

# Contributed Lectures D

Lecture Hall AI

August 30, Tuesday, 14:30 – 16:30

## Line Space Theory of Resonant Four-Wave Mixing by Rotationally Anisotropic Photofragments

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Based on the line-space (Liouville) quantum formalism, the potential of Resonant Four-Wave Mixing (RFWM) spectroscopy as a new tool to study rotational and translational anisotropy of photofragments produced by absorption of plane-polarized photons is theoretically addressed. Due to synergy of the flexible polarization setup, fine quantum state resolution and of the possibility to study translational recoil distributions, the tool is unsurpassed among the all-optical means to interrogate the photofragment states.<sup>1</sup> It furnishes a direct way to separate signals induced by the rotational anisotropy which remain silent in laser-induced fluorescence spectra and, as such, constitutes a promising approach to study rotational helicity, one of the crucial signatures of the photolytic bond rupture mechanism.<sup>2</sup> A Fortran code to calculate a set of irreducible polarization tensors appearing in the case of collinear RFWM geometry is also reported.

### References

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## Anomalous centrifugal distortion in NH<sub>2</sub>

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The NH<sub>2</sub> radical, first observed by Herzberg and Ramsay,<sup>1</sup> is dominated by a strong Renner-Teller effect, evidenced by Dressler and Ramsay,<sup>2</sup> giving rise to two electronic states: the bent  $X^2B_1$  ground state and the quasi-linear  $A^2A_1$  excited state. The NH<sub>2</sub> radical has been the subject of numerous high-resolution investigations and its electronic,<sup>3</sup> ro-vibrational,<sup>4</sup> and pure rotational transitions<sup>5</sup> have been measured. A value of the rotational quantum number  $N$  as large as 26 could be reached recently for the latter type of transitions using an experimental setup based on synchrotron radiation.<sup>6</sup>

In the  $X^2B_1$  ground state, the NH<sub>2</sub> radical behaves like a light triatomic molecule displaying spin-rotation splittings. Due to the large value of the rotational constants, there exists a strong coupling between the overall rotation and the bending  $\nu_2$  mode whose effects increase with the rotational quantum number  $N$  and lead to the anomalous centrifugal distortion observed by Martin-Drumel *et al.*<sup>6</sup>

In this talk the Bending-Rotation approach<sup>7</sup> developed to account for the anomalous centrifugal distortion of the water molecule<sup>8</sup> is modified to include spin-rotation coupling and is applied to the fitting of high-resolution data pertaining to the ground electronic state of NH<sub>2</sub>. In the modified approach, a 4-dimensional Hamiltonian is written using the bending coordinate  $t = \cos \theta$ , where  $\theta$  is the Radau<sup>9</sup> bending angle. A variation of the spin-rotation coupling with the bending coordinate is introduced.

A preliminary line position analysis of the pure rotational transitions reported by Martin-Drumel *et al.*<sup>6</sup> up to  $N = K_a = 12$  and the (010) state allowed us to reproduce the wavenumber of 600 (143) transitions belonging to the ground (excited) vibrational state with an RMS value of  $0.6 \times 10^{-3}$  ( $1.2 \times 10^{-3}$ ) cm<sup>-1</sup> using 71 parameters. The highest order distortion rotational operators considered are of the form  $N^{2p}N_z^{2q}$  with  $p + q = 4$ . This seems to imply that the present approach is more physical than the Watson-type Hamiltonian used by Martin-Drumel *et al.*<sup>6</sup> since they were led to use distortion rotational operators with  $p + q$  as large as 9 although for a larger maximum value of  $N$ .

### References

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## Calculated rotation-bending energy levels of $\text{CH}_5^+$ and a comparison with experiment<sup>1</sup>

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We report  $J > 0$   $\text{CH}_5^+$  levels computed by fixing stretch coordinates. They are computed by using a simple product basis, exploiting symmetry, and carefully parallelizing the calculation. The  $J > 0$   $\text{CH}_5^+$  levels are compared with those obtained from other theoretical methods and with experimental ground state combination differences of Asvany et al. [Science, **347**, 1346 (2015)]. If the assignment of Asvany et al. is correct, there are important differences between the levels we compute and those observed. We propose a different assignment of the experimental levels that reduces the maximum error from 34 to 2  $\text{cm}^{-1}$ . The new assignment can only be correct if states of both parities exist in the experiment. Although, ro-vibrational levels of  $\text{CH}_5^+$  cannot be associated with individual vibrational states, they do occur in blocks separated by gaps.

Calculated and experimental energy differences.

| $G_2^-$    |        |             | $H_2^-$    |        |             |
|------------|--------|-------------|------------|--------|-------------|
| $\Delta E$ |        | Expt. Set 1 | $\Delta E$ |        | Expt. Set 2 |
| $J = 0$    | (10.9) |             | $J = 1$    | (26.6) |             |
| $J = 2$    | 40.9   | 26.5        | $J = 2$    | 5.7    | 39.7        |
| $J = 1$    | 49.5   | 30.3        | $J = 0$    | 15.5   | 47.3        |
| $J = 2$    | 53.5   | 36.4        | $J = 2$    | 31.0   | 51.8        |
| $G_2^+$    |        |             | $H_2^+$    |        |             |
| $\Delta E$ |        |             | $\Delta E$ |        |             |
| $J = 1$    | (24.2) |             | $J = 1$    | (32.9) |             |
| $J = 2$    | 26.8   |             | $J = 2$    | 8.1    |             |
| $J = 1$    | 32.5   |             | $J = 0$    | 24.2   |             |
| $J = 3$    | 37.4   |             | $J = 2$    | 25.9   |             |

