*J. Phys. Chem.* **1995,** *99,* 5961−5966

# Anharmonic Force Field of Formamide. A Computational Study

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*Received: December 1, 1994; In Final Form: January 31, 1995*[⊗]

Vibrational energies of $HCONH_2$ and $DCONH_2$ molecules are calculated and compared to experiment. Rotational constants of formamide and water molecules are calculated for several vibrational states. The anharmonic force fields are calculated ab initio on HF and MP2 levels and using local and nonlocal density functional theory. Possible applications of DFT anharmonic force field in a prediction of vibrational properties are discussed. Dipolar derivatives are calculated to second order on the HF level. The phase integral quantum concept is introduced as a tool for an efficient diagonalization of the vibrational Hamiltonian.

## Introduction

Formamide, similar to the water molecule, belongs to a relatively small group of model molecules that are biologically important or serve as models for biological systems but that are small enough to be investigated by thorough calculations. Today extensive interest in these systems suggests that only a fraction of their basic properties is completely understood and explored. The formamide dimer, for example, serves as a model for the peptide amide group as well as for the base−base interactions in nucleic acids.[1]

We attempt to calculate vibrational energies of formamide molecule behind the harmonic approximation. A pure harmonic treatment is not possible, because of the well-known anharmonicity of the lowest-frequency, out-of-plane nitrogen vibration.[2] In the past, IR and Raman vibrational spectra of formamide and its isomers were measured and the fundamental vibrational modes were assigned.[2−4] Also extensive theoretical studies of this molecule were performed.[5,6] But calculated results do not fully explain experimentally observed frequencies and intensities. The energies and absorption intensities of the transitions below 1000 $cm^{-1}$ are extremely sensitive to molecular environment. The intensities of combinational and hot bands are comparable with intensities of fundamental transitions, which makes the assignment difficult. Often a nonplanar equilibrium geometry is found, if calculated within the harmonic approximation.[6] In ref 7 an attempt is made to introduce an anharmonic potential for two degrees of freedom of formamide, calculated frequencies are, however, higher by more than 100% than expected for the lowest frequency modes. Thus we feel a strong need to describe basic vibrational properties of this molecule consistently including the anharmonic effects.

Previously, we used a combined variational and perturbational calculation of the vibrational energies of *trans*-dideuteriooxirane.[8] The oxirane molecular force field is dominated by the harmonic terms. For the formamide, however, the perturbational theory cannot be used. Providing that a complete molecular force field is known, the problem would be solved if a Hamiltonian could be diagonalized in a sufficiently large harmonic basis. In fact, any basis set, including plane waves, is applicable. Utilization of Fourier-transformed wave functions in the discrete variable representation[9] leads to accurate prediction of vibrational energies of smaller systems.[10] Here, with respect to the computer limitations, we propose a reduction of the harmonic basis based on the idea of phase integrals.

**Phase Integrals.** For an effectively one-dimensional, linear motion, a condition for phase (Planck(−Bohr)−Somerrfeld) integrals can be derived[11] by an expansion of the wave function phase according to the powers of the Planck constant $h$: $\oint \mathbf{p}\cdot d\mathbf{r} = (v + {}^1/_2)h$, $v = 0, 1, ..., \infty$. If $p^2 = 2m(E - V(\mathbf{r}))$, allowed energy levels $E$ can be obtained for any potential $V$. Vibrational energies of diatomic molecules and other suitable systems are often calculated by this procedure.[12]

The phase integrals can be written for each of the $3N-6$ modes in normal coordinates[13] $Q_i$ as

$$\int_a^b \sqrt{E - V(Q_i)}\, dQ_i = (v + {}^1/_2)\pi\hbar/\sqrt{2} \qquad (1)$$

where $\hbar = h/(2\pi)$, the potential is defined according to the diagonal expansion coefficients

$$V(Q_i) = \omega_i^2 Q_i^2/2 + C_{iii}Q_i^3/6 + D_{iiii}Q_i^4/24 \qquad (2)$$

and the integral limits are given by the condition $V(a) = V(b) = E$. Thus, if there were no coupling among normal modes, allowed vibrational energies could be determined exactly from eq 1.

Nevertheless the off-diagonal anharmonic terms in the potential contribute to energies to the same extent as the diagonal part. To solve the Schrödinger equation, a new harmonic basis can be introduced, partially corrected for the diagonal anharmonic terms. Let us define new normal mode frequencies $\omega_i'$ according to the condition $\hbar\omega_i' = E^i_{\rm PI}(1) - E^i_{\rm PI}(0)$, where $E^i_{\rm PI}(0)$ and $E^i_{\rm PI}(1)$ are the ground and first excited states of each oscillator with the potential $V(Q_i)$. Note that for a harmonic potential $\omega_i' = \omega_i$. See Figure 1 for a graphical representation for the amino wagging mode (an MP2 calculated potential). The physical meaning of the choice of the new basis is simple: a system with the potential 1 (see Figure 1) is better described by a harmonic wave function of potential 3 rather than of potential 2. The energy levels $E^i_{\rm PI}(j)$ are obtained exactly by a numerical solution of eq 1. For the nitrogen out-of-plane motion a natural harmonic basis may not exist, if $\omega$ is close to zero or negative.

To implement the basis set substitution, a new Hamiltonian was constructed with the diagonal potential:

$$V(Q_i') = \omega_i'^2 Q_i'^2/2 + C_{iii}Q_i'^3/6 + D_{iiii}Q_i'^4/24 + V_i' \qquad (3)$$

where $V_i' = (\omega_i^2 - \omega_i'^2)Q_i'^2/2$. Although the potentials 2 and 3 are equal, the latter is more suitable for calculation of the

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[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1995.

