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The Effects of Vibrational Averaging on the Calculated Nuclear Spin–Spin Coupling Constants of Ammonia

Paul Solomon and Jerome M. Schulman*

Contribution from the City University of New York, Department of Chemistry, Queens College, Flushing, New York 11367.

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Abstract: The effects of including molecular vibrations on the calculated nuclear spin–spin coupling constants of a molecule have been studied for the case of ammonia. Both ${}^1J_{\mathrm{NH}}$ and ${}^2J_{\mathrm{HH}}$ were calculated by semiempirical coupled Hartree–Fock perturbation theory as a function of the six internal degrees of freedom and a subsequent vibrational average was computed at two levels of approximation. The first was an averaging over the normal modes, i.e., the small vibrations approximation, while the second procedure treated the inversion motion as a global problem. Rather large vibrational corrections were obtained with ${}^1J_{\mathrm{NH}}$ and ${}^2J_{\mathrm{HH}}$ being reduced ca. 15 and 9%, respectively, from their values calculated at the experimental equilibrium geometry.

I. Introduction

The quantum mechanical calculation of J_{AB}, the isotropic nuclear spin–spin coupling constant between nuclei A and B, remains an active area of theoretical study.[1] Yet most of the calculations of J_{AB} performed assume fixed nuclei at their equilibrium positions, thereby neglecting the role of nuclear motion. When nuclear motion is explicitly considered its treatment is more or less trivial; for example, coupling constants involving methyl protons are reported as statistical averages over a set of conformers. This treatment presumes that the rotamers are to a great degree localized in their respective wells. However, since rotamer interconversion is often quite rapid and the hindered rotational mode is appreciably anharmonic, there could be important contributions to the coupling constant from geometries other than the local minima.

A second example is spin–spin coupling to the nitrogen atom of amines. Here, interconversion between right and left pyramidal forms is rapid, and the inversion mode is anharmonic, so that a consideration of solely one or both quasi-equilibrium structures may be insufficient for a theoretical determination of J. Other situations where nuclear motion may make important corrections to the equilibrium value of J_{AB} are couplings to the proton in a hydrogen bond for which there can be tunneling, and coupling to the central atom of a fluxional molecule.

The correct way to incorporate nuclear motion into a theoretical calculation of the coupling constant within the Born adiabatic approximation[2] is to average J_{AB}, which depends parametrically on a set of nuclear displacements $\mathbf{Q} = (Q_1, Q_2, \ldots)$, over the ground state vibrational wave function. The temperature dependence of J_{AB}, if indeed it is of interest, can be subsequently determined by Boltzmann averaging of the contributions from excited vibrational states.

The only authentic examples of the vibrational averaging of a coupling constant to date appear to have been made for J_{HH} in the hydrogen molecule,[3a–c] J_{HF} in hydrogen fluoride,[4] and for ${}^2J_{\mathrm{HH}}$ in ammonia[5] (over the two totally symmetric degrees of freedom).

Our interest in the possible importance of corrections to spin–spin coupling constants arises from two considerations. Firstly, to the extent to which nuclear motion influences coupling constants in molecules undergoing inversion, hindered rotation, or other fluxional motion, the inferences drawn from the observed coupling constant about the electronic structure at the equilibrium geometry, e.g., hybridizations, may be subject to error. Secondly, since J_{AB} is at present most frequently calculated by INDO finite perturbation theory[6] or some other semiempirical approximate electronic theory,[7] the effects of vibrations could influence the choice of parameters, e.g., spin densities at the nuclei, which are selected to fit experimental data. Important vibrational corrections to J_{AB} for nonrigid molecules might then require that they be treated separately from rigid molecules, or more pessimistically, that J_{AB} might have to be averaged over vibrations before the parameters were chosen.

A possible example of this problem is afforded by the one-bond proton–nitrogen coupling constant in amines, ${}^1J_{\mathrm{NH}}$, where a single product of spin densities, $S_{\mathrm{N}}{}^2(0)S_{\mathrm{H}}{}^2(0)$, fails to fit all the experimental values. In particular, the experimentally observed difference between J_{NH} in pyramidal amines and nearly planar amines or amides is ca. half the difference that is calculated.[8] It is known that J_{NH} is very sensitive to the degree of nitrogen planarity.[8a] Could vibrational effects be the cause of this disparity?

