# THEORETICAL QUANTITATIVE SPECTROSCOPY: COMPUTER SIMULATION OF MOLECULAR SPECTRA

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**Abstract.** We present the results of theoretically simulating, by variational methods, rotation-vibration spectra of $NH_3$ and $PH_3$. The simulations carried out for $NH_3$ are based solely on *ab initio* calculations, i.e., they are purely theoretical and involve no fitting to experiment. The $PH_3$ simulations are made from a potential energy function refined to reproduce experimental data and from an *ab initio* dipole moment function. We show that our simulations reproduce observed rotation-vibration intensities with an accuracy approaching that obtained in fittings to these intensities in terms of models involving an effective dipole moment operator. Our results suggest that theoretical simulations of spectra are now close to attaining a level of accuracy where they can successfully compete with quantitative-spectroscopy measurements of intensities and thus assist in the interpretation of remote-sensing spectra.

**Keywords:** spectrum simulations, line intensities, $NH_3$, $PH_3$

## 1. Introduction

In atmospheric studies, remote-sensing techniques are important tools for determining molecular concentrations in the upper layers of the atmosphere. These techniques employ the methodology of high-resolution molecular spectroscopy;

*A. Perrin et al. (eds.), Remote Sensing of the Atmosphere for Environmental Security*, 171–183.

in principle the molecular concentrations are obtained from experimental molecular spectra. To determine a molecular concentration, or a column density, from the measured intensity of a molecular transition in emission or absorption, it is necessary to know the ‘molecule-intrinsic’ factors that influence the intensity, in particular the line strength (see below). Obviously line strength values can be obtained from laboratory measurements of intensities for molecules with known concentrations. Such measurements, however, appear to be exceedingly difficult. For example, for the molecules ozone $O_3$ and formaldehyde $H_2CO$, there exist several recent measurements of the intensities of the same molecular transitions whose results seriously disagree (Flaud, 2005). It is sometimes said that in present-day science, computer simulation of phenomena occurring in nature constitutes an alternative not only to experiment, but also to traditional theoretical work involving (simple) mathematical models. Computer simulations of rotation-vibration spectra are a potential alternative to the very difficult experimental intensity measurements. Also, they can assist in the assignment of complicated spectra, in locating ‘dark’ states, and in providing spectral information about molecules under conditions where the experiment is difficult.

In exploratory calculations, we have sought to assess the accuracy to which the simulation of rotation-vibration spectra can be carried out. As example molecules, we have chosen $NH_3$ and $PH_3$ for which there is a large amount of experimental wavenumber and intensity data available for comparison with the simulations. For selected bands of $^{14}NH_3$ and $^{31}PH_3$, we have made detailed simulations of the rotational structure. The calculations are carried out by means of recently developed computational procedures for describing the nuclear motion and are based on a high-level *ab initio* potential energy surface, and high-level dipole moment surfaces, for the electronic ground states of $NH_3$ and $PH_3$ [see Lin *et al.* (2002) and Yurchenko *et al.* (2003; 2005a; 2005b; 2005c; 2005d; 2005f)].

The paper is structured as follows: In Section 2 we give a very brief outline of the theory involved in the direct computer simulation of spectra by variational methods that we present here. Section 3 describes some of the results we have obtained, and Section 4 offers conclusions.

## 2. Theory

### 2.1. THE LINE STRENGTH

The intensities of electric dipole absorption transitions are determined by the absorption coefficient $\epsilon(\tilde{\nu})$ entering into the Lambert-Beer law [see, for example, Bunker & Jensen (2004)]; $\epsilon(\tilde{\nu})$ depends on the absorption wavenumber $\tilde{\nu}$. If we assume the absorbing molecules to be in thermal equilibrium at an absolute temperature $T$, the integral of $\epsilon(\tilde{\nu})$ over an absorption line is given as

$$\begin{aligned} I(f \leftarrow i) &= \int_{\text{Line}} \epsilon(\tilde{\nu})\, d\tilde{\nu} \\ &= \frac{8\pi^3 N_A \tilde{\nu}_{if}}{(4\pi\epsilon_0)3hc} \frac{\mathrm{e}^{-E_{\text{rve}}^{(n'',j'')}/kT}}{Q} [1 - \exp(-hc\tilde{\nu}_{if}/kT)]\, S(f \leftarrow i). \end{aligned} \tag{1}$$

This expression is valid for the transition from the state $i$ with energy $E_{\text{rve}}^{(n'',j'')}$ to the state $f$ with energy $E_{\text{rve}}^{(n',j')}$, where $hc\tilde{\nu}_{if} = E_{\text{rve}}^{(n',j')} - E_{\text{rve}}^{(n'',j'')}$, $N_A$ is the Avogadro constant, $h$ is Planck's constant, $c$ is the speed of light in vacuum, $k$ is the Boltzmann constant, $\epsilon_0$ is the permittivity of free space, and, finally, $Q$ is the partition function defined as $Q = \sum_j g_j \exp(-E_j/kT)$, where $g_j$ is the total degeneracy of the state with energy $E_j$ and the sum runs over all energy levels of the molecule. Experimental values of $I(f \leftarrow i)$ are obtained by numerical integration of experimentally determined $\epsilon(\tilde{\nu})$-values.

