

**MOLECULAR CHIRALITY: ENANTIOMER DIFFERENTIATION
BY HIGH-RESOLUTION SPECTROSCOPY**

Eizi Hirota

The Central Office, The Graduate University for Advanced Studies,
Hayama, Kanagawa 240-0193, JAPAN

Quantum mechanics faced a difficulty at its start in explaining the stability of an enantiomer, because the Hamiltonian was symmetric with respect to the inversion. Hund [1] circumvented this difficulty (referred to as Hund's paradox) by assuming a high potential barrier between enantiomers. In 1956 Lee and Yang [2] discovered that, when they took into account the weak interaction, the parity was not conserved, but the product of parity and charge CP was, that is, the two enantiomers were no more degenerate in energy, the phenomenon referred to as parity violation PV. Highly sophisticated spectroscopic systems were employed to detect the effect of PV in the molecular spectral lines, as exemplified by the study of Bordé's group [3]. This investigation is continuing [4], but the spectral resolution still remains nearly four orders of magnitude lower than the theoretical estimate. As a result, most people thought that conventional high-resolution spectroscopy would be unable to differentiate enantiomers. However, this view now has to be changed because of the findings of the present author (EH) [5] made in 2009.

Let us consider a C_1 symmetry chiral molecule. All the three components of the electric dipole moment are finite, making a -, b -, and c -types rotational transitions allowed. An infinite number of three-rotational-level group are available for such a molecule, in which one level is connected to the other two by two different types of rotational transitions. We may observe the three transitions in such a system one by one by conventional microwave spectroscopy, but it should be noted that a fundamental selection rule for the dipole transition $+ \leftrightarrow -$ does not hold for such a three-level system. EH examined the behavior of a C_1 symmetry chiral molecule, when it is subjected to triple resonance on the three-level system, and found that we could observe signals opposite in phase for the enantiomers, which meant enantiomer differentiation possible. This prediction was realized by Doyle's group [6].

Some C_2 and C_n ($n \geq 3$) symmetry chiral molecules have been known to exist, in which the electric dipole moment is located on the C_2 and C_n axis, respectively, making the argument on C_1 molecules inapplicable. However, if we take into consideration an excited vibrational or vibronic state, we may treat these molecules in a similar way as for C_1 cases.

[1] F. Hund, Z. Phys. **43**, 805 (1927).

[2] T. D. Lee and C. N. Yang, Phys. Rev. **104**, 254 (1956).

[3] Ch. Daussy, T. Marrel, A. Amy-Klein, C. T. Nguyen, Ch. J. Bordé, and Ch. Chardonnet, Phys. Rev. Lett. **83**, 1554 (1999).

[4] Ch. Chardonnet, B. Darquié, S. Tokunaga, C. Daussy, A. Amy-Klein, J. Crassous, P. Asselin, P. Soulard, T. Huet, and T. Saue, Spectroscopic Studies on Molecular Chirality, Kyoto, December 2013.

[5] E. Hirota, 3rd Molecular Science Symposium, Nagoya, September 2009; Proc. Jpn. Acad. Ser. B, **88**, 120 (2012).

[6] D. Patterson, M. Schnell, and J. M. Doyle, Nature **497**, 475 (2013); D. Patterson and J. M. Doyle, Phys. Rev. Lett. **111**, 023008 (2013).

CHIRALITY SYNCHRONIZATION IN TRIFLUOROETHANOL DIMER REVISITED: THE MISSING HETEROCHIRAL DIMERJavix Thomas, Yunjie Xu

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2

Chirality self-recognition in the dimer of transient chiral 2,2,2-trifluoroethanol (TFE) is studied using chirped pulse and cavity based Fourier transform microwave spectroscopy with the aid of ab initio calculations. The broadband and extreme high resolution capabilities enable us to assign rotational spectra of the most stable homo- and heterochiral dimers and analyze their structural and dynamical properties in detail. A strong preference for the homochiral over the heterochiral diastereomers is observed. The current study unambiguously identifies the structure of the most stable homochiral dimer and supports the identification by the previous low resolution infrared study [1]. More importantly, it also indisputably detects the so far elusive, most stable heterochiral dimer. Comparison to the other related systems [2] will be discussed.