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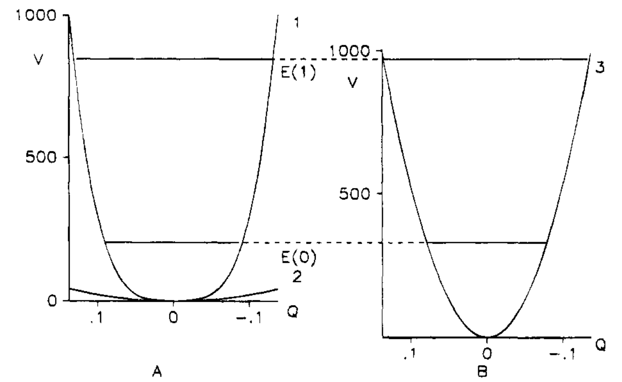

**Figure 1.** Basis set replacement (example for the amino wagging of $HCONH_2$). $V = V(Q)$, the diagonal part of the potential; $Q$, normal-mode coordinate. (A) Calculated potential (1) and its harmonic part (2). (B) Harmonic potential, from which the harmonic basis is derived (3).

fundamental vibrational energies in an incomplete harmonic basis derived from $\omega_i'$. For practical reasons, the computation was done in the dimensionless coordinates[14] $q_i = \omega_i^{1/2}Q_i$. An implementation of molecular symmetry can further reduce the size of the Hamiltonian block to be diagonalized.

**Eigen-Problem for Vibrational Hamiltonian.** Similarly as in the case of the electronic configuration interaction method,[15] leaving the harmonic approximation leads to a diagonalization of a large matrix. In most cases, the matrix is sparse with off-diagonal elements much smaller than diagonals. States that cover measured IR spectrum are desired, typically lowest energies up to about 4000 cm$^{-1}$. On the contrary, usually only the ground state is required for the electronic problem. When the matrix can be stored in a computer memory, straightforward and fast diagonalization methods can be applied,[16] particularly the diagonalization paths using the Sturm sequence property showed to be suitable for the vibrational problem.[8] For a larger matrix only few vectors (columns) can be kept in memory. Known numerical recipes[15,17,18] lead to a consecutive search for eigenvectors, by iterative procedures based on a matrix-vector multiplication rather than on a matrix transformation. The conjugate gradient methods,[15] working well for the electronic case, gives rather poor convergence for higher excited vibrational states. It also does not lead to a complete diagonalization of the matrix, if desired. We have achieved better results with the modified Mitin's gradient vector algorithm.[18] According to our experience, rather confusing explanation of the algorithm is given in the original paper. A modification suitable for the vibrational problem with a variable dimension of the iterative subspace is described in the Appendix.

## Computational Method

The geometry of the $HCONH_2$ molecule was optimized by energy minimization, using the Cadpac 5 ab initio quantum programs,[19] on the MP2 level with the 631GE basis set.[20] The energy second and first dipolar derivatives were calculated by a one-point numerical differentiation with a step of 0.001 bohr (0.000 53 Å). Because of computer limits, lower levels of calculations were used for higher derivatives. The third and fourth energy derivatives were calculated by a two-point numerical differentiation,[8] with a step of 0.003 bohr, on the MP2/DZP[21] level. Second dipolar derivatives were calculated on the HF/631GE level and the polarizability derivatives on the HF/DZP level, using a one-point fromula with the step of 0.005 bohr. The results were independent on the step used for the numerical differentiation at least at the region 0.0005−0.01 bohr. Test calculations in smaller bases were done.

**TABLE 1: Fundamental Vibrational Modes of $DCONH_2$[e]**

| | harm | anharmonic | | | | | dipolar strengths | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| mode | $\omega_{MP2}$ | $\omega_{PER}$ | $\omega_{var}$ | $\omega_{PI}$[a] | $\omega_{PI}$[b] | $\omega_{exp}$[c] | $D_H$ | $D_{HA}$ | $D_{AA}$ | $D_{exp}$[c] |
| 1a | 136 | −75 | 657 | 239 | 221 | 289[d] | 6313 | 13e3 | 14e3 | |
| 2 | 554 | 520 | 574 | 545 | 536 | 591 | 76 | 72 | 87 | w |
| 3a | 625 | 462 | 815 | 605 | 599 | 563 | 73 | 459 | 463 | s |
| 4a | 873 | 855 | 948 | 898 | 890 | ?890 | 4 | 6 | 5 | |
| 5 | 966 | 939 | 1001 | 966 | 957 | 955 | 28 | 12 | 12 | m |
| 6 | 1130 | 1087 | 1162 | 1111 | 1154 | 1142 | 2 | 7 | 10 | w |
| 7 | 1264 | 1215 | 1241 | 1260 | 1257 | 1241 | 280 | 280 | 287 | s |
| 8 | 1625 | 1584 | 1596 | 1605 | 1617 | 1582 | 78 | 30 | 10 | m |
| 9 | 1762 | 1712 | 1814 | 1771 | 1763 | 1740 | 990 | 916 | 796 | s |
| 10 | 2227 | 2126 | 2241 | 2209 | 2199 | 2135 | 132 | 75 | 85 | m |
| 11 | 3613 | 3486 | 3920 | 3477 | 3439 | 3438 | 55 | 26 | 17 | m |
| 12 | 3766 | 3615 | 3920 | 3686 | 3601 | 3563 | 60 | 16 | 7 | m |

[a] $v = 0.01$, 523 functions. [b] $v = 0.005$, 895 functions). [c] Reference 2. Dipolar strengths in $10^{-4}$ D$^2$: H, the harmonic limit; HA, first dipole derivatives were used only; AA, second dipole derivatives included. [d] For $HCONH_2$. a, an out-of-plane mode. Frequencies in cm$^{-1}$: PER, perturbational calculation; var, variational calculation ($v = 0.01$, 628 basis functions); PI, variational in the phase integral basis.