The 'molecule-intrinsic' factor $S(f \leftarrow i)$ in Eq. 1 is called the *line strength*. It is given as

$$S(f \leftarrow i) = \sum_{\Phi_{\text{rve}}^{(n',j')},\Phi_{\text{rve}}^{(n'',j'')}} \sum_{A=X,Y,Z} \left| \left\langle \Phi_{\text{rve}}^{(n',j')} \right| \mu_A \left| \Phi_{\text{rve}}^{(n'',j'')} \right\rangle \right|^2 \tag{2}$$

where $\Phi_{\text{rve}}^{(n',j')}$ and $\Phi_{\text{rve}}^{(n'',j'')}$ are eigenfunctions of the molecular Hamiltonian corresponding to the eigenvalues $E_{\text{rve}}^{(n',j')}$ and $E_{\text{rve}}^{(n'',j'')}$, respectively. In the case of degeneracies, that is if there is more than one eigenfunction $\Phi_{\text{rve}}^{(n',j')}$ (or $\Phi_{\text{rve}}^{(n'',j'')}$) corresponding to the eigenvalue $E_{\text{rve}}^{(n',j')}$ (or $E_{\text{rve}}^{(n'',j'')}$), we obtain the line strength by adding the individual transition probabilities for all transitions between the degenerate states; this is indicated by the sum over $\Phi_{\text{rve}}^{(n',j')}$ and $\Phi_{\text{rve}}^{(n'',j'')}$ in Eq. 2. In this equation, $\mu_A$ is the component of the molecular dipole moment operator along the $A$ axis ($A = X$, $Y$, or $Z$); the $XYZ$ axis system having origin at the molecular center of mass and space fixed orientation. The operator $\mu_A$ is given by $\mu_A = \sum_q e_q A_q$ with $e_q$ and $A_q$ as the charge and $A$ coordinate of the $q$th particle in the molecule, where $q$ runs over all nuclei and electrons.

The intensities of electric dipole emission transitions are determined from the Einstein coefficients [see, for example, Penner (1959) or Woodgate (1970)]; these coefficients are proportional to the line strength in Eq. 2 as explained in Section 2.2 of Yurchenko *et al.* (2005b).

In the Born-Oppenheimer approximation [see, for example, Bunker & Jensen (2000)], the rovibronic wavefunction of a molecule is expressed as

$$\Phi_{\text{rve}}^{(n,j)} = \Phi_{\text{elec}}^{(n)}\, \Phi_{\text{rv}}^{(n,j)} \tag{3}$$

where $\Phi_{\text{elec}}^{(n)}$ is the electronic wavefunction, depending on electronic and nuclear coordinates, and $\Phi_{\text{rv}}^{(n,j)}$ is the nuclear wavefunction, depending on the nuclear coordinates only. The index $n$ labels the electronic states, and $j$ labels the rovibrational states associated with a given electronic state. The wavefunction $\Phi_{\mathrm{elec}}^{(n)}$ is an eigenfunction of the electronic Hamiltonian, obtained with the nuclei fixed in space, and the corresponding eigenvalue is the Born-Oppenheimer potential energy function $V_{\mathrm{BO}}$ which depends on the nuclear coordinates.

Having determined $V_{\mathrm{BO}}$ as a function of the nuclear coordinates in *ab initio* calculations, we solve the rotation-vibration Schrödinger equation

$$\hat{H}_{\mathrm{rv}}\Phi_{\mathrm{rv}}^{(n,j)} = E_{\mathrm{rv}}^{(n,j)}\Phi_{\mathrm{rv}}^{(n,j)}, \tag{4}$$

with

$$\hat{H}_{\mathrm{rv}} = \hat{T}_{\mathrm{rv}} + V_{\mathrm{BO}}, \tag{5}$$

where $\hat{T}_{\mathrm{rv}}$ is the kinetic energy operator associated with rotation and vibration.