In order to gain some insight into this question we have calculated J_{NH} for ^{15}N of ammonia as a function of its six internal coordinates and averaged $J_{NH}(\mathbf{Q})$ over the corresponding vibrational wave functions. Two cases have been considered: (a) the small vibrations limit where the extent of displacement along the normal coordinates is small, and; (b) the case where the inversion mode is treated globally, while the five other internal displacements are kept small. In addition to studying the vibrational corrections to J_{NH} we have also examined the corrections to $^2J_{NH}$ for cases (a) and (b). Our results extend those of Kowalewski et al.[5] who considered only the totally symmetric modes. The theory, method, and results are described below.

II. Theory

A. Vibrational Averaging in the Small Vibrations Limit. The effects of nuclear motion on J_{NH} other than inversion can be treated in the small vibrations limit. The reasons for this are (1) all internal nuclear displacements except the inversion coordinate change relatively little as ammonia vibrates, and (2) J_{NH} is found to be much less sensitive to normal coordinates other than the inversion coordinate.

Let $\mathbf{Q}$ be a sextuple of normal coordinates corresponding to the representations of C_{3v} symmetry—Q_1, $Q_2 \subset A_1$; Q_3, $Q_4 \subset E_a$; Q_5, $Q_6 \subset E_b$—and (Q_3,Q_5) and (Q_4,Q_6) are pairs of degenerate partners of bending and stretching E modes, respectively. At the C_{3v} equilibrium geometry, designated by $\mathbf{O}$, $\angle$HNH = 106.67°, r_{NH} = 1.0136 Å.[9] Normal coordinate Q_1 is essentially pure HNH angle bending[10] (we calculate the angle between the Q_1 displacement vector at a proton and its NH bond as 88°[10]), and Q_2 is the symmetric stretch.

The Taylor series for $J_{NH}(\mathbf{Q}) - J_{NH}(\mathbf{O})$ to second order in the Q_i is

$$J_{NH}(\mathbf{Q}) - J_{NH}(\mathbf{O}) = \sum_i \frac{\partial J_{NH}}{\partial Q_i}\bigg|_{\mathbf{O}} Q_i + \tfrac{1}{2}\sum_i \sum_j \frac{\partial^2 J_{NH}}{\partial Q_i \partial Q_j}\bigg|_{\mathbf{O}} Q_i Q_j + \theta(Q_i{}^3) \quad (1a)$$

In the small vibrations approximation the Q_i can be obtained in the conventional manner as eigenvectors of the *FG* matrix and the vibrational wave function is a product of harmonic oscillator functions in the variable Q_i with quantum number n_i. (In the vibrational ground state all $n_i = 0$.)

$$\Psi_{vib} = \prod_{i=1}^{6} \psi_i{}^{n_i}(Q_i) \quad (2a)$$

Thus, from the well-known harmonic oscillator selection rules, it is readily established that

$$\langle \Psi_{vib} | J_{NH} | \Psi_{vib} \rangle - J_{NH}(\mathbf{O}) = \tfrac{1}{2} \sum_{i=1}^{6} \frac{\partial^2 J_{NH}}{\partial Q_i{}^2}\bigg|_{\mathbf{O}} \langle \psi_i{}^{n_i} | Q_i{}^2 | \psi_i{}^{n_i} \rangle \equiv \sum_i \Delta J_i \quad (3a)$$

to order $(Q_i)^3$. The linear and bilinear terms vanish since they are odd functions of Q_i whereas $|\psi_i{}^{n_i}|^2$ is even. Moreover, it can be shown, vide infra, that the ΔJ_i of degenerate partners are equal, viz., $\Delta J_3 = \Delta J_5$, $\Delta J_4 = \Delta J_6$. Thus, at this level of approximation the vibrational correction may be written

$$\langle J_{NH}(\mathbf{Q}) \rangle - J_{NH}(\mathbf{O}) = \Delta J_1 + \Delta J_2 + 2\Delta J_3 + 2\Delta J_4 \quad (4a)$$

corresponding, respectively, to the effects of A_1 bending (inversion), A_1 stretching, E bending, and E stretching motions.