[1] T. Scharge, T. Häber, M. A. Suhm, *Phys. Chem. Chem. Phys.* **8**, 4664(2006); T. Scharge, C. Cezard, P. Zielke, A. Schutz, C. Emmeluth, M. A. Suhm, *Phys. Chem. Chem. Phys.* **9**, 4472(2007); T. Scharge, D. Luckhaus, M. A. Suhm, *Chemical Physics*. **346**, 167(2008).

[2] X. Liu, N. Borho, Y. Xu, *Chem. Eur. J.* **15**, 270(2009); J. Thomas, W. Jäger, Y. Xu, *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.201403838.

OBSERVATION BY CHIRPED-PULSE ROTATIONAL SPECTROSCOPY AND PROPERTIES OF THE $(\text{H}_2\text{O})_3\text{HCl}$ AND $(\text{H}_2\text{O})_2(\text{HCl})_2$ HYDROGEN-BONDED CLUSTERS

Zbigniew Kisiel¹, Cristóbal Pérez², Justin L. Neill², Matt T. Muckle², Luca Evangelisti², Simon Lobsiger², Brooks H. Pate²

¹Institute of Physics, Polish Academy of Sciences, Warszawa, Poland

²Department of Chemistry, University of Virginia, Charlottesville, Virginia, USA

The quest for understanding of the process of protolytic dissociation at the molecular scale has been an important theme of small cluster research. The favoured system for such studies is the formation of hydrochloric acid, which appears to take place on dilution of a hydrogen chloride molecule in four molecules of water. Rotational spectroscopy of supersonic expansion allows studying successively larger clusters in the hydrogen chloride/water system allowing insight into the evolution of cluster properties with size. Detailed studies of $\text{H}_2\text{O}\cdots\text{HCl}$ [1], $(\text{H}_2\text{O})_2\text{HCl}$ [2,3], and $(\text{H}_2\text{O})(\text{HCl})_2$ [4] have already been performed. Presently we report observation and properties of two tetramer clusters in this system: $(\text{H}_2\text{O})_3\text{HCl}$ and $(\text{H}_2\text{O})_2(\text{HCl})_2$.

The clusters were observed in Virginia by using the configurations of the chirped pulse, supersonic expansion rotational spectrometer, as described in the studies of iodobenzene [5] and the heptamer water cluster [6]. The identification of the cluster species was confirmed by assignment also of the ^{37}Cl (natural abundance) and ^{18}O (enriched) isotopic species and analysis of the chlorine hyperfine structure. The isotopic rotational constants allow determination of the heavy atom distances in the clusters, while the hyperfine results provide independent information on the angular orientation of the HCl monomers, and thus on the hydrogen bond angles. The experimental results are compared with those for the smaller clusters and with results of *ab initio* calculations.

[1] Z.Kisiel, B.A.Pietrewicz, P.W.Fowler, A.C.Legon, E.Steiner, J.Phys.Chem.A **104**, 6970 (2000)

[2] Z.Kisiel, E.Białkowska-Jaworska, L.Pszczółkowski, A.Milet, C.Struniewicz, R.Moszyński, J.Sadlej, J.Chem.Phys. **112**, 5767 (2000)

[3] Z.Kisiel, J.Kosarzewski, B.A.Pietrewicz, L.Pszczółkowski, Chem.Phys.Lett. **325**, 523 (2000)

[4] Z.Kisiel, A.Lesarri, J.L.Neill, M.T.Muckle, B.H.Pate, PCCP **13**, 13912 (2011)

[5] J.L.Neill, S.T.Shipman, L.Alvarez-Valtierra, A.Lesarri, Z.Kisiel, B.H.Pate, J.Mol.Spectrosc. **269**, 21 (2011)