As a first step towards computing the matrix elements in the expression for the line strength (Eq. 2), we express the space-fixed dipole moment components in terms of the components $(\mu_x, \mu_y, \mu_z)$ along the *molecule-fixed axes xyz*. This axis system is chosen such that it follows the rotational motion of the molecule; for details of the general theory see, for example, Papoušek & Aliev (1982), Bunker & Jensen (1998), or Sarka & Demaison (2000), and for the application to $XY_3$ molecules, see Yurchenko *et al.* (2005a). We have

$$\mu_A = \sum_{\alpha=x,y,z} \lambda_{\alpha A}\, \mu_\alpha, \tag{6}$$

where the $\lambda_{\alpha A}$ are direction cosines [see, for example, Bunker & Jensen (1998)] effecting the transformation between the $xyz$ and $XYZ$ axis systems.

When we consider the intensities of transitions within a single electronic state $\Phi_{\mathrm{elec}}^{(n)}$, they depend on the electronically averaged dipole moment

$$\bar{\mu}_\alpha^{(n)} = \left\langle \Phi_{\mathrm{elec}}^{(n)} \,|\, \mu_\alpha \,|\, \Phi_{\mathrm{elec}}^{(n)} \right\rangle_{\mathrm{el}}, \quad \alpha = x, y, z; \tag{7}$$

where the subscript ‘el’ indicates that integration is over the electronic coordinates only. The quantity $\bar{\mu}_\alpha$ depends on the nuclear coordinates and, for given values of these coordinates, we can calculate the value of $\bar{\mu}_\alpha$ by *ab initio* methods.

### 2.2. VARIATIONAL CALCULATIONS

Experimental intensity studies normally analyze the observed intensities in terms of a model involving an *effective Hamiltonian* and an *effective dipole moment operator* [see Papoušek & Aliev (1982) or the review articles by Aliev & Watson (1985) and Sarka & Demaison (2000), respectively]; these operators are obtained from the nuclear Hamiltonian $\hat{H}_{\mathrm{rv}}$ and the dipole moment components $\mu_A$ ($A = X, Y, Z$), respectively, by means of perturbation theory and contain parameters whose values can be determined in fittings to experimental data. In a variational calculation we – at least initially – calculate the energies and intensities from first principles. We solve the Schrödinger equation in Eq. 4 by diagonalizing numerically (i.e., without the use of perturbation theory) a matrix representation of $\hat{H}_{\mathrm{rv}}$ set up in a suitable basis set. The potential energy function $V_{\mathrm{BO}}$ is represented by a suitable parameterized function, the parameter values being determined by fitting to a set of $V_{\mathrm{BO}}$-values obtained *ab initio*. In the present work, we are concerned with variational calculations for $XY_3$ pyramidal molecules, for which we choose the basis functions so that the rotation-vibration wavefunctions $|\Phi_{\mathrm{rv}}^{(n,j)}\rangle$ can be expressed as given in Eq. (65) of Yurchenko *et al.* (2005a):

$$|\Phi_{\mathrm{rv}}^{(n,j)}\rangle = \sum_{VK\tau_{\mathrm{rot}}} C_{VK\tau_{\mathrm{rot}}}^{(n,j)} \, |V\rangle \, |J\,K\,m\,\tau_{\mathrm{rot}}\rangle, \; K \geq 0, \tag{8}$$

where $C_{VK\tau_{\mathrm{rot}}}^{(n,j)}$ is an expansion coefficient obtained as an eigenvector component in the diagonalization of the Hamiltonian matrix (Yurchenko *et al.*, 2005a), and the vibrational basis functions $|V\rangle$ are

$$|V\rangle = \; |n_1\rangle \, |n_2\rangle \, |n_3\rangle \, |n_{\mathrm{b}}, l_{\mathrm{b}}, \tau_{\mathrm{bend}}\rangle \, |n_{\mathrm{i}}, J, K, \tau_{\mathrm{inv}}\rangle; \tag{9}$$