B. Vibrational Averaging Including the Anharmonic Effects of Inversion. In order to ascertain the importance of anharmonicity in the inversion mode we will replace Ψ_{vib} of eq 2a with the "ansatz"

$$\tilde{\Psi}_{vib} = \tilde{\psi}_1{}^{n_1}(\tilde{Q}_1) \prod_{i=2} \psi_i{}^{n_i}(Q_i) \quad (2b)$$

This is probably the most practicable way to retain a simple form for the vibrational function and yet include the important effects of inversion. The function $\tilde{\psi}_1{}^{n_1}(\tilde{Q}_1)$ is a solution of the empirical Schrodinger equation for ammonia inversion obtained by Swalen and Ibers,[11] who fitted parameters in a one-dimensional treatment to reproduce the inversion frequencies. The quantum number n_1 which ranges over 0S, 0A, 1S, 1A, etc., refers to representations of the Longuet-Higgins group isomorphic with D_{3h}[12], and S and A refer to states which are symmetric and antisymmetric with respect to the planar configuration. This treatment replaces the normal coordinate for inversion with the new variable $r_{NH}\phi$, denoted $\tilde{Q}_1$. Here ϕ is the angle between a given NH bond and the line connecting that proton with the midpoint of the H_3 equilateral triangle. The variable $\tilde{Q}_1$ ranges from $-(\pi/2)r_{NH}$ to $+(\pi/2)r_{NH}$, passing through zero at the planar configuration; it is more suitable than Q_1 in the inversion problem since it takes on both positive and negative values, i.e., it has different signs for the right and left pyramids.

Corresponding to eq 2b we may write the Taylor series counterpart of eq 1a by expanding J_{NH} $(\tilde{Q}_1, Q_2, Q_3, \ldots)$ about about J_{NH} $(\tilde{Q}_1, 0, 0, \ldots)$ as

$$J_{NH}(\tilde{\mathbf{Q}}) = J_{NH}(\tilde{Q}_1, 0, 0, \ldots) + \sum_{i \neq 1} \frac{\partial J_{NH}}{\partial Q_i}\bigg|_{(\bar{Q}_1, 0, 0, \ldots)} Q_i + \tfrac{1}{2} \sum_{i=2}^{6} \sum_{j=2}^{6} \frac{\partial^2 J_{NH}}{\partial Q_i \partial Q_j}\bigg|_{(\bar{Q}_1, 0, 0, \ldots)} Q_i Q_j \quad (1b)$$

to second order in $Q_{i \neq 1}$, where $\tilde{\mathbf{Q}} = (\tilde{Q}_1, Q_2, \ldots, Q_6)$. That is, a function of the form $J(\tilde{Q}_1, Q_2, Q_3, \ldots)$ for $Q_2, Q_3, \ldots$, near zero can be expanded about $J(\tilde{Q}_1, 0, 0, \ldots)$. The only tractable procedure is to evaluate the derivatives at the equilibrium geometry. When this expansion is averaged over $|\tilde{\Psi}|^2$ we obtain

$$\langle J_{NH}(\mathbf{Q}) \rangle - J_{NH}(\mathbf{O}) = \Delta\tilde{J}_1 + \Delta J_2 + 2\Delta J_3 + 2\Delta J_4 \quad (4b)$$

where $\Delta\tilde{J}_1$ replaces ΔJ_1 of eq 4a and

$$\Delta\tilde{J}_1 = \langle \tilde{\psi}_1{}^{n_1} | J_{NH}(\tilde{Q}_1, 0, 0, \ldots) | \tilde{\psi}^{n_1} \rangle \quad (3b)$$

It is clear that the above analysis has decoupled the contribution of inversion motion to the coupling constant from contributions from the other modes. Again, the rationale is the presumption that the other modes undergo only small vibrations and for J_{NH} the fact that the coupling constant is much more sensitive to inversion motion than to any other, as will be seen.

III. Method

The various aspects of the method of calculation are (1) determination of the normal coordinates in the small vibrations case; (2) determination of the inversion wave function $\tilde{\psi}_1{}^{n_1}(\tilde{Q}_1)$; (3) calculation of the second derivatives of eq 3a and $J_{^{15}NH}(\tilde{Q}_1, Q_{i \neq 1} = 0)$ of eq 1b, which we will write hereafter as $J_{NH}(\tilde{Q}_1)$; and (4) averaging over the vibrational wave functions to obtain the corrections ΔJ_1, $\Delta\tilde{J}_1$, ΔJ_2, etc.

