower curve only, and are determined entirely by the form of the upper curve $U^+(r)$. By an exactly analogous argument one may show that the $\Sigma^-$ levels are determined solely by the form of the function $U^-(r)$. These statements hold, furthermore, to all orders in the perturbation (3.1).

The $\Pi, \Delta, \Phi, \Gamma, \ldots$ levels, with $K = 1, 2, 3, 4, \ldots$ respectively, present a more complicated situation. As Renner showed, a small quadratic perturbation of the form

$$H' = fr^2 \cos 2\zeta$$

(3.5)
The Renner effect in \( \text{NH}_2 \) splits each pair of degenerate functions in figure 3 into their sum and their difference, in the first order, and we shall see that the same is true of the perturbation

\[
H' = \frac{1}{2} f r^2 [1 - \exp(2ix) - \exp(-2ix)].
\]

By analogy with the behaviour of the \( \Sigma \) functions one might therefore speak of the combination

\[
[|1, 3, 0\rangle + |3, 2\rangle] / \sqrt{2}
\]

as a \( \Pi^+ \) function, and a combination of the type

\[
[|1, 3, 0\rangle - |3, 2\rangle] / \sqrt{2}
\]

as a \( \Pi^- \) function. Closer examination reveals, however, that the perturbation (3.6), and the more general perturbation (3.1), has non-vanishing matrix elements between, for example, different \( \Pi^+ \) functions, and also between \( \Pi^+ \) and \( \Pi^- \), or \( \Delta^+ \) and \( \Delta^- \) functions. As a consequence, every vibronic level with \( |K| > 1 \) is determined by both the upper and lower potential energy curves. It is for this reason, as Renner showed, that the vibronic wave function can no longer be factorized into an electronic and a vibrational term. Nevertheless, in calculating the energies of the upper vibronic levels we shall make the simplifying assumption that their wave functions are adequately represented by the combinations which we have called \( \Pi^+, \Delta^+, \Phi^+, \Gamma^+ \) etc., at least for large values of \( n - |K| \). This assumption is admittedly somewhat questionable, but we think it sufficiently near the truth to yield results which are at least approximately correct.

4. Calculation of energy levels for quartic potential surfaces

We shall now apply the theory of the previous sections to the calculation of the upper vibronic energy levels when the potentials \( U^+ \) and \( U^- \) are of the type \( ax^2 + br^4 \). Such functions can give a reasonable representation of the situation illustrated by figure 1 (b). In view of the simple properties of the harmonic oscillator, we shall adopt a slightly different procedure in which \( U^0 \) will be taken as the parabola which closely approximates to \( U^+ \) (the upper Born-Oppenheimer potential curve) for small \( r \). It is convenient to adopt units of energy and distance such that

\[
hv = 1, \quad \kappa = 1
\]

where \( \nu \) and \( \kappa \) are the classical frequency and force constant of the bending vibration in the upper state. Thus, in these units,

\[
U^0 = \frac{1}{2} r^2
\]

and the upper curve will be

\[
U^+ = U^0 + hr^4,
\]

\( h \) being a constant allowing for anharmonicity. The presence of this effect in \( \text{NH}_2 \) is indicated by the unequal spacing in the \( \Sigma^+ \) levels. We must also include a quartic term in the expression for the lower curve ; this we write as

\[
U^- = (\frac{1}{2} - f)r^2 + g r^4,
\]

where \( f > \frac{1}{2} \) and \( g > 0 \). By equation (2.9), therefore,

\[
V_0 = - \frac{1}{2} f r^2 + \frac{1}{2} (g + h)r^4
\]

and

\[
V_2 = + \frac{1}{2} f r^2 - \frac{1}{3} (g - h)r^4
\]
The energy of one of the upper vibronic levels is then given by

\[ E^+(\hat{n}, K) = n + \frac{1}{2} \left( (1, n, K - 1) + (-1, n, K + 1) \right) V_0 + 2V_2 \cos \theta \{ (1, n, K - 1) + (-1, n, K + 1) \}, \]  

(4.7)

where we have made the assumption, discussed in §3, that its wave function is the sum (here unnormalized) of two degenerate eigenfunctions of the unperturbed Hamiltonian.