$V$ is used as a short-hand notation for all the quantum numbers and symmetry labels $n_1$, $n_2$, $n_3$, $n_{\mathrm{b}}$, $l_{\mathrm{b}}$, $\tau_{\mathrm{bend}}$, $n_{\mathrm{i}}$, and $\tau_{\mathrm{inv}}$ that label the vibrational basis functions. All the functions $|J\,K\,m\,\tau_{\mathrm{rot}}\rangle$, $|n_1\rangle$, $|n_2\rangle$, $|n_3\rangle$, $|n_{\mathrm{b}}, l_{\mathrm{b}}, \tau_{\mathrm{bend}}\rangle$, and $|n_{\mathrm{i}}, J, K, \tau_{\mathrm{inv}}\rangle$ occurring in Eqs. 8-9, and the quantum numbers labeling them, are defined in detail in Yurchenko *et al.* (2005a): $|J\,K\,m\,\tau_{\mathrm{rot}}\rangle$ is a symmetrized rotational wavefunction defined in Eqs. (66) and (67) of Yurchenko *et al.* (2005a), $|n_1\rangle$, $|n_2\rangle$, and $|n_3\rangle$ are one-dimensional Morse oscillator eigenfunctions describing the stretching motion of the $XY_3$ molecule, $|n_{\mathrm{b}}, l_{\mathrm{b}}, \tau_{\mathrm{bend}}\rangle$ is a symmetrized eigenfunction of the two-dimensional harmonic oscillator modelling the small-amplitude bending motion, and $|n_{\mathrm{i}}, J, K, \tau_{\mathrm{inv}}\rangle$ is a symmetrized inversion basis function obtained by numerical solution of a zero-order inversion Schrödinger equation. Concerning the quantum numbers, it suffices to say here that each of the three quantum numbers $\tau_{\mathrm{rot}}$, $\tau_{\mathrm{bend}}$, and $\tau_{\mathrm{inv}}$ assumes the values 0 or 1 in such a way that the parity (Bunker & Jensen, 1998) of $|J\,K\,m\,\tau_{\mathrm{rot}}\rangle$ is $(-1)^{\tau_{\mathrm{rot}}}$, the parity of $|n_{\mathrm{b}}, l_{\mathrm{b}}, \tau_{\mathrm{bend}}\rangle$ is $(-1)^{\tau_{\mathrm{bend}}}$, and the parity of $|n_{\mathrm{i}}, J, K, \tau_{\mathrm{inv}}\rangle$ is $(-1)^{\tau_{\mathrm{inv}}}$.

As a prerequisite to computing line strengths from the variationally-determined wavefunctions in Eq. 8, we compute *ab initio* values of the electronically averaged dipole moment (Eq. 7) and fit analytical, parameterized functions through the computed values. We then simply insert Eqs. 6, 7, and 8 in the expression for the line strength (Eq. 2). The resulting expression is simplified by use of the techniques described, for example, in Chapter 14 of Bunker & Jensen (1998) and the simplified form can be used for computing the line strengths numerically. The application of this strategy to $XY_3$ pyramidal molecules is described in detail by Yurchenko *et al.* (2005b; 2005c). Analogous work for triatomic molecules is described by Jensen & Špirko (1986) and by Jensen (1988) [see also Tennyson (2000) and references therein]. Having made the initial, *ab initio* calculation of molecular energies and line strengths we can, of course, refine the parameters of the analytical representations of the potential energy and the dipole moment components by fitting to experimental data.

In the variational approach to calculating intensities, *resonances* (i.e., energetically close-lying vibrational states) cause no problems. All resonances are explicitly treated in the variational calculation and, in consequence, the resulting intensity stealing (Bunker & Jensen, 1998) is accounted for. This is in contrast to the conventional theoretical approach involving an effective Hamiltonian and an effective dipole moment operator, where the theoretical model must normally be modified to describe the resonances of a particular molecule so that different models are sometimes required for isotopically substituted molecules.

## 3. Applications

We present here some results of applying our spectrum-simulation computer program to the molecules $^{14}NH_3$, $^{15}NH_3$, and $^{31}PH_3$. The calculations for $^{14}NH_3$ and $^{15}NH_3$ are based on the *ab initio* potential energy surface CBS**-51816 described in detail by Yurchenko *et al.* (2005d) [see also Lin *et al.* (2002)]. Further, we employ the *ab initio* ATZfc dipole moment function described by Yurchenko *et al.* (2005b; 2005c). Thus it should be noted that the $NH_3$ calculations presented here are purely theoretical; they do not involve any fitting to experiment.

The simulations are made with a basis set [see Yurchenko *et al.* (2005b)] defined by

$$P = 2(n_1 + n_2 + n_3) + n_i + n_b \leq 8, \tag{10}$$

where the principal quantum numbers $n_1$, $n_2$, $n_3$, $n_i$, and $n_b$ are defined in connection with Eq. 9; we consider transitions involving states with $J \leq 18$. In calculating the integrated absorption coefficients from Eq. 1, we set $T = 295$ K, the temperature appropriate for the experimental spectra (Cottaz *et al.*, 2000; Fabian *et al.*, 1995; Kleiner *et al.*, 1995; Kleiner *et al.*, 1999) with which we compare the simulations, and we use a value of the partition function obtained at this temperature from the $J \leq 18$ term values calculated variationally below 6000 cm$^{-1}$ [see Yurchenko *et al.* (2005b)].