[6] C.Perez, S.Lobsiger, N.A.Seifert, D.P.Zaleski, B.Temelso, G.C.Shields, Z.Kisiel, B.H.Pate, Chem.Phys.Lett. **571**, 1 (2013)

**ROTATIONAL SPECTRUM AND STRUCTURE OF THE FORMIC
ACID...CARBON DIOXIDE MOLECULAR COMPLEX**

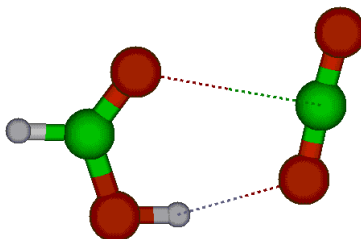
Annalisa Vigorito, Camilla Calabrese, Qian Gou, Sonia Melandri, Walter Caminati and Assimo Maris

Department of Chemistry, University of Bologna, Via Selmi 2, I-40126 Bologna (Italy).

In recent years much attention has been devoted to the CO₂ molecule due to its key role in the Earth's greenhouse effect. In this study the interaction between CO₂ and formic acid, another compound of chemical and atmospheric relevance, has been investigated with rotational spectroscopy. It is the first complex of CO₂ with an organic acid investigated with this technique.

By *ab initio* calculations, performed both at the MP2/6-311++G(d,p) and MP2/cc-pVTZ level, three planar minima have been obtained. Each one of these shows a structure held together through a H...O hydrogen bond and a van der Waals interaction O...C.

The rotational spectra have been recorded in the 6-18 GHz and 59.6-74.4 GHz frequency ranges with a pulsed jet Fourier transform microwave spectrometer and Stark modulated free jet absorption millimeter wave spectrometer respectively. Spectroscopic constants are reported for the normal species and for its monodeuterated isotopologues. The spectral lines showed no evidence of tunneling splitting. Only the most stable conformer has been observed (see picture).



Based on the assumption that the monomer geometries are unchanged upon formation of the complex, the relative orientation of the two molecules has been determined. The obtained results are compared with the ones obtained for other CO₂ complexes.

**FOURIER-TRANSFORM MICROWAVE AND MILLIMETERWAVE
SPECTROSCOPY OF THE H₂-HCN MOLECULAR COMPLEX**

Keiichi. Tanaka^{1,2}, M. Ishiguro¹, K. Harada^{1,2}, Y. Sumiyoshi³, M. Nakashima³, and Y. Endo³

¹ Department of Chemistry, Faculty of Sciences, Kyushu Univ. Fukuoka, 812-8581 Japan

² ICSWSE, Kyushu Univ. Fukuoka, 812-8581 Japan

³ Department of Pure and Applied Sciences, Univ. of Tokyo, Tokyo 153-8902 Japan
ktanaka@chem.kyushu-univ.jp



Fourier-Transform microwave (FTMW) spectroscopy has been applied to observe the $J = 1 - 0$ rotational transitions of the H₂-HCN/DCN complexes containing both the *para* ($I_{H_2}=0$) and *ortho*-H₂ ($I_{H_2}=1$) hydrogen molecule[1]. Rotational spectra of H₂-HCN/DCN up to $J = 5 - 4$ were also observed in the millimeter-wave (MMW) region below 150 GHz[2].

Observed FTMW lines for H₂-HCN/DCN split into hyperfine components due to the nuclear quadrupole interaction of N and D nuclei. For the *ortho*-H₂ species, the hyperfine splitting due to the magnetic interaction between the hydrogen nuclear spin of H₂ part ($j_{H_2}=1$, $I_{H_2}=1$) was also observed, but not for the *para*-H₂ species ($j_{H_2}=0$, $I_{H_2}=0$). From the observed nuclear spin-spin coupling constants of *ortho*-H₂ species, $d = 21.90(47)$ and $24.66(68)$ kHz for the HCN and DCN complexes, respectively, the average values of $\langle P_2(\cos \theta) \rangle = 0.380(8)$ and $0.439(10)$ were derived indicating that H₂ is nearly-free rotating in the complex with $j_{H_2} = 1$ and $k_{H_2} = 0$. The nuclear quadrupole interaction constants, due to N and D nuclei, show that the HCN/DCN part execute a floppy motion with a large mean square amplitude of about 29/25 and 33/30 degree for the *para* and *ortho*-H₂ species, respectively.

