

Contributed Lectures P

Lecture Hall AII

September 3, Saturday, 9:00 – 10:30

Diatomic molecules in supersonic expansion beam experiment – from separation of overlapped profiles to determination of interatomic potential

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We present methods, which are used to analyse data collected in experiments of detection of LIF excitation spectra in supersonic molecular beam, which are conducted in our laboratory. In the first part, we present a method of separation of overlapped spectra of different molecules that is based on their lifetimes [1]. In the second part, we methods of determination of proper representation of interatomic potential which should be used in the simulation to provide proper agreement with experimental spectrum. It shown, that even in the case of a simple analytical representation of interatomic potential (e.g., a Morse function), it can exist a strong correlations between parameters of the potential (e.g., between vibrational constants ω_e and $\omega_e x_e$), which leads to difficulties in the assessment of errors of these parameters. We present the methods to overturn the limitation (e.g., agreement plot method developed in our laboratory).

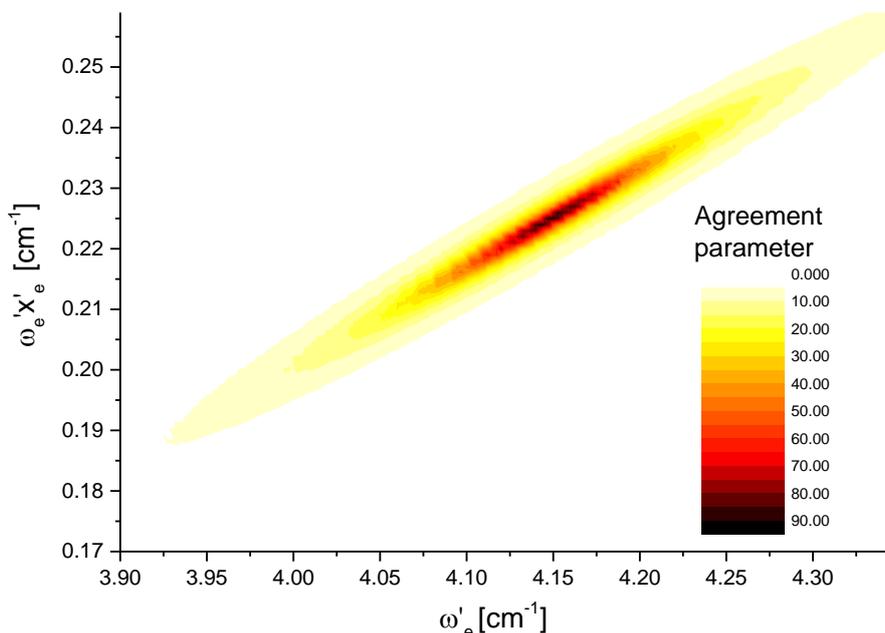


Fig. 1: Agreement plot for $E^3\Sigma^+(6^3S_1) \leftarrow B^3\Sigma_1^+(5^3P_1)$ transition in CdAr. Plot shows which combination of vibrational constants lead to high simulation-to experiment agreement (the higher value of the agreement parameter the better simulation-to experiment agreement).

References

[1] T. Urbanczyk; J. Koperski, Mol. Phys. **112**, 2486-2494, 2014

Acknowledgements

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Ortho-para dependence of pressure effects observed in the C_2H_2 $\nu_1 + \nu_3$ band by dual-comb spectroscopy

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We have observed the ortho-para dependence of pressure-broadening coefficients for the ro-vibrational transitions from $P(26)$ to $R(29)$ in the $^{12}C_2H_2$ $\nu_1 + \nu_3$ band at six pressures ranging from 25 to 2654 Pa by using a dual-comb spectrometer [1]. Each observed line profile has been analyzed by employing the Voigt function, and the parameters for the intensity, pressure broadening and shift have been determined accurately. The determined pressure broadening coefficients vary alternatively with the rotational angular momentum quantum number (J) of the transitions; those for the ortho transitions are larger than those for para transitions. It suggests that the collision cross-section is larger between molecules in the identical rotational level than that between those in different rotational levels. We also observed the J dependence of the pressure shift coefficients, but they do not indicate the ortho-para dependence so clearly.