In Fig. 1 we show simulations of the $\nu_1$, $\nu_2$, $\nu_3$, and $\nu_4$ fundamental absorption bands of $^{14}NH_3$. In these stick diagrams, the heights of the sticks represent integrated absorption coefficients computed from Eq. 1 in units of cm$^{-2}$ atm$^{-1}$. The $\nu_1$ and $\nu_3$ bands are artificially separated according to the assignment of the upper state. That is, in the 3000–3800 cm$^{-1}$ wavenumber region we plot in

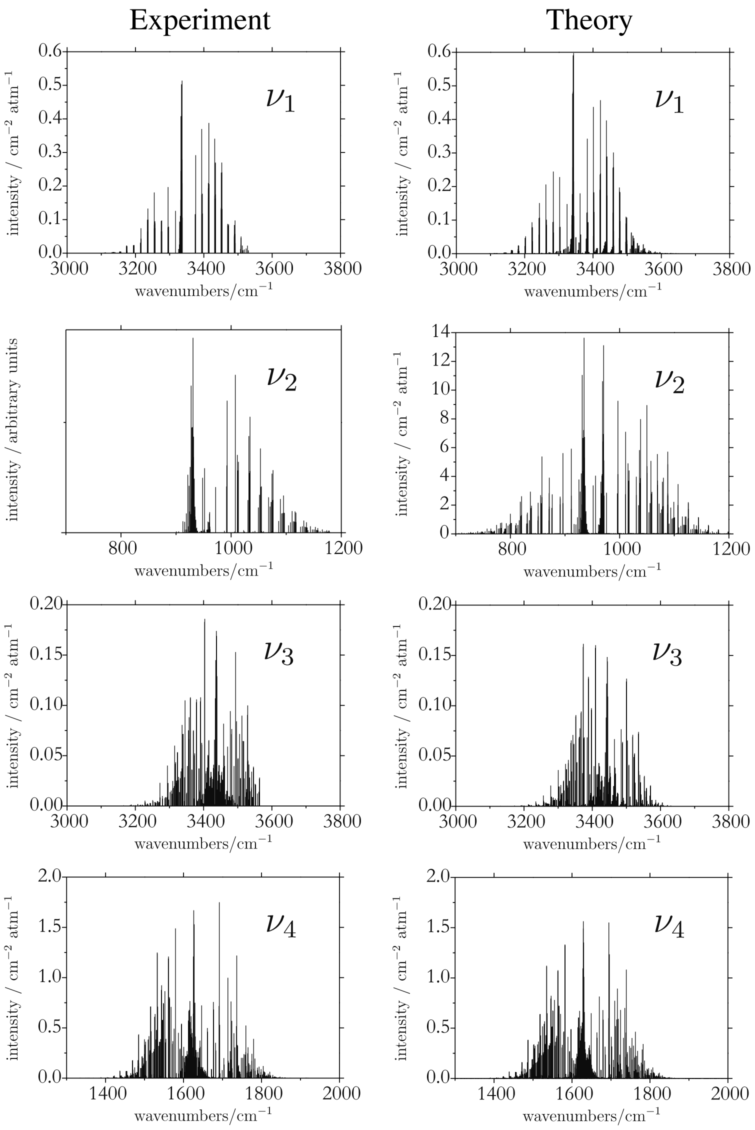

*Figure 1.* Comparison of simulated and observed absolute intensities for the $\nu_1$ (Kleiner *et al.*, 1999), $\nu_2$ (Fabian *et al.*, 1995), $\nu_3$ (Kleiner *et al.*, 1999), and $\nu_4$ (Cottaz *et al.*, 2000) bands of $^{14}NH_3$, where the references are to the experimental work providing the observed intensities. For the $\nu_2$ band, the only available experimental intensity data are relative intensities for transitions in the wavenumber region 900–1180 cm$^{-1}$ (Fabian *et al.*, 1995).

*Table 1.* Calculated integrated absorption coefficients $I_{\mathrm{calc}}$ (in cm$^{-2}$ atm$^{-1}$) for the strongest rotation-vibration transitions in the $\nu_1$ bands of $^{14}$NH$_3$ and $^{15}$NH$_3$, together with the available observed transition wavenumbers $\tilde{\nu}_{\mathrm{obs}}$ (in cm$^{-1}$) and intensities $I_{\mathrm{obs}}$ (in cm$^{-2}$ atm$^{-1}$) for $^{14}$NH$_3$ (Kleiner *et al.*, 1999). In the transition labels, $J_i$, $K_i$, and $\Gamma_i$ ($J_f$, $K_f$, $\Gamma_f$) are the $J$-value, $K$-value, and $\boldsymbol{D}_{3\mathrm{h}}$(M) rotation-vibration symmetry, respectively, of the initial (final) state. The relative deviation $\Delta(\%) = 100 \times |I_{\mathrm{obs}} - I_{\mathrm{calc}}|/I_{\mathrm{obs}}$.