Fig. 1: A comparison of calculated and experimental energy differences of Asvany et al. [Science, **347**, 1346 (2015)]

### References

- [1] X.-G. Wang and T. Carrington Jr. J Chem. Phys. **144**, 204304, (2016)

## AN EMPIRICAL POTENTIAL ENERGY SURFACE FOR THE ELECTRONIC GROUND STATE OF HCO<sup>+</sup>

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Our work on calculating rovibronic energies and simulating spectra of small molecules involves an analytical, parameterized representation of the potential energy surface for a particular electronic state of the molecule in question. The values of the parameters in the function can, in principle, be obtained (1) by a least-squares fitting of theoretical *ab initio* energies or, (2) by a least-squares fitting of experimentally determined rovibronic energy spacings. In practice, the amount of experimentally determined energy spacings is normally too limited to allow the determination of a complete potential energy surface, and so Method (1) is customarily used to determine initial values for the potential-surface parameters and these parameters are then refined by Method (2), leading to an improved reproduction of the available experimental data. In many cases the available experimental data are so limited that even the refinement poses a problem. With very limited experimental data, only very few parameters can be varied in the refinement, and it is difficult to choose which parameters to vary.

In such cases, we have been able to proceed successfully by simultaneously least-squares fitting to the experimental data and the *ab initio* energies, applying an appropriate weighting of the two types of input data. This procedure was first implemented in the program TROVE<sup>1</sup> which simulates rovibronic spectra for any molecule in an isolated electronic state, and then (as MORBID requires significantly less computer resources than TROVE for doing the same calculation) in the older program MORBID<sup>2</sup> applicable to triatomic molecules only.

The experimental data are compiled by Neese<sup>3</sup> and the *ab initio* energies are newly calculated at the core-valence RCCSD(T)/[aug-cc-pCVQZ(C, O), aug-cc-pVQZ(H)] level of theory. Further details and results of the fits will be given at the conference.

### References

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## Dispersion and relativistic corrections to the spectral line shapes

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The growing requirements in the measurements of the physical constant variations, metrological applications as well as the diagnostics of stellar and planetary systems stimulate the development of spectroscopic techniques and spectral line-shape theories. Modern spectrometers are capable of providing spectra with very high signal-to-noise-ratios exceeding  $10^5$ . Such precise data require proper analysis in terms of the line-shape models going beyond the commonly used Voigt profile. It is well known that the speed dependence of collisional broadening and shifting, Dicke narrowing and the correlations between velocity-changing collisions and dephasing collisions have to be included in the line-shape analysis. Here we show that at this level of accuracy other, neglected so far, very subtle physical effects have to be taken into account. We present the dispersion and relativistic corrections to the line-shape models on an example of simple Gaussian and Voigt profiles.

We discuss the dispersion corrections including the frequency dependence of the Doppler shifting caused by dispersion<sup>1,2</sup> as well as by light frequency variation over the whole spectral line shape.<sup>2</sup> These effects can have non-negligible influence on the spectral line shape and can affect it even at the level of  $10^{-5}$ . The dispersion correction may influence the determination of the line position at the level of kHz.<sup>2</sup>

Moreover, we provided the relativistic formula describing the Voigt profile in the case of spontaneous emission.<sup>3</sup> We verified that our formula has a proper behaviour in two asymptotic cases: the relativistic Gaussian profile and the classical Voigt profile.<sup>4</sup> We presented an alternative expression, which simplify numerical evaluation for the most physically meaningful weak-relativistic regime. We estimated that at room temperature the relativistic correction can be at the level of  $10^{-6}$ .

The presented results might be crucial for the Doppler-width thermometry<sup>1</sup>, astrophysical applications and precise molecular spectroscopy for fundamental studies.<sup>5</sup>

### References

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## Spin-Rotation Hyperfine Splittings at Moderate to High $J$ Values in Methanol

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This talk presents an explanation based on torsionally mediated proton-spin–overall-rotation interaction for the observation of doublet hyperfine splittings in some Lamb-dip sub-millimeter-wave transitions between ground-state torsion-rotation states of E symmetry in methanol. These unexpected doublet splittings, some as large as 70 kHz, were observed for rotational quantum numbers in the range of  $J = 13$  to 34, and  $K = -2$  to  $+3$ . Because they increase nearly linearly with  $J$  for a given branch, we confined our search for an explanation to hyperfine operators containing one nuclear-spin angular momentum factor  $I$  and one overall-rotation angular momentum factor  $J$  (i.e., to spin-rotation operators), and ignored both spin-spin and spin-torsion operators, since they contain no rotational angular momentum operator. Furthermore, since traditional spin-rotation operators did not seem capable of explaining the observed splittings, we constructed totally symmetric “torsionally mediated spin-rotation operators” by combining the E-species spin-rotation operator with an E-species torsional-coordinate factor. The resulting operator is capable of connecting the two components of a degenerate torsion-rotation E state. This has the effect of turning the hyperfine splitting pattern upside down for some nuclear-spin states, which leads to bottom-to-top and top-to-bottom hyperfine selection rules for some transitions, and thus to an explanation for the unexpectedly large observed hyperfine splittings. The constructed operator has no nonzero matrix elements within the set of torsion-rotation  $A_1$  and  $A_2$  states, and thus cannot contribute to hyperfine splittings in the A manifold. The theory developed here fits the observed large doublet splittings to a root-mean-square residual of less than 1 kHz, and predicts much smaller splittings for a number of transitions in which no doublet splitting was detected. New measurements of more complicated splitting patterns in the excited torsional states, having triplet and quartet forms, are yet to be explored.