For the density functional theory (DFT) calculations, the DeFT program[22] was adapted. Analytical second energy derivatives are not implemented in DeFT, so second and higher derivatives had to be calculated numerically. The program has basis sets optimized for density functional calculations.[23] Bases of 72 orbital and 171 auxiliary basis functions was used for formamide. The geometry was optimized and the numerical differentiation done with the step of 0.005 Å. Here a smaller step may lead to wrong results, because of the limited numerical accuracy—a numerical integration of electron density is performed over a grid of points in space. It appeared useful to check translational and rotational invariance as well as the symmetric properties of obtained cubic and quartic force field tensors. The local (spin) density approximation (LSDA, LDA) is based on the Vosko−Wilk−Nusair functional,[24] while the nonlocal correction uses a combination of Becke[25] and Perdew[26] functionals.

For calculation of the vibrational energy levels and spectral intensities the S4 program[8] was used. The basis set was selected from all of the 6188 states less than 6 times excited, according to their interaction parameter[8] $v(s) = |\langle i|V|s\rangle/(E_i - E_s)|$, where $|i\rangle$ is ground or a monoexcited state.

## Results and Discussion

**$DCONH_2$.** For this isomer, we want to illustrate the advantage of the harmonic basis based on the phase integrals. The utilization of a Cartesian force field allows an easy isotopic substitution without repeating the numerical differentiation according to normal modes.

In Table 1 frequencies and dipolar strengths of fundamental modes are listed. The harmonic frequencies mostly differ by less than 5% from experimental values. The difference exceeds 100 cm$^{-1}$ for the highest energy (hydrogen stretching) modes. Calculated harmonic frequency of the first mode (out-of-plane nitrogen wagging) is by about 50% lower than experimental (supposed to be close to the $HCONH_2$ amino wagging).

A straightforward perturbational calculation of the anharmonic terms is not conceivable, because the harmonic term is the minor part of the amino-wagging potential. Rather a calculation based on the phase integral harmonic basis was performed. Second-order perturbational calculation ($\omega_{PER}$ in Table 1) gives poor results for six lowest energy modes. Higher frequencies compare better to experiment, for example for the eighth mode $\omega_{PER}$ = 1584 cm$^{-1}$, experimentally 1582 cm$^{-1}$. The carbonyl stretching is underestimated by 28 cm$^{-1}$. The perturbational

**TABLE 2: Frequencies of Fundamental Transitions of $HCONH_2$[f]**

| | harmonic | | | anharmonic | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| mode | $\omega_{MP2}$ | $\omega_{DFT}{}^a$ | $\omega_{DFT}{}^b$ | $\omega_{PI}$ | $\omega_{PER}$ | $\omega_{MP2}$ | $\omega_{MP2}{}^c$ | $\omega_{DFT}{}^a$ | $\omega_{DFT}{}^b$ | $\omega_{DFT}{}^{b,d}$ | $\omega_{exp}{}^e$ | $\lvert c_{ii}\rvert^2$ |
| 1a | 136 | 237 | 187 | 649 | −62 | 221 | 216 | 233 | 236 | 252 | 289 | 73 |
| 2 | 560 | 524 | 532 | 582 | 526 | 543 | 538 | 488 | 498 | 536 | 581 | 85 |
| 3a | 637 | 612 | 633 | 743 | 492 | 617 | 616 | 595 | 603 | 580 | 603 | 81 |
| 4a | 1042 | 969 | 985 | 1083 | 1010 | 1042 | 1041 | 969 | 960 | 1012 | 1046 | 88 |
| 5 | 1049 | 988 | 1011 | 1079 | 1010 | 1012 | 1007 | 982 | 987 | 1016 | 1021 | 75 |
| 6 | 1279 | 1217 | 1231 | 1277 | 1235 | 1269 | 1267 | 1210 | 1234 | 1253 | 1258 | 80 |
| 7 | 1421 | 1334 | 1315 | 1431 | 1385 | 1422 | 1419 | 1345 | 1325 | 1389 | 1390 | 52 |
| 8 | 1630 | 1512 | 1555 | 1629 | 1567 | 1577 | 1596 | 1532 | 1525 | 1587 | 1577 | 43 |
| 9 | 1780 | 1727 | 1740 | 1778 | 1743 | 1780 | 1779 | 1734 | 1790 | 1769 | 1754 | 86 |
| 10 | 3011 | 2895 | 2861 | 2898 | 2894 | 2879 | 2876 | 2854 | 2750 | 2732 | 2883 | 62 |
| 11 | 3614 | 3512 | 3480 | 3546 | 3472 | 3452 | 3424 | 3213 | 3313 | 3441 | 3439 | 29 |
| 12 | 3767 | 3661 | 3629 | 3841 | 3611 | 3634 | 3629 | 3458 | 3483 | 3600 | 3564 | 27 |

[a] LDA. [b] Nonlocal DFT. [c] Bigger harmonic basis of 1737 states used [d] MP2 normal modes used. [e] Reference 2. See Table 1 for other symbols. [f] $c_{ii}$ is the diagonal coefficient for the expansion into harmonic basis (MP2 calculation).

calculation has the advantage that a great number of basis functions can be included (6188), but the results may be affected by Fermi resonances and are, in principle, unreliable. For states with a dominant contribution of the anharmonic part, a perturbational calculation fails completely, as documented by the negative frequency of the first mode.

A simple variational calculation ($\omega_{var}$, with the coupling parameter $v = 0.01$, 628 basis functions) gives vibrational energy of the first mode by about 130% higher than experiment and most of other frequencies are worse than the harmonic limit, almost 500 cm$^{-1}$ off for N−H stretching modes.

On the contrary, the basis set based on the diagonal phase integrals (frequencies $\omega_{PI}{}^a$ in Table 1) leads to a substantial improvement. Even the singular first mode frequency is only by 17% below the expected experimental value. For the highest frequency out-off-phase N−H stretching, the error becomes 3%, half of the error of the harmonic limit. For this calculation the same interaction parameter $v = 0.01$ was used (523 basis functions).

