

Contributed Lectures F

September 5, Wednesday, 11:00 – 12:30

On the relation between properties of long-range diatomic bound states

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Long-range states of diatomic molecules have average values of internuclear separations $\langle R \rangle$ at least one order of magnitude larger than the equilibrium value of R . For example, the helium dimer $4\text{He}-4\text{He}$ has a single bound state with $\langle R \rangle$ of about 50 Å. We show that the properties of these states as $\langle R \rangle$, the dissociation energy, or the s -wave scattering length, can be related by simple, yet very accurate formulas if a potential curve is known. By examining a range of ab initio and empirical helium dimer potentials, we found that the formulas remain accurate even if very approximate potentials are used. In addition to $4\text{He}-4\text{He}$, we present results for Be-Be, Ne-Ne, and KRb.

Vibrational assignment and vibronic interaction for the nitrate radical NO₃ in the ground electronic state

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Ishiwata *et al.* [1] determined three of the four normal mode frequencies from the dispersion spectra: $\nu_1 = 1060$, $\nu_3 = 1480$, and $\nu_4 = 380$ in cm^{-1} . Ishiwata *et al.* [2] and Kawaguchi *et al.* [3] later observed the ν_3 band at high resolution and derived the band origin to be $1492.3936 \text{ cm}^{-1}$. These results were supplemented by $\nu_2 = 762.327 \text{ cm}^{-1}$, as reported by Friedl and Sander [4], to complete the assignment, which we shall refer to as Assign I. In 2007 Stanton [5,6] proposed the ν_3 band to be near 1000 cm^{-1} , based upon an *ab initio* calculation, and the 1492 cm^{-1} band was assigned to $\nu_3 + \nu_4$: the assignment called Assign II. Kawaguchi *et al.* [7] searched for the basis in support of Assign II, by reanalyzing the 1492 cm^{-1} band as the $\nu_3 + \nu_4$ and also by observing transitions from the ν_4 fundamental state to the $\nu_3 + \nu_4$ state. Unfortunately, their analysis suffered from miss-assignment for the rotational quantum numbers N and K of a part of the observed transitions and yielded some unrealistic results, which clearly indicate Assign II unacceptable. In parallel with this study, I re-examined the 1492 cm^{-1} band, by primarily paying attention to perturbations on $K' = 7$ in the upper vibrational state of the band, the origin of which was previously not fully clarified [3], and convinced this time that the perturbations were caused by the interaction between the ν_3 and $2\nu_2$ states. In fact, I succeeded in reproducing all the observed spectra including hot bands from the ν_4 state, thereby eliminating all the anomalous features reported in [7]. I conclude that the traditional vibrational assignment Assign I is correct, and I am suspecting that Stanton has overestimated the effects of vibronic interactions.

References

- [1] T. Ishiwata, I. Fujiwara, Y. Naruge, K. Obi, I. Tanaka, *J. Phys. Chem.* **87**, 1349, 1983.
- [2] T. Ishiwata, I. Tanaka, K. Kawaguchi, E. Hirota, *J. Chem. Phys.* **82**, 2196, 1985.
- [3] K. Kawaguchi, E. Hirota, T. Ishiwata, I. Tanaka, *J. Chem. Phys.* **93**, 951, 1990.
- [4] R. R. Friedl, S. P. Sander, *J. Phys. Chem.* **91**, 2721, 1987.
- [5] J. F. Stanton, *J. Chem. Phys.* **126**, 134309, 2007.
- [6] J. F. Stanton, *Mol. Phys.* **107**, 1059, 2009.
- [7] K. Kawaguchi, N. Shimizu, R. Fujimori, J. Tang, T. Ishiwata, I. Tanaka, *J. Mol. Spectrosc.* **268**, 85, 2011.

High Resolution Infrared Spectra of Larger Molecular Clusters: (N₂O)₅, (CO₂)₃-(C₂H₂)₂, and (CO₂)₄-(C₂H₂)₂

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There is an extensive history of high-resolution spectroscopy of weakly-bound gas-phase molecular dimers. To a lesser extent trimers and tetramers have also been studied. But there are few high-resolution microwave or infrared spectra of larger clusters, which are more difficult to produce in abundance and more difficult to identify and resolve. Recently, we assigned specific infrared rotation-vibration bands to a number of carbon dioxide clusters in the range (CO₂)₆ to (CO₂)₁₃.¹ Here, we present new spectra of pentamers and a hexamer.