| | | | | | | $^{14}$NH$_3$ | | | | $^{15}$NH$_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $J_i$ | $K_i$ | $\Gamma_i$ | $J_f$ | $K_f$ | $\Gamma_f$ | $\tilde{\nu}_{\mathrm{obs}}$ | $I_{\mathrm{obs}}$ | $I_{\mathrm{calc}}$ | $\Delta(\%)$ | $I_{\mathrm{calc}}$ |
| 3 | 3 | $A''$ | 3 | 3 | $A'$ | 3336.39046 | 0.514 | 0.598 | 16.3 | 0.598 |
| 3 | 3 | $A'$ | 3 | 3 | $A''$ | 3334.59825 | 0.503 | 0.591 | 17.5 | 0.592 |
| 6 | 6 | $A'$ | 6 | 6 | $A''$ | 3333.02520 | 0.408 | 0.482 | 18.1 | 0.489 |
| 6 | 6 | $A''$ | 6 | 6 | $A'$ | | | 0.477 | | 0.484 |
| 3 | 0 | $A'$ | 4 | 0 | $A''$ | 3414.63633 | 0.388 | 0.457 | 17.8 | 0.430 |
| 2 | 0 | $A''$ | 3 | 0 | $A'$ | 3393.80352 | 0.370 | 0.437 | 18.1 | 0.415 |
| 4 | 0 | $A''$ | 5 | 0 | $A'$ | 3431.88520 | 0.341 | 0.397 | 16.4 | 0.369 |
| 1 | 0 | $A'$ | 2 | 0 | $A''$ | 3367.26976 | 0.292 | 0.343 | 17.5 | 0.330 |
| 4 | 4 | $E'$ | 4 | 4 | $E''$ | 3335.97602 | 0.278 | 0.287 | 3.2 | 0.300 |
| 4 | 3 | $A''$ | 4 | 3 | $A'$ | | | 0.294 | | 0.302 |
| 4 | 3 | $A'$ | 4 | 3 | $A''$ | 3335.63576 | 0.277 | 0.291 | 5.1 | 0.299 |
| 4 | 4 | $E''$ | 4 | 4 | $E'$ | 3334.16807 | 0.272 | 0.283 | 4.0 | 0.296 |
| 5 | 0 | $A'$ | 6 | 0 | $A''$ | 3452.52248 | 0.270 | 0.302 | 11.9 | 0.280 |
| 4 | 3 | $A''$ | 5 | 3 | $A'$ | 3433.97824 | 0.270 | 0.290 | 7.4 | 0.277 |
| 4 | 3 | $A'$ | 5 | 3 | $A''$ | 3432.22513 | 0.267 | 0.287 | 7.5 | 0.274 |
| 5 | 5 | $E''$ | 5 | 5 | $E'$ | 3335.47572 | 0.258 | 0.261 | 1.2 | 0.276 |
| 5 | 5 | $E'$ | 5 | 5 | $E''$ | 3333.64481 | 0.245 | 0.258 | 5.3 | 0.272 |

separate displays the transitions to the $\nu_1$ and $\nu_3$ states, respectively. Each simulated band is compared to an ‘experimentally derived’ stick spectrum drawn with experimental values for transition wavenumbers and intensities taken from Kleiner *et al.* (1999) for $\nu_1$ and $\nu_3$, Fabian *et al.* (1995) for $\nu_2$, and Cottaz *et al.* (2000) for $\nu_4$. The experimentally derived spectra show only the transitions assigned in the respective experimental studies (Kleiner *et al.*, 1999; Fabian *et al.*, 1995; Cottaz *et al.*, 2000) and this explains why the experimental spectra generally contain less lines than the simulated ones. Note that the same absolute intensity scale is used for the two members of each theoretical/experimental spectrum pair except in the case of the $\nu_2$ band, where the experimental results from Fabian *et al.* (1995) are given in arbitrary units as these authors report relative intensities only. In this case, we have drawn the ‘Experimental’ display such that the stick representing the strongest absorption transition has the same height as in the corresponding ‘Theory’ display. Furthermore, Fabian *et al.* (1995) recorded spectra in the wavenumber region 900–1180 cm$^{-1}$ only; this explains the lack of lines below 900 cm$^{-1}$ in the ‘Experimental’ $\nu_2$ display of Fig. 1.