To explore the convergence of energies with respect to the size of the basis, the calculation was repeated for the interaction parameter $v = 0.005$ (895 basis functions, $\omega_{PI}{}^b$ in Table 1). Frequency changes of a few cm$^{-1}$ are observed, mostly toward experimental values. Nevertheless, a substantial part of the anharmonic correction could be calculated already in the smaller basis. Such a convergence was not seen in the variational calculation based on the natural harmonic basis.

The harmonic dipolar strengths ($D_H$ in Table 1) may be a sufficient approximation for fundamental modes, with respect to available experimental data. It would cause difficulties to integrate the complicated rotational−vibrational pattern in the gaseous spectra to obtain experimental intensities, because of band-overlapping and vast Coriolis interactions. Data from solutions or frozen matrices cannot be used, since formamide spectra are extraordinary sensitive on molecular environment. Dipolar strength doubles for the first mode and rises 6 times for the third mode, if the anharmonicity is included. Changes on the order of 50% can be seen also for the hydrogen/deuterium stretching modes, where also higher dipolar derivatives start to contribute substantially, similar to for the case of the oxirane molecule.[8]

**$HCONH_2$.** On the case of $HCONH_2$ we want to demonstrate the performance of the density functional theory. Within the harmonic approximation, several applications of DFT to $HCONH_2$ were already explored,[6] including the hydrogen bonding.[23] A DFT calculation of the anharmonic terms for any molecule is not known to us.

Calculated energies are listed in Table 2. For modes 1−9 the MP2 and DFT (both the LDA and with the nonlocal functional) energies harmonic energies are in a good agreement. The DFT frequencies for the modes 10−12 are by the order of 100 cm$^{-1}$ lower than the MP2 harmonic limit, which may appear like a shift to experimental frequencies. There is little qualitative difference between the LDA and nonlocal DFT results.

For calculation of the anharmonic energies, harmonic basis based on the phase integrals was used. The first diagonal excitation energies are listed in Table 2 as $\omega_{PI}$. Since $\omega_{PI}$ is equal to the harmonic limit for a pure harmonic potential, substantial anharmonic parts in the diagonal part of potentials of the first and third modes can be expected, as follows from the comparison of $\omega_{PI}$ and $\omega_{MP2}$. For other modes $\omega_{PI}$ differs from the harmonic limit by few percent, by 74 cm$^{-1}$ for the highest energy mode, for example, while the carbonyl stretching (ninth mode) can be apparently well described by a harmonic diagonal potential.

The second-order perturbational calculation, based on the phase integral basis, gives good estimates of frequencies 6−12 ($\omega_{PER}$). It fails for the lower frequency modes, similar to for $DCONH_2$.

Finally, a variational calculation based on the substituted basis ($v = 0.005$, 937 basis functions, anharmonic $\omega_{MP2}$ in the Table 2) gives the best values of vibrational energies, including the lowest energy modes. To test the effect of limited basis set, calculation with 1737 harmonic states was done ($\omega_{MP2}{}^c$). An excellent convergence is observed, with energies varied by few cm$^{-1}$; for modes 8 and 11 greater differences of about 20 cm$^{-1}$ emerge.

For all modes the diagonal and off-diagonal anharmonic energy contributions can be estimated: For the first mode, for example, the diagonal term in the potential is very big, $\omega_{PI} = 649$ cm$^{-1}$ is by 380% higher than the MP2 harmonic limit, see also the magnitude of the $d_{1111}$ coefficient in Table 3. But the coupling to other modes lowers the transitional frequency to about 220 cm$^{-1}$, mainly due to the cubic force constants; see Table 3. A good starting choice of the basis indicates the high value of the diagonal expansion coefficient of the wave function, $|c_{11}|^2 = 73\%$. Clearly, previous efforts to rely on only the diagonal part of the potential had to fail,[2,7] neglecting the coupling. For the N−H stretching modes the diagonal anharmonicity contributes by about 2% to harmonic energy and $|c|^2 \simeq 28\%$ indicates strong coupling to other vibrations.

The fourth- and fifth-mode frequencies are switched for the MP2 calculation, if compared to the harmonic limit and to the earlier assignment.[2] They have a weak IR signal, and the energy separation is only 25 cm$^{-1}$.

**TABLE 3: Selected[a] Anharmonic Force Constants for $HCONH_2$**

| $ij(k)$ | HF/431G | HF/631G** | MP2 | DFT/LDA | DFT/nonlocal |
|---|---|---|---|---|---|
| | | | Cubic $c_{ijk}$[b] | | |
| 1 1 8 | 1515 | 1717 | 1617 | 1465 | 1340 |
| 1 1 11 | 5733 | 6337 | 6606 | 6015 | 5706 |
| 1 1 12 | 2899 | 3067 | 3200 | 2741 | 2746 |
| 1 3 12 | 2463 | 2612 | 2736 | 2434 | 2402 |
| 3 3 11 | 1028 | 1063 | 1109 | 988 | 981 |
| 10 10 10 | 2030 | 2009 | 2061 | 1878 | 1871 |
| 11 11 11 | 1637 | 1642 | 1685 | 1526 | 1522 |
| 11 12 12 | 1624 | 1629 | 1666 | 1507 | 1504 |
| 12 12 12 | 542 | 542 | 552 | 499 | 510 |
| | | | Quartic $d_{iijj}$ | | |
| 1 1 | 43533 | 53036 | 56085 | 51204 | 46489 |
| 1 3 | 4733 | 5137 | 5475 | 4749 | 4577 |
| 1 11 | −3415 | −3520 | −3589 | −3368 | −3266 |
| 1 12 | -4004 | −4108 | −4185 | −3978 | −3944 |
| 10 10 | 1197 | 1158 | 1154 | 1050 | 1035 |
| 11 11 | 685 | 679 | 674 | 593 | 569 |
| 12 12 | 733 | 721 | 715 | 619 | 614 |

[a] Constants bigger than 1000 $cm^{-1}$ (in dimensionless MP2/631GE normal coordinates) and diagonal for hydrogen stretchings. [b] Sign of cubic constants depends on the phase of normal modes.