The normal coordinates, Q_i, were obtained by diagonalizing the *FG* matrix in a basis of external Cartesian coordinate displacements. Force constants were computed from a

Table I. Variation of $J_{^{15}NH}$ with Q_i for the Normal Modes of NH_3 (Hz)[a,b]

Q_i	$-J_{NH}(Q_1)$	$-J_{NH}(Q_2)$[d]	$-J_{NH}(Q_3)$	$-J_{NH}(Q_4)$
0.32	14.23 (93.0)[c]	36.78	37.97	46.50
0.24	18.14 (96.6)	36.77	36.54	39.82
0.16	22.75 (100.1)	36.53	35.64	36.80
0.08	28.32 (103.5)	35.96	35.16	35.41
0.04	31.52 (105.1)	35.54	35.05	35.10
0.00	35.01 (106.6)	35.01	35.01	35.01
−0.04	38.88 (108.2)	34.34	35.05	35.11
−0.08	43.04 (109.6)	33.51	35.15	35.37
−0.16	52.33 (112.3)	31.26	35.53	36.46
−0.24	62.79 (114.7)	27.89	36.14	38.33
−0.32	74.09 (116.6)	22.77	37.94	41.20

[a] Q_i is varied while $Q_{j \neq i}$ is kept fixed at 0. The Q's are in (amu)$^{1/2}$ Å. [b] Q_1 = A_1 inversion, Q_2 = A_1 stretch, Q_3 = E bend, Q_4 = E stretch. [c] The HNH angle for the Q_1 mode in degrees. [d] A negative Q_2 corresponds to increased NH bond lengths.

Table II. Vibrational Corrections to $J_{^{15}NH}(\mathbf{O})$ of Ammonia (Hz)

Inversion correction		Small vibrations corrections				
n_1	$\Delta\tilde{J}_1$	n_i	ΔJ_1	ΔJ_2	$2\Delta J_3$	$2\Delta J_4$
0S	−4.55	0	−1.54	0.20	−0.50	−0.54
0A	−4.42	1	−4.62	0.60	−1.50	−1.62
1S	−18.86					
1A	−13.99					

$J_{NH}(\mathbf{O}) = -35.01$ Hz

Correction to $J_{NH}(\mathbf{O})$, eq 4a = −2.38 Hz
Correction to $J_{NH}(\mathbf{O})$, eq 4b = −5.33 Hz
for the ground state

MINDO/3 potential surface[13] by optimizing the geometry,[14] calculating the first derivatives analytically, and then finite differencing these derivatives again numerically.[15] The frequencies obtained were (cm^{-1}) ν_1 (inversion) = 1113, ν_2 (A_1 stretch) = 3555, $\nu_3 = \nu_5$ (E bend) = 1517, and $\nu_4 = \nu_6$ (E stretch) = 3578; they are in reasonable agreement with the reported harmonic values (1022, 3506, 1691, and 3577, respectively).[16]

For the vibrational wave function $\tilde{\psi}_1(\tilde{Q}_1)$ we solved the empirical Schrodinger equation of Swalen and Ibers[11] numerically using the Numerov method; $\tilde{Q}_1 = r_{NH}\phi$ was varied from −0.624 to +0.624 Å on a grid of 5000 points. The resulting eigenvalues, e_{n_1}, duplicated those of Swalen and Ibers who used an expansion in Hermite polynomials. Relative to the ground state energy e_{0S} they were (cm^{-1}) $e_{0A} = -0.830$, $e_{1S} = 930.2$, and $e_{1A} = 996.5$, which compare well with the experimental values (0.7935, 932.51, and 968.32).[17]

The second derivatives, $(1/2)(\partial 2J_{NH}/\partial Q_i^2)|_{\mathbf{O}}$, were obtained by calculating J_{NH} for various Q_i with $Q_j \neq i$ held at zero and fitting the values to a fifth degree polynomial in Q_i. A seventh-degree polynomial was employed for $J_{NH}(\tilde{Q}_1)$. The method used to calculate the coupling constants was the INDO coupled Hartree–Fock method,[7] which is equivalent to finite perturbation theory,[6] with spin density parameters $S_H{}^2(0) = 0.3724a_0{}^{-3}$ and $S_N{}^2(0) = 6.9265a_0{}^{-3}$. Our J_{NH} values were very close to those obtained by Wasylishen and Schaefer;[8a] for $^2J_{HH}$ our values agreed quite well with the ab initio results of ref 5. The semiempirical method used here for J_{NH} appears to be the most suitable method available at present.

The vibrational corrections for the small vibrations case were obtained from the product of the second derivatives and the expectation values of $(Q_i)^2$ employing

$$\langle \psi_i{}^{n_i} | (Q_i)^2 | \psi_i{}^{n_i} \rangle = (n_i + 1/2)h/4\pi^2\nu_i \qquad (5)$$

with the Q_i expressed as mass-weighted coordinates. For the correction term $\Delta\tilde{J}_1$ a numerical integration by Simpson's rule was performed, the full polynomial $J(\tilde{Q}_1)$ being averaged.