In order to evaluate the vibronic energy given by (4.7) we require the matrix elements of \( r^2, r^4, r^2 \cos 2\theta \) and \( r^4 \cos 2\theta \) within the pair of functions \(|1, n, K-1\rangle\) and \(|-1, n, K+1\rangle\). According to (2.6) this amounts to finding the matrix elements of \( r^2, r^4, r^2 \exp (2i\phi) \) and \( r^4 \exp (2i\phi) \) between the vibrational wave functions \(|n, K-1\rangle\) and \(|n, K+1\rangle\). These matrix elements are determined as follows.

Setting

\[ r \exp (i\phi) = z \]  

(4.8)

we observe that the four operators in question may be written as \( z \bar{z}^p, z^2, z^2 \bar{z}, \) and \( z^2 (z^2 \bar{z}) \), where \( \bar{z} \) is the complex conjugate of \( z \). If, then, we can find the matrix elements of \( z \) and \( \bar{z} \) within the system of functions of \(|n, l\rangle\), we can obtain those of \( z \bar{z}, (z \bar{z})^2, z^2 \) and \( z^2 (z \bar{z}) \) from them by the ordinary rules of matrix multiplication. But it has been shown by various authors (Moffitt and Liehr [3], Longuet-Higgins et al. [4]) that all the matrix elements of \( z \) and \( \bar{z} \) in the system \(|n, l\rangle\) vanish except those of the two types

\[ \langle n, l | z | n+1, l-1 \rangle = \langle n+1, l-1 | \bar{z} | n, l \rangle = \sqrt{\frac{1}{2} (n-l+1)} \]  

and

\[ \langle n+1, l+1 | z | n, l \rangle = \langle n, l | \bar{z} | n+1, l+1 \rangle = \sqrt{\frac{1}{2} (n+l+1)}. \]  

(4.9)

(4.10)

Hence the required matrix elements may be evaluated without further ado. As an example of our procedure, consider the matrix of the quadratic part of \( H' \), namely

\[ -\frac{1}{2} fr^2 + \frac{1}{2} fr^2 (2 \cos 2\theta) = \frac{1}{2} f \{ r^2 \exp (2i\phi) - r^2 + r^2 \exp (-2i\phi) \}. \]  

(4.11)

The three terms on the right-hand side are treated separately, as follows:

\[ \langle 1, n, K-1 | z^2 \exp (2i\phi) | -1, n, K+1 \rangle = \langle n, K-1 | \bar{z} | n, K+1 \rangle \]

\[ = \langle n, K-1 | \bar{z} | n+1, K \rangle \langle n+1, K | \bar{z} | n, K+1 \rangle \]

\[ + \langle n, K-1 | \bar{z} | n-1, K \rangle \langle n-1, K | \bar{z} | n, K+1 \rangle \]

\[ = \sqrt{\left[ \frac{1}{2} (n+K) \right]} \sqrt{\left[ \frac{1}{2} (n-K) \right]} + \sqrt{\left[ \frac{1}{2} (n-K) \right]} \sqrt{\left[ \frac{1}{2} (n+K) \right]} = \sqrt{(n^2 - K^2)}; \]  

(4.12)

\[ \langle -1, n, K+1 | z^2 | -1, n, K+1 \rangle = \langle n, K+1 | \bar{z} | n, K+1 \rangle \]

\[ = \langle n, K+1 | \bar{z} | n+1, K \rangle \langle n+1, K | \bar{z} | n, K+1 \rangle \]

\[ + \langle n, K+1 | \bar{z} | n-1, K \rangle \langle n-1, K | \bar{z} | n, K+1 \rangle \]

\[ = \sqrt{\left[ \frac{1}{2} (n-K) \right]} \sqrt{\left[ \frac{1}{2} (n-K) \right]} + \sqrt{\left[ \frac{1}{2} (n+K) \right]} \sqrt{\left[ \frac{1}{2} (n+K) \right]} = n. \]  