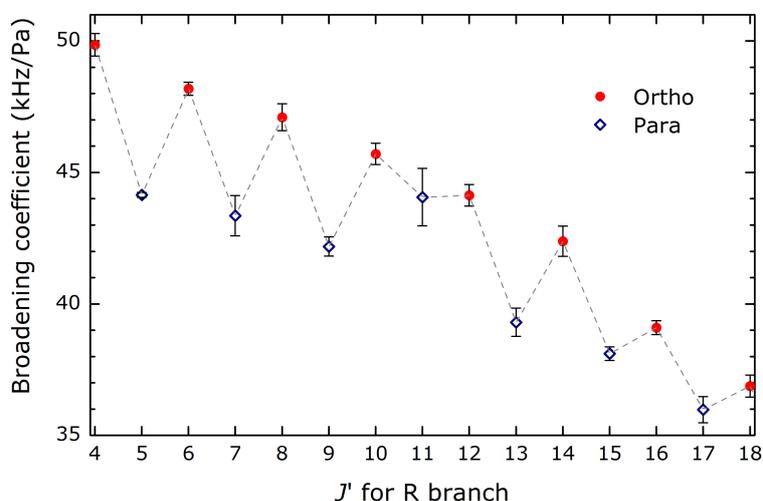


Fig. 1: The observed ortho-para dependence of the pressure broadening coefficients.

- [1] S. Okubo, K. Iwakuni, H. Inaba, K. Hosaka, A. Onae, H. Sasada, and F.-L. Hong, *Appl. Phys. Express* **8**, 082402 (2015).

Precise determination of line shapes and positions of self-perturbed oxygen B-band transitions

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We report set of line shape parameters for several lines observed due to $b^1\Sigma_g^+ - X^3\Sigma_g^-$ ($1 \leftarrow 0$) transitions in oxygen molecule. Measurements were performed in the low pressure range with the Pound-Drever-Hall locked, frequency stabilised cavity ring-down spectrometer (PDH-locked FS-CRDS) linked to the optical frequency comb (OFC)¹⁻³. The data analysis was performed in terms of speed-dependent Voigt profile with the use of multispectrum fitting technique. This approach enabled us to reduce numerical correlations between fitted parameters and obtain consistent set of line shape parameters, including pressure broadening, shifting, speed-dependent parameters, and line intensities⁴. The transition frequencies were determined with accuracies reaching 150 kHz⁴. We have shown that in our conditions use of the simple Voigt profile is insufficient and may lead to significant systematic errors on determined line shape parameters. Those errors can be as high as several percent.

Recently the spectrometer was optically linked via OFC to the atomic optical lattice clock working on $^{88}\text{Sr } ^1\text{S}_0 - ^3\text{P}_0$ transition^{5,6}. In our experiment all frequency counters and generators are referenced to the same 10 MHz signal from the hydrogen maser⁷, which is transferred by the 330 km fibre link^{6,8}. This approach enables us to determine line central frequency against the frequency of the atomic optical clock and avoid systematic uncertainties which have been present in earlier measurements. We have performed measurement of the position of the P7P7 line from the oxygen B-band which lead to about one order of magnitude reduction of uncertainty comparing to previous data. This is a proof-of-principle experiment presenting the use of atomic optical clocks in molecular spectroscopy.

References

- [1] J. Domysławska *et al*, J. Chem. Phys. **139**, 194312, 2013
- [2] S. Wójtewicz *et al*, J. Quant. Spectrosc. Radiat. Transfer **144**, 36, 2014
- [3] J. Domysławska *et al*, J. Quant. Spectrosc. Radiat. Transfer **155**, 22, 2015
- [4] J. Domysławska *et al*, J. Quant. Spectrosc. Radiat. Transfer **169**, 111, 2016
- [5] M. Bober *et al*, Meas. Sci. Technol. **26**, 0075201, 2015
- [6] P. Morzyński *et al*, Sci. Rep. **5**, 17495, 2015
- [7] Z. Jiang *et al*, Metrologia **52**, 384, 2015
- [8] P. Krehlik *et al*, Metrologia **52**, 82, 2015

Unifying Hydrogen Bonding with Vibrational Stark Effect

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Replace Vibrational spectroscopy has been a very powerful tool to investigate the formation of X–H···Y hydrogen bonds. The formation of X–H···Y hydrogen bonding leads to changes in the X–H stretching frequency. In most of the hydrogen bonds the X–H stretching frequency shifts to the red. However, hydrogen bonds wherein the X–H stretching frequency experiences either blue shift or no-shift have also been reported.^{1,2} There have been attempts to unify the entire spectrum of hydrogen bonding irrespective of the nature of the shift in the X–H stretching frequency.³ An alternate but physically simplistic model based on electrostatics and vibrational Stark effect,⁴ is used to understand the nature of the shift in several hydrogen bonded complexes. Examples of hydrogen bonded complexes with both the red-shifted and the blue-shifted have been used to demonstrate this model.⁵