A final point should be made regarding the present calculation, which is a composite of MINDO/3 and INDO semiempirical methods. INDO coupling constants are usually computed at the experimental equilibrium geometry, $\mathbf{O}_{expt}$ (here, r_{NH} = 1.0136 Å and ∠HNH = 106.67°), whereas the MINDO/3 **O**, from which the normal coordinates were determined, was slightly different (r_{NH} = 1.0311 Å, ∠HNH = 104.23°). In order to reconcile these two equilibrium geometries we have somewhat arbitrarily referred the MINDO/3 normal coordinates to the experimental equilibrium geometry. Of course, this presumes that the "experimental" surface parallels and is merely displaced from the MINDO/3 surface, which is strictly speaking incorrect since the vibrational frequencies obtained differ somewhat from their experimental counterparts. It seems doubtful, however, that this assumption introduces more error than the other approximations which are made here, especially since it is not of issue in the most important instance, namely, the computation of $\Delta\tilde{J}_1$, where the HNH angle is varied over all possible values.

IV. Results

Table I contains J_{NH} as a function of Q_i for the various modes in case (a); in each column the $Q_{j \neq i}$ have been held constant at zero. The most significant variation found is for the inversion mode Q_1, that is, J_{NH} is most sensitive to the symmetric HNH angle bending. (For each of the ten distortions tabulated the actual HNH angle corresponding to Q_1 is given adjacent to the J_{NH} value.) It varies from −14 Hz at 93° to −74 Hz at 116.6°, the value at equilibrium being −35.01 Hz.

The actual values are proportional to $S_N(0)^2S_H(0)^2$ and are not so meaningful in themselves; for example, this parameter could be adjusted to give perfect agreement with the vapor phase J_{NH} of ammonia, −61.2 ± 0.3 Hz,[18a] but the good agreement for J_{NH} in formamide (−87.5 Hz calculated vs. −91.3 Hz observed[19]) would then be lost. What is significant is the change in J_{NH} relative to $J_{NH}(\mathbf{O})$ for the Q_i. It is clear from Table I that the vibrational corrections to mode Q_1 might be appreciable, whereas the corrections ΔJ_2, ΔJ_3, and ΔJ_4 are expected to be small since J_{NH} is insensitive to displacements along these modes. With regard to the values tabulated for the E modes it should be mentioned that the average J_{NH} over all three protons is reported. The individual protons behave differently from each other under E distortions since the spin Hamiltonian for a given pair of protons is not totally symmetric in C_{3v}; on the other hand, the spin Hamiltonian for the sum of the three NH couplings is totally symmetric.

In the global inversion case (b), $J_{NH}(\tilde{Q}_1)$ is rather similar to the values given for J_{NH} vs. Q_1 in Table I since the NH stretching turns out to be of little consequence. For that reason it is not separately tabulated; several values are contained in ref 8a.

Table II contains the various ΔJ_i obtained in case (a) by averaging over the harmonic oscillator functions. There, the values for the lowest two quantum states, n_i = 0, 1 are given for each ΔJ_i. For the vibrational ground state the total correction is −2.38 Hz or 6.8% of $J_{NH}(\mathbf{O})$. The various modes have rather similar ΔJ_i's, a result which is rather surprising given the much greater sensitivity of J_{NH} to Q_1 than to the other normal coordinates. However, when in case (b) the coupling constant is averaged over the inversion wave function $\tilde{\psi}_1{}^{n_1}(\tilde{Q}_1)$, large corrections, $\Delta\tilde{J}_1$ = −4.55 and −4.42 Hz, are found for the 0S and 0A states, respectively. Since their splitting, 0.8 cm^{-1} ≈ 2 cal/mol, is small they are almost equally populated at room temperature and an average correction, −4.49 Hz, can be used. This value is 12.8% of $J_{NH}(\mathbf{O})$, and the

Table III. Vibrational Corrections to $J_{HH}(\mathbf{O})$ for Ammonia (Hz)

Inversion correction		Small vibrations correction				
n_1	$\Delta\tilde{J}_1$	n_i	ΔJ_1	ΔJ_2	$2\Delta J_3$	$2\Delta J_4$
0S	0.83	0	0.10	−0.27	−0.88	−0.36
0A	0.81					
1S	3.80					
1A	2.76					

$J_{HH}(\mathbf{O}) = -7.88$ Hz

Correction to $J_{HH}(\mathbf{O})$, eq 4a = −1.41 Hz
Correction to $J_{HH}(\mathbf{O})$, eq 4b = −0.69 Hz
for the ground state

total correction for case (b) is $\Delta\tilde{J}_1 + \Delta J_2 + 2\Delta J_3 + 2\Delta J_4 = -5.33$ Hz or 15.2% of the equilibrium value.