We calculate the vibrational transition moment of the $\nu_1$ band as $\mu_{if}$(Calc.) = 0.027 D, in very good agreement with the experimental value $\mu_{if}$(Obs.) =

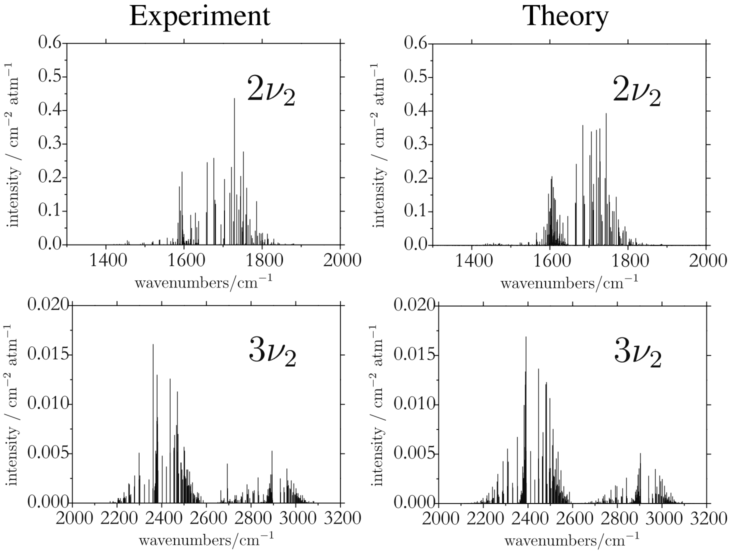

*Figure 2.* Comparison of simulated and observed absolute intensities for the $2\nu_2$ (Cottaz *et al.*, 2000) and $3\nu_2$ (Kleiner *et al.*, 1995) bands of $^{14}$NH$_3$, where the references are to the experimental work providing the observed intensities.

0.0262(1) D (Kleiner *et al.*, 1999), where we give in parentheses the quoted uncertainty in units of the last digit. For this band, we present in Table I the integrated absorption coefficients for the strongest, individual rotation-vibration transitions of $^{14}$NH$_3$ and $^{15}$NH$_3$. In the table, the states involved in the transitions are labeled by the 'standard' quantum numbers $J$ and $K$ together with $\Gamma$, the rovibrational symmetry in the molecular symmetry group $\boldsymbol{D}_{3\mathrm{h}}$(M) (Bunker & Jensen, 1998) of NH$_3$. For $^{14}$NH$_3$, the calculated intensity values are compared with experimental values from Kleiner *et al.* (1999). Two strong calculated lines, $^{Q}Q$ transitions with $(J_i, K_i)$ = (4,3) and (6,6), respectively, apparently have not been assigned since they cannot be found in Appendix 1 of Kleiner *et al.* (1999) but for completeness we include their calculated intensities in Table I. The calculated intensities in the table are systematically larger than the measured ones, in keeping with the fact that $\mu_{if}$(Calc.) > $\mu_{if}$(Obs.). For the 15 transitions in Table I, where a comparison between theory and experiment is possible, the percentage deviation $\Delta$(%) lies between 1.2% and 18.1% with an average of 11.2%.

In Fig. 2, we compare the simulations of the overtone band $2\nu_2$, and the second-overtone band $3\nu_2$, of $^{14}$NH$_3$ with experiment in a manner analogous to the comparisons in Fig. 1. For the $2\nu_2$ and $3\nu_2$ bands, the experimental intensities are determined by Cottaz *et al.* (2000) and Kleiner *et al.* (1995), respectively.

We compare in Fig. 3 simulations of the $\nu_2$ and $\nu_4$ fundamental absorption bands of $^{31}$PH$_3$ with experimental results (Brown *et al.*, 2002). The simulations

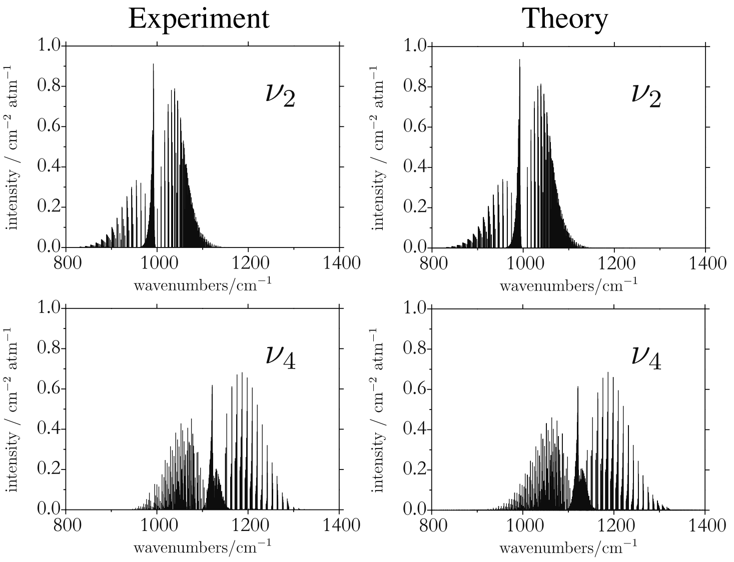

*Figure 3.* Comparison of simulated and observed absolute intensities for the $\nu_2$ and $\nu_4$ fundamental bands of $PH_3$. The observed intensities are from Brown *et al.* (2002).