**TABLE 4: Spectral Intensities for $HCONH_2$[a]**

| | dipolar strength | | | | Raman | | | |
|---|---|---|---|---|---|---|---|---|
| | $D_{MP2}{}^H$ | $D_{DFT}{}^H$ | $D_{HA/AA}$ | $D_{exp}{}^b$ | $I^H$ | $I$ | $\varrho^H$ | $\varrho$ |
| 1 | 6296 | 764 | 13012/13534 | | 2 | 7 | 0.75 | 0.75 |
| 2 | 76 | 98 | 72/87 | m | 222 | 184 | 0.39 | 0.35 |
| 3 | 74 | 65 | 521/525 | m | 11 | 13 | 0.75 | 0.75 |
| 4 | 21 | 11 | 6/7 | w | 97 | 99 | 0.75 | 0.75 |
| 5 | 21 | 20 | 6/24 | w | 509 | 588 | 0.25 | 0.24 |
| 6 | 347 | 520 | 341/316 | s | 431 | 376 | 0.09 | 0.15 |
| 7 | 13 | 19 | 33/7 | w | 431 | 133 | 0.26 | 0.69 |
| 8 | 111 | 93 | 43/16 | m | 241 | 133 | 0.47 | 0.40 |
| 9 | 933 | 1134 | 885/775 | vs | 688 | 652 | 0.37 | 0.37 |
| 10 | 115 | 26 | 76/81 | s | 4033 | 2774 | 0.26 | 0.26 |
| 11 | 55 | 15 | 25/17 | m | 2996 | 1011 | 0.08 | 0.14 |
| 12 | 59 | 9 | 23/10 | m | 1060 | 581 | 0.71 | 0.36 |

[a] Dipolar strengths in $10^{-4}$ $D^2$, for values behind slash first dipole derivatives used only. H: harmonic approximation. Raman intensity in atomic units, $\varrho$ the depolarization ratio. [b] Reference 2.

**TABLE 5: $HCONH_2$ Combinational Vibrational Transitions**

| state[a] | $\omega_{MP2,H}$ | $\omega_{DFT,A}$ | $\omega_{MP2,A}$ | $\omega_{exp}{}^b$ | $D_{MP2}$ |
|---|---|---|---|---|---|
| $1^2$ | 272 | 813 | 830 | 658 | 42/2669 |
| $1^1 3^1$ | 772 | 1093 | 1142 | 1159 | 66/352 |
| $3^2$ | 1273 | 1324 | 1403 | 1340 | 6/5 |
| $1^3$ | 409 | 1465 | 1534 | 1570 | 4/11 |
| $1^2 2^1$ | 832 | 1533 | 1609 | 1620 | 44/18 |
| $1^2 3^1$ | 905 | 1653 | 1721 | 1738 | 94/105 |
| $1^1 5^1$ | 1185 | 1991 | 1836 | 1844 | 14/20 |
| $1^1 6^1$ | 1415 | 2218 | 2108 | 2133 | 9/9 |
| $1^4$ | 545 | 2329 | 2420 | 2349 | 2/49 |
| $1^2 8^1$ | 1766 | 2576 | 2682 | 2746 | 1/70 |

[a] Highest contribution in the expansion into the harmonic basis (MP2 calcd), symbols and units same as in previous Tables. [b] Reference 2 (Figure 2).

The DFT frequencies are mostly underestimated, apparently due to the low harmonic values (second derivatives). This handicap of DFT is almost totally corrected, when the MP2/631GE normal modes (harmonic force constants) are combined with the DFT third and fourth energy derivatives, see frequencies $\omega_{DFT}b,d$ in Table 2. Frequencies number 1, 5, 6, 7, 9, 11, and 12 are even closer to experiment than sole MP2 results. For five modes the difference between calculated and experimental frequencies is less than 10 $cm^{-1}$.

Calculation within the harmonic approximation may lead to wrong suggestions about molecular symmetry and geometry. Some ab initio approximations for $HCONH_2$ give an imaginary frequency for the amino wagging, predicting a nonplanar equilibrium geometry.[6] An HF/631G** calculation, for example, yields $\omega_1 = 476$ $cm^{-1}$, an MP2/DZP calculation $\omega_1 = -129$ $cm^{-1}$ (we keep the usage to express imaginary frequencies as negative), while the 631GE basis leads again to a positive value of $\omega_1 = 136$ $cm^{-1}$. The DFT calculation gives the energy by about 38% higher, 187 $cm^{-1}$. This inconsistency can be easily overcome behind the harmonic approximation. The excitation energies derived from the diagonal phase integral are 744, 630, 649, and 617 $cm^{-1}$ for the HF/631G**, MP2/DZP, MP2/631GE, and DFT force fields, respectively. Here the usual characteristics of molecular force fields are conserved: the DFT gives usually most flat, shallow potentials, while the HF forces are overestimated.

Selected higher energy derivatives (related to dimensionless MP2/631GE normal coordinates) are given in Table 3. The constants vary by less than about 10% if calculated by HF, MP2, or DFT methods. The performances of LDA a nonlocal DFT are comparable, if the MP2 calculation is considered superior.

Spectral intensities are listed in Table 4. They approximately match experimental spectrum, although a qualitative comparison with the gaseous spectrum may be misleading. The dipolar strength for the first mode is surprisingly high, and the difference between the MP2 and DFT values rather big. We consider the MP2 values more realistic, since the mode is associated with a significant change of electronic structure on nitrogen ($sp^2 \rightarrow sp^3$) and large changes of dipole moment may be expected. For Raman intensities first polarizability derivatives were calculated only. Small vapor presure of formamide prevents a Raman measurement in the gas phase,[27] although spectra in the condensed phase were studied, see ref 28 and references therein. We want to point out a big influence of anharmonic forces on intensities and also polarization ratios of the hydrogen stretching modes.