(4.13)

Similarly,

\[ \langle -1, n, K+1 | z^2 \exp (-2i\phi) | 1, n, K-1 \rangle = \langle n, K+1 | \bar{z} | n, K-1 \rangle = \sqrt{(n^2 - K^2)} \]  

(4.14)

and

\[ \langle 1, n, K-1 | z^2 | 1, n, K-1 \rangle = \langle n, K-1 | \bar{z} | n, K-1 \rangle = n. \]  

(4.15)

Hence the matrix of (4.11) within the system \(|1, n, K-1\rangle, |-1, n, K+1\rangle\) is
simply
\[ \frac{1}{2} f \begin{bmatrix} n^2 - K^2 & \sqrt{n^2 - K^2} \\ \sqrt{n^2 - K^2} & -n \end{bmatrix} \] (4.16)

The symmetry of this matrix substantiates our earlier statement that the quadratic perturbation (3.6) splits each such pair of degenerate functions into their sum and difference; the energies of these two combinations are seen to be, in the quadratic approximation,

\[ n - \frac{1}{2} f [n - \sqrt{(n^2 - K^2)}] \quad \text{and} \quad n - \frac{1}{2} f [n + \sqrt{(n^2 - K^2)}] \] (4.17)

respectively. Two things will be noted: first, that the energy of the sum is invariably higher than that of the difference, the correction to the energy of the former being relatively slight; and secondly, that if \( K = 0 \) the perturbation (3.6) has no effect on the energy of the combination, as our more general argument has already established.

The matrices of \( r^2 \) and \( r^4 \cdot 2\cos 2\alpha \) within the pair of functions may be evaluated in an exactly similar manner. They are, respectively,

\[ \begin{bmatrix} \frac{3}{2} n^2 - \frac{1}{2} K(K - 2) & 0 \\ 0 & \frac{3}{2} n^2 - \frac{1}{2} K(K + 2) \end{bmatrix} \] (4.18)

and

\[ \begin{bmatrix} 0 & \frac{3}{2} n \sqrt{(n^2 - K^2)} \\ \frac{3}{2} n \sqrt{(n^2 - K^2)} & 0 \end{bmatrix} \] (4.19)

Hence the complete matrix of \( H' \), with \( V_0 \) and \( V_2 \) given by (4.5) and (4.6), is

\[ \begin{bmatrix} -\frac{1}{2} fn + \frac{1}{2} (g + h)(\frac{3}{2} n^2 - \frac{1}{2} K(K - 2)), \frac{1}{2} f \sqrt{(n^2 - K^2)} - \frac{1}{2} (g - h) n \sqrt{(n^2 - K^2)} \\ \frac{1}{2} f \sqrt{(n^2 - K^2)} - \frac{1}{2} (g - h) n \sqrt{(n^2 - K^2)}, -\frac{1}{2} fn + \frac{1}{2} (g + h)(\frac{3}{2} n^2 - \frac{1}{2} K(K + 2)) \end{bmatrix} \] (4.20)

The approximate energy of an upper vibronic level, is therefore, by (4.7)

\[ E^+(n, K) = n - \frac{1}{2} f [n - \sqrt{(n^2 - K^2)}] + \frac{1}{2} (g + h)(3n^2 - K^2) - \frac{3}{2} (g - h)n \sqrt{(n^2 - K^2)}. \] (4.21)

For small values of \( K(K \ll n) \) an expansion to order \( K^2 \) gives

\[ E^+(n, K) = n + \frac{3}{2} h n^2 - \frac{1}{2} K^2[2fn^{-1} - g + 5h]. \] (4.22)

Two points about this expression are worth noting. In the first place, for the \( \Sigma^+ \) levels \( (K = 0) \) the energy reduces to \( n + \frac{3}{2} h n^2 \) confirming once again that these levels are independent of the lower energy curve \( U^-(r) \). Secondly, the coefficient in square brackets will probably be positive so that a lowering of levels with \( K > 0 \) is predicted, approximately proportional to \( K^2 \).