are made with a ‘spectroscopic’ potential energy surface, obtained by adjusting the *ab initio* CCSD(T)/aug-cc-pVTZ potential energy surface from Wang *et al.* (2000) in a simultaneous fit to *ab initio* data and to the available, experimentally determined vibrational term values of $PH_3$. The $PH_3$ potential energy surface and the dipole moment surface employed in the present work will be described elsewhere (Yurchenko *et al.*, 2005e). The potential energy surface is a further refinement of that reported by Yurchenko *et al.* (2003) and used by Yurchenko *et al.* (2005f) to calculate the rotational energy structure for $J \leq 80$ in the vibrational ground state of $PH_3$. Yurchenko *et al.* (2005f) showed that the rotational levels form near-degenerate six-fold energy clusters analogous to the four-fold clusters formed in triatomic dihydrides $H_2X$ (see, for example, Jensen (2000) and references therein). In the $PH_3$ calculations of the present work, we considered states with $J \leq 18$, and we used the basis set defined by Eq. 10.

## 4. Conclusion

One of the most important aims of our theoretical work is to assist the interpretation and understanding of high-resolution molecular spectroscopy experiments. We have already been able (Yurchenko *et al.*, 2005a) to provide assistance of this kind in that, with our calculated values for the rotational energies in the $4\nu_2^+$ vibrational state of $^{14}NH_3$, we could verify (and, for a few transitions, refute) the tentative assignment to the $4\nu_2^+$ band made by Kleiner *et al.* (1999) for 55 weak transitions that they had observed in their experimental study of the $\nu_1$, $\nu_3$, and $2\nu_4$ bands of $^{14}NH_3$. Also, it is obvious that there is a high degree of similarity between the simulated and experimental spectra in Figs. 1-3 and, in view of this, we believe that with the computational method presented here, in conjunction with high-quality *ab initio* potential energy and dipole moment surfaces, we can simulate rotation-vibration spectra of $XY_3$ pyramidal molecules prior to observation with sufficient accuracy to facilitate the observation and interpretation of these spectra.

But are our theoretical absolute intensities sufficiently accurate that they can be of assistance in quantitative spectroscopy and in the interpretation of remote sensing experiments? At this point in time, we have not yet made extensive, line-by-line comparisons between the simulated and observed spectra. However, inspection of Figs. 1-3 and the figures in Yurchenko *et al.* (2005b; 2005c) suggests that the 10-20% deviations found for the transitions in Table I are not untypical, at least for the strong lines dominating the spectra. For comparison, Kleiner *et al.* (1999) have fitted their observed line intensities for the $\nu_1$, $\nu_3$, and $2\nu_4$ bands of $^{14}NH_3$ in terms of a model involving an effective dipole moment function. In these fittings, they obtain root-mean-square relative deviations of 5.0% for 165 lines in the $\nu_1$ band, 11.9% for 325 lines in the $\nu_3$ band, 13.9% for 123 lines in the $2\nu_4(\ell_4 = 0)$ band, and 14.6% for 328 lines in the $2\nu_4(\ell_4 = 2)$ band. Better agreement (1.5% for 399 lines in the $\nu_2$ band and 2.1% for 580 lines in the $\nu_4$ band) was achieved by Brown *et al.* (2002) in fittings of the $\nu_2/\nu_4$ 'dyad' intensities for $PH_3$. The agreement with experiment obtained in our theoretical calculations is poorer than that obtained in fittings to experimental intensities, but not hopelessly so. Our results suggest that theoretical simulations of spectra are now approaching a level of accuracy where they can successfully compete with quantitative-spectroscopy measurements of intensities. They should thus be capable of resolving problems such as those mentioned by Flaud (2005), where different measurements of the intensities of the same transitions are in serious disagreement.

## Acknowledgements

We acknowledge support from the European Commission through contract no. HPRN-CT-2000-00022 “Spectroscopy of Highly Excited Rovibrational States” (SPHERS) and contract no. MRTN-CT-2004-512202 “Quantitative Spectroscopy for Atmospheric and Astrophysical Research” (QUASAAR).

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