Two bands in the N₂O ν₁ fundamental region near 2233.9 and 2236.4 cm⁻¹ are assigned to nitrous oxide pentamers. Although similar in appearance, the bands have slightly different lower state rotational parameters and are assigned to distinct (N₂O)₅ isomers. These isomers probably have the same basic ‘backbone’ structure (which is unsymmetrical) but differ in the alignment (N-N-O or O-N-N) of one or two monomers.

A band centered near 2355.0 cm⁻¹ in the CO₂ ν₃ fundamental region is assigned to (CO₂)₃-(C₂H₂)₂, which is a near-symmetric rotor with C_{2v} symmetry. Another band near 2357.7 cm⁻¹ is assigned to (CO₂)₄-(C₂H₂)₂, which has a highly symmetric (D_{2d}) structure. This structure and part of the spectrum are shown in Fig. 1. The (CO₂)₃-(C₂H₂)₂ structure is similar to that shown, but with one ‘end’ CO₂ removed.

The assignments are supported by structural calculations using available intermolecular potential models and by resonant dipole interaction model calculations of vibrational shifts and intensities.

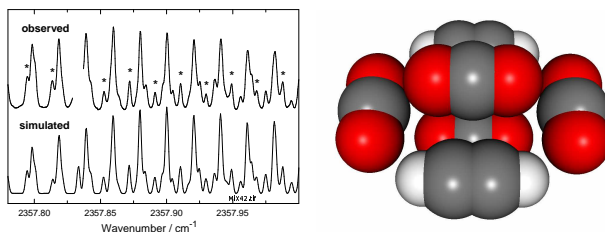


Fig. 1: Partial spectrum and calculated structure of (CO₂)₄-(C₂H₂)₂. Asterisks indicate a series showing intensity alternation which helps to confirm the indicated structure.

References

- [1] J. Norooz Oliiae, M. Deghany, A.R.W. McKellar, and N. Moazzen-Ahmadi, J. Chem. Phys. **135**, 044315, 2011.

The rotational spectra of $D_2^{17}O$ and $HD^{17}O$: accurate spectroscopic and hyperfine parameters

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The Lamb-dip technique was employed to resolve the hyperfine structure of the rotational lines of $D_2^{17}O$ and $HD^{17}O$. The high resolution of this technique allowed us to obtain the hyperfine parameters with high accuracy. The experimental determination was supported by highly accurate quantum-chemical calculations of the hyperfine parameters involved. The experimental spin-rotation constants of ^{17}O were used to evaluate the paramagnetic contribution to the nuclear magnetic shielding constants, whereas the diamagnetic contribution was accurately determined by means of CCSD(T) calculations. These steps are part of a well-tested procedure, which also involves the determination of vibrational and temperature corrections. The present study is part of a wider project which aims at establishing an alternative experimental absolute NMR scale for oxygen and which has been started with an analogous investigation on $H_2^{17}O$.¹ Due to the lack of information on spectroscopic parameters, the rotational spectra of $D_2^{17}O$ and $HD^{17}O$ were also investigated at Doppler-limited resolution, spanning a large frequency range: from the millimeter-wave region up to the THz frequency domain. The recorded transitions allowed to determine rotational and centrifugal-distortion constants to a good accuracy.

References

[1] C. Puzzarini, G. Cazzoli, M. E. Harding, J. Vázquez, J. Gauss, *J. Chem. Phys.* **131**, 234304, 2009.

Large Amplitude Bending Motion: A Computational-Molecular-Spectroscopy Approach

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Our version of Computational Molecular Spectroscopy has a history of more than 12 years. We analyse the rovibronic spectrum of a (triatomic) molecule in three steps: 1) Construction of a potential energy surface (PES) by very accurate *ab initio* molecular orbital calculations, 2) Solution of the ro-vibrational Schrödinger equation, and 3) Determination of molecular constants as expectation values involving MORBID and/or RENNER wavefunctions. We successfully applied this method to many molecules such as MgNC, FeNC, FeCN, CoCN, NiCN, BrCN⁺, CsOH, FeOH, FeCO that show large amplitude bending motion. Meanwhile we noticed that from the conventional spectroscopy analysis developed for the case of small amplitude bending motion, physically sound molecular geometries (and hence an accurate PES) cannot be derived. We will discuss the problems associated with large amplitude bending motion from the viewpoint of computational molecular spectroscopy.