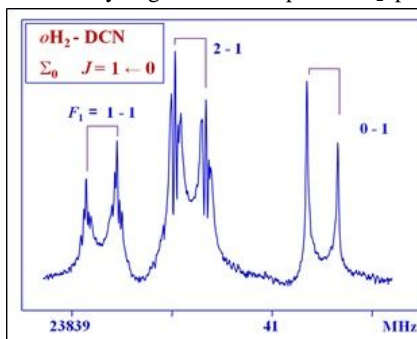


Fig. 1 $J = 1-0$ line of *ortho*-H₂-DCN

From the observed rotational constants, the center-of-mass distances of H₂ and HCN/DCN were derived to be 3.9617(5)/4.00356 (43) Å for the *ortho* species and 4.1589(13)/4.1596 (36) Å for the *para* species, by 0.20-0.15 Å longer than those for the *ortho*-H₂ species. The isotope effect on rotational constants confirmed the totally different configurations for the *ortho* and *para*-H₂ species: H₂ is attached to the H/D end of HCN/DCN in the *para*-H₂ species, while to the N end in the *ortho*-H₂ species, as suggested by IR spectroscopy [3] and theoretical study [4] (see top Figure).

[1] M. Ishiguro, *et al.* Chem. Phys. Lett. **554**, 33 (2012).

[2] M. Ishiguro, *et al.* J. Chem. Phys. **115**, 5155 (2001).

[3] D. T. Moore, *et al.* J. Chem. Phys. **115**, 5144 (2001).

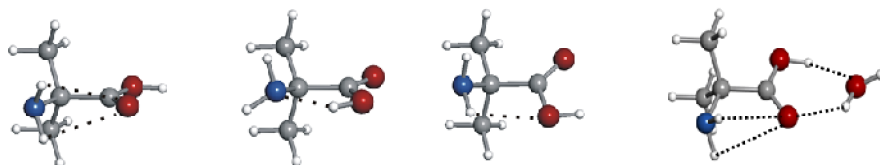
[4] D. T. Moore, *et al.* J. Chem. Phys. **115**, 5137 (2001).

THE ROTATIONAL SPECTRA OF AMINOISOBUTYRIC AND ITS MONOHYDRATE

Juan C. López, Vanesa Vaquero, Elena R. Alonso, Isabel Peña and José L. Alonso¹

¹ Grupo de Espectroscopía Molecular (GEM), Edificio Quifima, Laboratorios de Espectroscopia y Bioespectroscopia, Universidad de Valladolid, 47011 Valladolid, Spain

The rotational spectra of laser ablated α -aminoisobutyric acid and its hydrated clusters have been studied using broadband chirped pulse Fourier transform microwave spectroscopy and conventional molecular beam Fourier transform microwave spectroscopy. Three conformers showing the three possible hydrogen bond types between the amino and acid groups of an α -amino acid have been observed. The most stable conformer has a type I bifurcated hydrogen bond linking both amino hydrogen atoms to the carbonyl oxygen (N–H \cdots O=C). The second conformer detected correspond to a type II a hydrogen bond from the hydroxyl group to the amino nitrogen atom (O–H \cdots N). The third type of amino acid backbone arrangement, type III is similar to type I but with the hydroxyl oxygen acting as the hydrogen bond acceptor (N–H \cdots O–H). Indeed, conformers stabilized by this interaction are predicted to be energetically accessible for all coded aliphatic α -amino acids, but have been observed only in amino acids with polar side chain [1]. These structures have been successfully identified by comparison of the experimental rotational and ¹⁴N nuclear quadruple coupling constants with those predicted theoretically. The large values of the centrifugal distortion constants of type II conformer have been attributed to vibration-rotation interaction effects arising from a double minimum potential function associated to the torsion around the C $_{\alpha}$ -COOH bond giving rise to two equivalent type II forms. As a continuation with our work with the microsolvation of amino acids [2] we have also studied the α -aminoisobutyric acid-H₂O rotational spectra. Only one rotamer has been found which has been identified to correspond to the hydrate of the most stable conformer, type I, of the bare amino acid. In this system as in previously observed monohydrates of amino acids the water molecule forms a cycle with the carboxylic group through two OH \cdots O bonds.