In the absence of angular coupling between the odd electron and the bending mode, the surfaces coincide \( (f = 0, g = h) \) and (4.22) reduces to

\[ E^+(n, K) = n + \frac{1}{2} h (3n^2 - K^2), \] (4.23)
a formula which applies also, of course, if the molecule is in a \( \Sigma \) electronic state \( (\Lambda = 0) \) and the bending vibration is anharmonic. Thus a Renner effect is only indicated if the \( K \)-dependence of the energy levels is greater than that predicted by (4.23).

5. APPLICATION TO \( \text{NH}_2 \)

Before applying the theory quantitatively, some remarks should be made about the relevance of the simple one-electron model to a radical such as \( \text{NH}_2 \).
In its linear form, the $\Sigma^+$ state of NH$_2$ has the electronic configuration

$$K\sigma^2_u\pi^2$$

where the $\pi$ molecular orbitals are approximately $2p\pi$ atomic orbitals of the nitrogen atom. There are two such orbitals $\pi_x$ and $\pi_y$ possessing a degeneracy which is removed when the nuclear framework is bent. The one with a node in the plane of the bent molecule ($\pi_y$, say) will have the higher energy so that the configuration corresponding to the lower curve of figure 1(b) will be $K\sigma^2_u\pi^2\pi_x$ and for the upper curve it will be $K\sigma^2_u\pi^2\pi_y\pi_x$. In absorption from the ground state, therefore, an electron is transferred from $\pi_y$ to $\pi_x$, that is from a symmetric orbital into one with a node in the molecular plane. This is opposite to the convention adopted at the end of §2. Nevertheless this convention is appropriate in the case of NH$_2$ for the total (rather than orbital) symmetry, since the lower state has a node in the molecular plane. We may think, if we like, of the angle $\theta$ as the angular coordinate of the missing electron.

In order to apply equation (4.21) to the NH$_2$ radical, it is necessary to have some means of finding the quantities $f$, $g$ and $h$. Of these the upper surface anharmonicity $h$ is obtained by fitting the observed energies of the $\Sigma^+$ levels to the formula with $K=0$. Dressler and Ramsay find that these levels have energies which can be represented numerically by

$$9650 + 597n + 11.5n^2$$  \hspace{1cm} (5.1)

in wave numbers above the ground state. The unit of energy is therefore 597 cm$^{-1}$ and the value of $h$ (from equation (4.22) with $K=0$) is found to be

$$h = 0.01284.$$  \hspace{1cm} (5.2)

We determine $f$ and $g$ from the valency angle in the ground state and the height of the barrier. If the valency angle is denoted as $(\pi - 2\chi)$ in radians, then the mean value of $\chi^2$ would be given by

$$\bar{\chi}^2 = \frac{h}{4\pi^2\nu MR^2},$$  \hspace{1cm} (5.3)

in the lowest state if both surfaces were coincident parabolae, where $\nu$ and $M$ are the frequency and reduced mass associated with the bending mode, and $R$ the NH bond length. Setting

$$M = 2M_NM_H/(M_N + 2M_H),$$
$$\nu/c = 597 \text{ cm}^{-1}$$

and

$$R = 1.02 \text{ Å} \ (\text{as given by Dressler and Ramsay})$$

we obtain

$$\bar{\chi}^2 = 3.077 \times 10^{-2} \text{ radian}^2.$$  \hspace{1cm} (5.4)

Hence the root mean square value of $\chi$ would be 10.03°. But in the natural units which we have adopted the mean square value of the amplitude would be unity in this state; hence our natural unit for NH$_2$ must be taken as 10.03°. The value of $\chi$ in the ground state, given by Dressler and Ramsay as 38.5°, is therefore 3.84 of our units.