Combinational transitions that should be visible in the absorption spectrum are listed in Table 5. The assignment is, however, more speculative than for fundamental transitions. Also, the convergence of eigenvectors is slower than that of energies. The DFT and MP2 calculations differ by the order of 100 $cm^{-1}$. An extensive rotational−vibrational coupling for combinational and hot transitions can be expected.

Calculated absorption spectra are compared to the experiment in Figure 2. Spectra were simulated with the bandwidth of 10 $cm^{-1}$. Calculated frequency of the $0 \rightarrow 1^2$ transition 830 $cm^{-1}$ is closer to the 770 $cm^{-1}$ band than previously assigned 658 $cm^{-1}$. The calculated frequency of the hot transition $1^1 \rightarrow 1^2$ (not shown in Figure 2) is 614 $cm^{-1}$. The calculations presented here are primarily optimized for fundamental transitions, and we feel that future work will be needed in the assignment of combinational modes. The nomenclature based on the harmonic basis may be misleading for higher excited states. Nevertheless good overall agreement between calculated and experimental frequencies is observed.

The contribution of second dipolar derivatives, as shown in Tables 4 and 5 and in Figure 2, is large for many transitions and can bring additional error to the intensities derived from first derivatives, calculated on a higher level of approximation. The intensity pattern of fundamental transitions is better described by first derivatives only. On the other side, second derivatives dominate in intensities of the combinational transitions.

**Rotational Constants.** Geometry changes caused by an anharmonic forces are usually too small for a direct comparison with experimental values.[8] Molecular rotational constants can

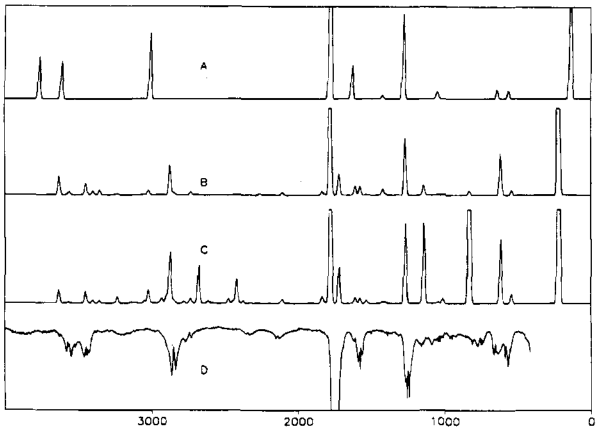

**Figure 2.** IR spectra of $HCONH_2$. (A) harmonic (MP2/631GE) approximation, (B) anharmonic force field, (C) anharmonic force field + second dipolar derivatives included, (D) experiment, redrawn from ref 2 (measured in a multiple-reflection cell, optical path set at 17.25 m, 20 °C, resolution 1 cm$^{-1}$). Arbitrary units on $y$ axis, one scale for A–C.

**TABLE 6: Rotational Constants for Nitrogen Wagging Excited States**[a]

| | calculation[b] | | | | | |
|---|---|---|---|---|---|---|
| const | $r_0$ | $\langle r\rangle$ | $H$ | $A$, MP2 | $A$, DFT | exp[c] |
| A$\|0\rangle$ | 2.4332 | 2.4044 | 2.3781 | 2.2931 | 2.3012 | 2.4256 |
| B$\|0\rangle$ | 0.3507 | 0.3480 | 0.3500 | 0.3467 | 0.3435 | 0.3537 |
| A$\|1\rangle$ | (0) | (−0.0195) | (−0.0869) | (−0.0934) | (−0.0635) | (−0.0327) |
| B$\|1\rangle$ | (0) | (0.0017) | (−0.0011) | (0.0002) | (0.0005) | (−0.0003) |
| A$\|2\rangle$ | (0) | (0.0081) | (−0.1738) | (−0.0986) | (−0.0730) | (−0.0450) |
| B$\|2\rangle$ | (0) | (0.0010) | (−0.0021) | (−0.0005) | (−0.0001) | (0.0000) |
| A$\|3\rangle$ | (0) | (0.0288) | (−0.2607) | (−0.0629) | (−0.0366) | (−0.0732) |
| B$\|3\rangle$ | (0) | (0.0027) | (−0.0032) | (−0.0010) | (0.0007) | (−0.0003) |
| error[d] (%) | | | 1.8 | 1.6 | 1.0 | |

[a] Constants in cm$^{-1}$, $B$ is an effective (averaged) rotational constant. [b] $r_0$, potential-well geometry (MP2/631GE); $\langle r\rangle$, constants calculated from average nuclear positions, H, harmonic limit; A, anharmonic values. In brackets the difference with respect to the ground state is given. [c] Reference 2. [d] Average error for a linear fit.

be, on the contrary, measured directly from a rotationally resolved spectra and serve as an indicator of geometry changes in various vibrational states. A second order expansion of the constants was used for calculation, $A(Q) = A_0 + A_iQ_i + A_{ij}Q_iQ_j$.

For the first, out-of-plane nitrogen wagging mode, the rotational constant $A$ was found to decrease from the ground state with a higher excitation, until the three-times excited mode.[2] An effective $B$ constant changes by less than 0.0003 cm$^{-1}$ for these four vibrational states. As can be seen in Table 6, both the MP2 and DFT calculations are in accord with this observation. For the three-times excited state, however, the change of constant $A$ is already underestimated. The density functional theory results are closer to experiment, except the change of A constant for the $|3\rangle$ state and the absolute value of the effective constant. Calculation on the harmonic level (H) reflects qualitatively changes of rotational constants, but the numbers are overestimated in most cases. Change of $A$ for the $|3\rangle$ state is higher by 260% than the experimental value, for example. Sole equilibrium ($r_0$) or potential minimum ($\langle r\rangle$) coordinates cannot be used to estimate correctly rotational constants in various vibrational states, as apparent from Table 6.