[1] See for example: S. Blanco, M. E. Sanz, J. C. López and J. L. Alonso, Proc. Natl. Acad. Sci. **104**, 20183(2007); M. E. Sanz, S. Blanco, J. C. López and J. L. Alonso, Angew. Chem. **120**, 6312(2008); Sanz, M. E.; López, J. C.; Alonso, J. L. Phys. Chem. Chem. Phys. **12**, 3573(2010); C. Pérez, S. Mata, S. Blanco, J. C. López, and J. L. Alonso, J. Phys. Chem. A **115**, 9653(2011); I. Peña, M. E. Sanz, J. C. López, and J. L. Alonso, J. Am. Chem. Soc. **234**, 2315(2012).

[2] J. L. Alonso, E. J. Cocinero, A. Lesarri, M. E. Sanz, J. C. López, Angew. Chem. Int. Ed. **45**, 3471(2006). Alonso, J. L.; Peña, I.; Sanz, M. E.; Vaquero, V.; Mata, S.; Cabezas C.; López, J. C. Chem. Commun. **49**, 3443 (2013). V. Vaquero, M. E. Sanz, I. Peña, S. Mata, C. Cabezas, J. C. López, J. L. Alonso, J. Phys. Chem. A. **118**, 2584(2014).

MILLIMETER-WAVE DETECTION OF THE NH₃-H₂ VAN DER WAALS
COMPLEXIvan Tarabukin¹, Victor Panfilov¹, Leonid Surin^{1,2}, Stephan Schlemmer²¹Institute of Spectroscopy of Russian Academy of Sciences, 142190 Troitsk, Moscow, Russia²I. Physikalisches Institut, University of Cologne, 50937 Cologne, Germany

The millimeter-wave spectra of the NH₃-H₂ van der Waals complex in a supersonic jet have been measured for the first time with the ultrahigh sensitivity intracavity spectrometer, OROTRON. This study is intended to reveal the intermolecular interaction between ammonia and dihydrogen and to test the recent *ab initio* potential energy surface (PES) calculations [1, 2]. Detailed knowledge of the NH₃-H₂ interaction parameters is important for a number of applications in astrophysics.

In the present work, we have observed the end-over-end rotational bands of the complex for four different nuclear spin modifications: (*ortho*)-NH₃-(*ortho*)-H₂, (*para*)-NH₃-(*ortho*)-H₂, (*ortho*)-NH₃-(*para*)-H₂, (*para*)-NH₃-(*para*)-H₂. The (*ortho*)-H₂ monomers led to considerably stronger binding than (*para*)-H₂ monomers, therefore it was necessary to use pure (*para*)-H₂ instead of normal hydrogen to detect the NH₃-(*para*)-H₂ species. The rotation transitions were measured in the frequency range of 110-140 GHz with OROTRON spectrometer directly and at lower frequencies of 75-80 GHz applying double resonance technique. The assignments of the observed lines were based on the recent bound levels calculations of NH₃-H₂ [3] using earlier reported *ab initio* interaction potential [2].

The authors acknowledge the Deutsche Forschungsgemeinschaft (Grants SU 579/1) and the Russian Foundation for Basic Research (Grants 12-03-00985; 12-02-91337) for financial support.

[1] M. Mladenović, M. Lewerenz, G. Cilpa, P. Rosmus, and G. Chambaud, Chem. Phys. **346**, 237 (2008).

[2] S. Maret, A. Faure, E. Scifoni, and L. Wiesenfeld, Mon. Not. R. Astron. Soc. **399**, 425 (2009).

[3] A. van der Avoird, private communication (2013).