It is interesting to note that the difference in vibrational corrections is negligible for the ground state inversion doublet; however, the $\Delta\tilde{J}_1$ for 1S and 1A, −18.86 and −13.99 Hz, respectively, are appreciably different. In fact, their splitting exceeds the total ground state $\Delta\tilde{J}_1$. Nonetheless, the temperature dependence of J_{NH} is nil because the 1S and 1A excited inversion states, which furnish an average correction of −16.4 Hz vs. −4.5 Hz for 0S and 0A, have a Boltzmann factor of $e^{-1343/T}$ or ca. 0.01 at room temperature.

Table III contains the various vibrational corrections to ${}^2J_{HH}$ for the small vibrations case (a) and the global inversion case (b). (The value actually reported is the average of the corrections for each of the three proton–proton couplings for the E modes, as discussed previously for ${}^1J_{NH}$.) We find in case (a) a rather large negative vibrational correction, −1.41 Hz, to the calculated value for the equilibrium geometry, $J_{HH}(\mathbf{O}) = -7.88$ Hz. The magnitude of J_{HH} in liquid ammonia is 10.35 ± 0.80 Hz,[18b] with the sign as yet undetermined. In the small vibrations case the contribution from the inversion mode, ΔJ_1, is small and positive, 0.10 Hz. However, when inversion is considered globally we obtain a larger correction, $\Delta\tilde{J}_1 = 0.82$ Hz. This, in turn, leads to a smaller total correction to $J_{HH}(\mathbf{O})$ of −0.69 Hz or 8.8% of the total.

V. Discussion

The dominant vibrational correction to ${}^1J_{NH}$ of ammonia is clearly that from inversion since it furnishes 85% of the total correction. This is due to the very high sensitivity of J_{NH} to a change in Q_1 and to the anharmonicity inherent in the global inversion problem. The latter is seen from the rather disparate small and global corrections: $\Delta J_1 = -1.54$, $\Delta\tilde{J}_1 = -4.55$ Hz.

Regarding the results for ${}^2J_{HH}$ the global correction for the A_1 modes in the global calculation was +0.55 Hz, which is similar to that found from ab initio calculations by Kowalewski and Roos[5] who obtained +0.24 for the correction to their equilibrium J_{NH}, −8.5 Hz. It is important to note that the INDO and ab initio results for J_{HH} vs. (Q_1) are in remarkably good agreement indicating that the vibrational results obtained here from coupling constants calculated semiempirically are probably similar to those which would be obtained by a more lengthy ab initio calculation for the other modes as well. Thus it is with added interest that we note that the corrections for the E modes outweigh the A_1 corrections and lead to a net negative vibrational correction to $J_{HH}(\mathbf{O})$ of ca. 9%. In other words, the ab initio result,[5] $J_{HH}(\mathbf{O}) = -8.5$ Hz, should be improved with respect to experiment −10.4 Hz when all six modes are considered (assuming, of course, that J_{HH} is negative), whereas the correction is in the wrong direction if only the totally symmetric modes are employed.[5]

Finally, we turn to the initial question of whether the vibrational corrections can account for the difference between calculated ${}^1J_{NH}$ values and experiment. The calculated vibrational correction for ammonia is −5.3 Hz or 15% of the equilibrium value owing, in part, to the preferential inclusion of flatter ammonia geometries in the average. By the same token, it is likely that an amine or amide which has a nearly planar geometry would have a vibrational correction which is positive owing to the inclusion of more pyramidal configurations. In other words, the vibrational corrections are in the correct directions, tending to reduce the larger calculated than observed difference between J_{NH} in pyramidal vs. nearly planar nitrogen moieties. They do not, however, seem to be of sufficient magnitude to account for the bulk of the effect which in INDO theory is on the order of a 100% error; the conclusion must be that there is inherently a deficiency in the INDO treatment of J_{NH} which exists above and beyond the use of vibrational averages.

Nonetheless, it is important to realize that there is a significant relative vibrational correction to the calculated ${}^1J_{NH}$ and ${}^2J_{HH}$ is ammonia at their equilibrium geometries. Moreover, the J_{NH} correction is substantial in absolute magnitude as well, −5.3 Hz relative to the equilibrium value of −35 Hz calculated here, or in terms of the observed value, −62 Hz, the correction would be 9.3 Hz!

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