The DFT theory gives comparable bond lengths with the MP2 calculation (Table 7). Within given experimental accuracy it is difficult to separate the anharmonic contribution and the error of an electronic ab initio level.

**TABLE 7: Ground-State Geometry of $HCONH_2$**

| | harmonic | | anharmonic | | |
|---|---|---|---|---|---|
| $d$ (Å) | MP2 | DFT | MP2 | DFT | exp[30] |
| CN | 1.361 | 1.368 | 1.373 | 1.379 | 1.368 ± 0.003 |
| CO | 1.222 | 1.227 | 1.224 | 1.230 | 1.212 ± 0.003 |
| $NH_H$ | 1.007 | 1.014 | 0.991 | 1.001 | 1.027 ± 0.006 |
| NH | 1.010 | 1.017 | 1.005 | 1.013 | 1.027 ± 0.006 |
| CH | 1.105 | 1.115 | 1.116 | 1.126 | 1.125 ± 0.012 |

**TABLE 8: DFT Frequencies and Rotational Constants of Water**

| | frequencies [cm−$^1$] | | | rotational constants (cm−$^1$) | | |
|---|---|---|---|---|---|---|
| mode | exp | MP2 | DFT/harm | ref 29 | MP2 A/harm | DFT A/harm |
| 0 | 0 | 0 | 0 | 9.29 | 9.12/9.40 | 8.94/9.21 |
| | | | | 14.50 | 14.32/14.71 | 13.91/14.31 |
| | | | | 27.79 | 26.90/27.74 | 26.78/27.58 |
| $2^1$ | 1575 | 1565 | 1527/1601 | 9.12 | 9.05/9.29 | 8.87/9.11 |
| | | | | 14.70 | 14.47/14.97 | 14.00/14.56 |
| | | | | 30.70 | 29.52/29.46 | 29.62/29.34 |
| $2^2$ | 3151 | 3107 | 3019/3202 | 9.00 | 8.98/9.18 | 8.81/9.00 |
| | | | | 15.00 | 14.62/15.24 | 14.11/14.81 |
| | | | | 35.80 | 32.27/31.19 | 32.64/31.10 |
| $1^1$ | 3651 | 3679 | 3537/3687 | 9.20 | 8.99/9.54 | 8.80/9.35 |
| | | | | 14.47 | 14.21/14.93 | 13.78/14.53 |
| | | | | 26.50 | 26.36/28.12 | 26.24/27.97 |
| $3^1$ | 3756 | 3792 | 3637/3805 | | 8.80/9.35 | 8.80/9.35 |
| | | | | | 14.04/14.64 | 13.63/14.24 |
| | | | | | 25.43/27.61 | 25.23/27.45 |
| error (see Table 7) | | | | | 1.3/2.5 | 0.8/1.99 |

The water molecule was chosen, to further explore applications of a DFT anharmonic molecular force field. Here, a complete set of 56 less than 6 times excited states of the 3-dimensional oscillator was used in the vibrational Hamiltonian. The results are summarized in Table 8. Nonlocal DFT calulations yield strongly underestimated harmonic frequencies and, consequently, underestimated transitional frequencies. On the contrary, rotational constants compare well with the orbital (MP2/6311G**) computation. For example, the experimental constant $C = 27.79$ cm$^{-1}$ for the ground state decreases by 1.29 cm$^{-1}$ for the $1^1$ state. Both MP2 and DFT calculations give a decrease of 0.54 cm$^{-1}$, while the harmonic values increase. MP2 rotational constants are closer to experimental absolute values, while the DFT results better describe changes under vibrations, see the error of the linear fit.

## Conclusions

The harmonic basis set derived from phase integrals is more convenient and more universal for calculation of vibrational energies than a basis based on sole second energy derivatives.

The density functional theory yields anharmonic force constants comparable to values from an orbital calculations. The DFT is particularly suitable for calculation of changes of molecular geometry under vibrations, as was shown for rotational constants of water and formamide molecules.

Calculated frequencies and intensities for the formamide molecule are in a good overall agreement with the experiment, including the hydrogen out-of-plane wagging mode and lower combinational transitions.

**Acknowledgment.** The work was supported by the grant of the Academy of Sciences of the Czech Republic (203/93/0714).

## Appendix

*Algorithm for Diagonalization of Large Matrixes.* The eigenvalue problem $\mathbf{A}\cdot\mathbf{X} = \lambda\mathbf{X}$ for a real symmetric matrix $\mathbf{A}$ of dimension $N$ is solved by a modified Mitin's algorithm[18] based on minimization of Rayleigh functional. The eigenvectors are built subsequently according to their ascending eigenvalues.

1. Select initial dimension of the iterative subspace $M$ for the *lth* eigenvalue, $2 < M \leq N - l + 1$; $M = 2$ for $l = N - 1$ and $M = 1$ for $l = N$.

2. Estimate the *lth* eigenvector $\mathbf{X}_1 = \mathbf{E}^l$ as a unit vector, $\mathbf{E}^l = (N)^{-1/2}$ (1, 1, ...., 1)$^t$ and the starting eigenvalue $\lambda_l$ ($\lambda_1 = 0$, $\lambda_l = \lambda_{l-1}$ for $l > 1$).

3. Orthogonalize $\mathbf{X}_1$ to previous eigenvectors $\mathbf{E}^i$, $i = 1, 2, ..., l - 1$ and normalize.

4. Form gradient vectors $\mathbf{X}_i$, $i = 2, 3, ..., M$, as

$$\mathbf{X}_i = (\mathbf{A} - \lambda_l \mathbf{1})\cdot\mathbf{X}_{i-1}$$

where **1** is the unit matrix. Orthogonalize each $\mathbf{X}_i$ to $\{\mathbf{X}_k, k = 1, 2, ..., i - 1\}$ and to the eigenvectors $\{\mathbf{E}^j, j = 1, 2, ..., l - 1\}$ and normalize.