References

- [1] P. Hobza, V. Spirko, Z. Havlas, K. Buchhold, B. Reimann, H. D. Barth, B. Brutschy, *Chem. Phys. Lett.* **299**, 180, 1999.
- [2] M. M. Nolasco, P. J. A. Ribeiro-Claro, *ChemPhysChem.* **6**, 496, 2005.
- [3] J. Joseph, E. D. Jemmis, *J. Am. Chem. Soc.* **129**, 4620, 2007.
- [4] M. Saggi, N. M. Levinson, S. G. Boxer, *J. Am. Chem. Soc.* 2007,, 17414, 2011.
- [5] A. Dey, S. I. Mondal, S. Sen, D. Ghosh, G. N. Patwari, *Phys. Chem. Chem. Phys.* **16**, 25247, 2014

Cavity-enhanced absorption and dispersion spectroscopy for molecular line-shape investigations

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Investigation on molecular line shapes finds applications in growing number of fields, including basic research, metrology and remote sensing. For weak absorption cavity-enhanced techniques, such as cavity ring-down spectroscopy (CRDS), proved excellent performance and spectra with extremely high signal-to-noise ratios^{1,2} were demonstrated using the frequency-stabilized CRDS³.

The exponential light decays measured in CRDS, are related to the spectral half-width of the cavity modes, measured in the cavity mode-width spectroscopy (CMWS)⁴⁻⁶. Properties of CRDS and CMWS methods make them complementary in terms of achievable accuracies at different levels of intra-cavity absorption⁵. For low absorptions, where the ring-down decays are long and mode widths are small, the best precision is expected with the CRDS. In the opposite case of high absorption the precision of CMWS should be higher.

Alternative method of accurate quantitative spectroscopy is provided by measurement of dispersive shifts of the cavity mode frequencies. Since frequency can be measured most accurately of all physical quantities, direct measurement of absolute or differential mode frequencies to obtain a spectrum in the one-dimensional cavity mode dispersion spectroscopy (1D-CMDS)^{7,8} should eliminate potential problems with nonlinearities of detection system and minimize systematic instrumental errors. Contrary to any absorption spectroscopy, in 1D-CMDS both axes of the spectrum can be linked to the primary frequency standard⁹.

Recent results of accurate line-shape investigations, using methods mentioned above, will be presented. These new cavity-enhanced techniques may be especially useful in applications that require high accuracy of weak absorption measurements, e.g. gas spectroscopy for atmospheric monitoring and gas metrology, Doppler thermometry, as well as fundamental study of spectral line shapes. Direct comparison of spectra obtained with various cavity-enhanced techniques enables identification of potential instrumental errors at sub-percent level of accuracy required in many modern applications.

References

- [1] A. Cygan, D. Lisak, S. Wójtewicz, et al., *Phys. Rev. A* **85**, 022508 (2012)
- [2] H. Lin, Z.D. Reed, V.T. Sironneau, J.T. Hodges, *J. Quant. Spectrosc. Radiat. Tr.* **161**, 11 (2015)
- [3] D.A. Long, A. Cygan, R.D. van Zee, et al., *Chem. Phys. Lett.* **536**, 1 (2012)
- [4] K. Nakagawa, T. Katsuda, A.S. Shelkovnikov, et al., *Opt. Commun.* **107**, 369 (1994)
- [5] A. Cygan, D. Lisak, P. Morzyński, et al., *Opt. Express* **21**, 29744 (2013)
- [6] D.A. Long, G.-W. Truong, R.D. van Zee, et al., *Appl. Phys. B* **114**, 489 (2014)
- [7] A. Cygan, P. Wcisło, S. Wójtewicz, et al., *Opt. Express* **23**, 14472 (2015)
- [8] A. Cygan, S. Wójtewicz, M. Zaborowski, et al., *Meas. Sci. Technol.* **27**, 045501 (2016)
- [9] A. Cygan, S. Wójtewicz, G. Kowzan, et al., *J. Chem. Phys.* accepted (2016)