- *The experimentally determined r_0 value of the ligand is too short.* The experimental $r_0(\text{N-C})$ value of $\tilde{X}^6\Delta$ FeNC is 1.03(8) Å [1], whereas our theoretical value of $\langle r(\text{N-C}) \rangle_0$ is 1.187 Å [2]. The experimental $r_0(\text{C-N})$ value 1.1590(2) Å of $\tilde{X}^2\Delta$ NiCN [3] is shown by MORBID analyses to be close to the projection average of the bond onto the molecular a axis and in reality, $r_0(\text{C-N}) = 1.171$ Å [4]. Since most recent experiments employ a free jet, the only method to determine physically sound r_0 -structure is limited at present to the method of computational molecular spectroscopy.

- *The ro-vibrationally averaged structure of any chain molecule is bent.* Since, for a linear molecule, we cannot consider bending and rotation separately, the ro-vibrationally averaged value of $\rho = \pi - \angle(\text{ABC})$, $\langle \rho \rangle$, is non-zero by necessity. For example, $\langle \rho \rangle = 13^\circ$ for $\tilde{X}^6\Delta$ FeNC and $\langle \rho \rangle = 17^\circ$ for $\tilde{X}^1\Sigma^+$ CsOH. Thus, it becomes difficult to distinguish linear and quasilinear molecules experimentally. We have demonstrated that the Yamada-Winnewisser quasilinearity index is useful in such cases.

- *Large amplitude bending motion coupled with stretching.* In cases where the ionic bond (e.g., Mg-N in $\tilde{X}^2\Sigma$ MgNC) is formed by electron-transfer from metal to ligand σ^* or the bond is formed as a coordinate-covalent bond, the relevant bond elongates significantly as the molecule bends (due to a significant value of the 3rd-order force-constant $f_{\text{stretch,bend,bend}}$). $\tilde{X}^2\Sigma$ MgNC and $\tilde{X}^2\Sigma$ CaNC are of the former type and $\tilde{X}^3\Sigma^-$ FeCO and $\tilde{X}^1\Sigma^+$ H⁺CO are of the latter. For these molecules we have to apply a method of analysis considering the PES variation in a wide range of configuration space. Second-order perturbation theory and conventional spectroscopy analysis, both of which consider the PES in a narrow range near the equilibrium structure only, are inappropriate. We will discuss this issue by taking $\tilde{X}^3\Sigma^-$ FeCO case as an example.

References

- [1] J. Lie and P.J. Dagdigan, *J. Chem. Phys.* **114** (2001) 2137. [2] T. Hirano et al, *J. Mol. Spectrosc.* **236** (2006) 234. [3] P.M. Sheridan and L.M. Ziurys, *J. Chem. Phys.* **118** (2003) 6370. [4] T. Hirano et al, *J. Mol. Spectrosc.* **250** (2008) 33.

The use of precise molecular spectroscopy for a search of m_e/m_p variations

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We report critical analysis of our recent radio astronomical measurement^{1,2} with Medicina-32m, Nobeyama-45m and Effelsberg-100m telescopes intended for a search of m_e/m_p variation from narrow line observations of HC_3N and NH_3 in dark clouds in comparison with laboratory frequencies. Using FTMW spectrometer measurements in a cold jet in the University of Hannover we confirm previously used laboratory frequencies for HC_3N and NH_3 and improved the line frequencies for H^{13}CCCN , HC^{13}CCN , HCC^{13}CN and HCCC^{15}N . A set of additional molecular spectra is improved significantly with sub-Doppler spectrometer developed at the IAP of the RAS, N.Novgorod.

References

[1] S.A. Levshakov, A.V. Lapinov, C. Henkel, P. Molaro, D. Reimers, M.G. Kozlov, I.I. Agafonova, *Astron. Astrophys.*, **524**, A32, 2010.

[2] S.A. Levshakov, P. Molaro, A.V. Lapinov, D. Reimers, C. Henkel, T. Sakai, *Astron. Astrophys.*, **512**, A44, 2010.