5. Check convergence on gradient, gradient = norm of $\mathbf{X}_2$ before normalization. If gradient < *gradlimit* change $l$ to $l + 1$ and go to 1 (if next eigenvector is desired).

6. Form vectors $\mathbf{A}\cdot\mathbf{X}_i$ and the subspace $M \times M$ matrix $\mathbf{F} = \mathbf{X}^{t}\cdot\mathbf{A}\cdot\mathbf{X}$.

7. Diagonalize **F** and take the lowest eigenvalue $\lambda_F$: $\mathbf{F}\cdot\mathbf{Y}^F = \lambda_F\mathbf{Y}^F$. Order the eigenvalues ($\lambda_F = \lambda_1 \leq \lambda_2 \leq ... \leq \lambda_M$).

8. Take new approximation of the eigenvalue $\lambda_l = \lambda_F$ and of the eigenvector $\mathbf{E}^l = \sum_{i=1}^{M} \mathrm{Y}^F{}_i\mathbf{X}_i$.

9. Check if the subspace is not redundant: if for some $M'|\mathbf{Y}^p|\langle\Delta$ for all $p = M' + 1, ..., M$, then $M = M'$.

10. Go to 4.

By the value of $M$ the speed of calculation and computer memory requirements can be tuned. The algorithm becomes a direct diagonalization for $M = N$ and is equivalent to a conjugate gradient method for $M = 3$. The algorithm can be used for the generalized problem $\mathbf{A}\cdot\mathbf{X} = \lambda\mathbf{B}\cdot\mathbf{X}$, if the form $\mathbf{X}_i = (\mathbf{A} - \lambda_l\mathbf{B})\cdot\mathbf{X}_{i-1}$ is used in 4 and $\mathbf{F}\cdot\mathbf{Y}^F = \lambda_F\mathbf{S}\cdot\mathbf{Y}^F$ is solved in 6, with $\mathbf{S} = \mathbf{X}^t.\mathbf{B}\cdot\mathbf{X}$. By a nonzero value of $\Delta$ greater numerical stability was observed than for $\Delta = 0$.

Values used for the 1737 × 1737 vibrational matrix of $HCONH_2$ are as follows:

Average magnitude of matrix element $a = 5$ cm$^{-1}$

Average magnitude of diagonal element $d = 6551$ cm$^{-1}$

*gradlimit* = sqrt(0.00000001$dN$)

Starting value of $M = 50$

$\Delta = 0.001$.

## References and Notes

(1) Hrouda, V.; Florian, J.; Polášek M; Hobza, P. *J. Phys. Chem.* **1994**, *98*, 4742.

(2) Sugawara, Y.; Hamada, Y.; Tsuboi, M. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1045.

(3) Suzuki, I. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 1359.

(4) King, S. T. *J. Phys. Chem.* **1971**, *75*, 405.

(5) Kwiatowski, J. S.; Leszynski, J. *J. Mol. Struct.* **1993**, *297*, 277.

(6) Florian, J.; Johnson, B. G. *J. Phys. Chem.* **1994**, *98*, 3681.

(7) Østergård, N.; Christiansen, P. L.; Nielsen, O. F. *J. Mol. Struct. (THEOCHEM)* **1991**, *235*, 423.

(8) Bouř, P. *J. Phys. Chem.* **1994**, *98*, 8862.

(9) Meyer, R. *J. Chem. Phys.* **1970**, *52*, 2053.

(10) Beil, A.; Luckhaus, D.; Marquardt, R.; Quack, M. *Faraday Discuss.*, in press.

(11) Blochincev, D. I. *Osnovy Kvantovoy Mechaniky,* Nauka: Moskva 1976; Chapter 37.

(12) Luck, A. P. W.; Wess, T. *Can. J. Chem.* **1991**, *69*, 1819.

(13) Papoušek, D.; Aliev, M. R. *Molecular Vibration-Rotational Spectra*; Academia: Prague, 1982.

(14) Green, W. H. Jr.; Willetts, A.; Jayatilaka, D.; Handy, N. C. *Chem. Phys. Let.* **1990**, *169*, 127.

(15) van Lenthe, J. H.; Pulay, P. *J. Comput. Chem.* **1990,** *11*, 1164.

(16) Gourlay, A. R.; Watson, G. A. *Computational Methods for Matrix Eigenproblems;* John Wiley & Sons: London, 1993.

(17) Davidson, E. R. *J. Comput. Phys.* **1975**, *17*, 87.

(18) Mitin, A. V. *J. Comput. Chem.* **1994**, *15*, 747.

(19) Amos, R. D. CADPAC version 5; SERC Laboratory: Daresbury, U.K., 1994.

(20) 631GE: a standard basis set of CADPAC, obtained by an extension from 631G by adding diffuse s and p functions with exponent one third that of the lowest exponent in the parent basis and by using two sets of polarization functions.

(21) DZP basis: double-ζ basis (see: Dunning, *J. Chem. Phys.* **1970**, *53*, 2823) + polarization functions.

(22) St-Amant, A. DeFT; Department of Chemistry, University of Ottawa: Ottawa, Canada, 1992.

(23) Sim, F.; St-Amant, A.; Papai, I.; Salahub, D. R. *J. Am. Chem. Soc.* **1992**, *114*, 4391.

(24) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(25) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(26) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(27) Vladimír Baumruk, Charles University, personal communication.

(28) Mortensen, A.; Nielsen, O. F.; Yarwood, J.; Shelley, V. *J. Phys. Chem.* **1994**, *98*, 5221.

(29) *Landolt-Börnstein Molekelnkonstanten*; Springer-Verlag: Berlin, 1951.

(30) Kitano, K.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 67.

JP9431907