The height of the ground state barrier is close to 9650 cm$^{-1}$, but must be slightly greater than this because of the zero-point energy of the ground state. Adopting the value 10000 cm$^{-1}$, which equals 16.75 natural units, and noting
Table 1. Calculated and (in brackets) observed vibronic term values in NH₂. Observed band origins are quoted to the nearest 10 cm⁻¹ since the upper state levels are split slightly both by spin-orbit coupling and by the slight dynamical asymmetry produced by the bending vibration.
that \( dU^-/dr = 0 \) for \( r = 3.84 \), we obtain the following two equations for \( f \) and \( g \):

\[
\begin{align*}
\frac{1}{2} - f + gr^2 &= -16.75/r^2 \\
(\frac{1}{2} - f) + 2gr^2 &= 0
\end{align*}
\]

\( r = 3.84 \). (5.4)

Solution of these equations yields

\[
f = 2.770, \quad g = 0.07695. \quad (5.5)
\]

It then only remains to insert these values of \( f \), \( g \) and \( h \) into equations (4.21), multiply by 597 to convert to wave numbers and add 9650 cm\(^{-1}\), which is the gap between the ground state and the top of the barrier, since the energy in (4.21) is measured from this point. The resulting theoretical frequencies, and their experimental counterparts, are given in Table 1.

6. DISCUSSION

The general agreement in Table 1 between the observed frequencies and those calculated from equation (4.21) leaves little doubt that Dressler and Ramsay were right in attributing the absorption spectrum of \( \text{NH}_2 \) to transitions between two real components of an electronic \( \Pi \) state which is split in the manner indicated in figure 1(b) by electronic-vibrational coupling, for the reasons given by Rennet. The corresponding calculation for a \( \Sigma \) electronic state using (4.23) yields a variation of \( E^+(n, K) \) with \( K \) which is too small by an order of magnitude.

The near coincidence between the experimental and theoretical energies of the \( \Sigma^+ \) levels in Table 1 is not, of course, particularly significant, as the coefficient \( h \) in (4.3) was chosen to fit these levels as well as possible. It is, however, interesting to note that the value of \( h \) is positive, and that the upper potential curve shows no trace of a shallow maximum at \( r = 0 \). As to the other levels, the agreement with experiment is clearly best for \( K = 1 \) and worst for \( K = 4 \). The reason for this is not, perhaps, difficult to appreciate; the larger the value of \( K \), the more strongly will the energy of an upper vibronic level be affected by the form of the lower potential energy curve, and errors as to its precise shape will therefore be most apparent at high \( K \) values.

In conclusion it should perhaps be stressed that our theory is limited by a number of severe approximations. An exact calculation along the lines laid down by Renner would necessitate the diagonalization of an infinite matrix, whose rows and columns correspond to the members of a complete orthonormal set of functions with a given value of \( K \), and whose matrix elements include contributions from all powers of \( r \) in \( U^+(r) \) and \( U^-(r) \). What we have done is to ignore all matrix elements except those between functions which are degenerate in the harmonic zeroth approximation, and to neglect all powers of \( r \) higher than the fourth. Not only this, but we have neglected all interactions between the bending mode and other modes, and have treated the bending mode as though its effective mass were independent of its amplitude, even at the very large amplitudes which are actually reached. Nevertheless, it appears from our results that these approximations are not so serious as might have been feared, and that the perturbation techniques similar to that which we have here adopted may be helpful in interpreting other instances of the Renner effect.

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On interprète quantitativement, par l'effet Renner, les observations de Dressler et Ramsay (1958) sur le spectre d'absorption vibronique du radical NH$_2$. L'emploi d'une méthode de perturbation mène à la prédiction de fréquences en bon accord avec l'expérience, et confirme l'opinion des auteurs cités que la bande d'absorption est associée à des transitions entre les composantes, largement séparées par l'interaction électronique-vibrationnelle, d'un état électronique II.


REFERENCES