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H2S Dimer is Hydrogen Bonded: Direct Confirmation from Microwave Spectroscopy

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Abstract:	The Ka = 1 transitions of H2S dimer and several isotopomers have been observed in a pulsed nozzle Fourier transform microwave spectrometer. These provide unambiguous evidence that H2S dimer has an anisotropic structure exhibiting S-H***S hydrogen bond. The hydrogen bond distance (H***S) is determined to be 2.777(9) Å, slightly smaller than the sum of van der Waals radii of H and S (3 Å). The hydrogen bond angle S-H***S is determined to be 176(7). The structure is similar to that of the well explored H2O dimer, though in bulk, ice and solid H2S appear very different. The structure determined from microwave spectroscopy is in very good agreement with the result from high level theoretical calculations.
Author Comments:	I am enclosing a manuscript entitled "H2S Dimer is Hydrogen Bonded: Direct Confirmation from Microwave Spectroscopy" authored by Arijit Das, Pankaj K. Mandal, Frank J. Lovas, Chris Medcraft, Nicholas R. Walker and E. Arunan. There are numerous investigations of H2O dimer and the data on H2S dimer is scarce. Pauling had concluded that H2O forms hydrogen bond and H2S has van der Waals interaction based on the observed structure of these molecules in solids. His conclusions were so influential that for a long time biologists and chemists accepted this view. Hydrogen bonds by SH groups and S as acceptor have been observed and still debated. The prototype for the S-H***S hydrogen bond would be the H2S dimer about which conclusive experimental results are yet to be reported. In this manuscript we report the microwave spectrum and observation of Ka=1 transitions for the H2S dimer which unambiguously prove that the structure is hydrogen bonded. Though part of the microwave spectrum of H2S dimer was observed several decades ago in NIST (Frank

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	Lovas) and IISc (Mandal and Arunan) decades ago, they were not published as the observed lines could only lead to a structure in which both H2S are essentially spherical, resulting in a pseudodiatomic molecule. Medcraft and Walker found some transitions during their work on H2S—MX (M = Ag/Au/Cu) which they thought may come from H2S dimer which led to these experiments and eventual observation and assignment of transitions from Ka = 1 transitions proving the structure to be hydrogen bonded. The results would be interest to chemists and biologists working on hydrogen bonding. We believe that Angewandte Chemie International Edition in English would be the right Journal to carry this for wide dissemination.
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H_2S Dimer is Hydrogen Bonded: Direct Confirmation from Microwave Spectroscopy

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Abstract: The K_a = 1 transitions of H_2S dimer and several isotopomers have been observed in a pulsed nozzle Fourier transform microwave spectrometer. These provide unambiguous evidence that H_2S dimer has an anisotropic structure exhibiting S-H···S hydrogen bond. The hydrogen bond distance (H···S) is determined to be 2.777(9) Å, slightly smaller than the sum of van der Waals radii of H and S (~3 Å). The hydrogen bond angle ∠S-H···S is determined to be 176(7)°. The structure is similar to that of the well explored H_2O dimer, though in bulk, ice and solid H_2S appear very different. The structure determined from microwave spectroscopy is in very good agreement with the result from high level theoretical calculations.

The water dimer, $(H_2O)_2$, is probably the most extensively studied hydrogen-bonded system, both experimentally[1][2][3][4][5][6][7] and theoretically[8][9][10][11][12][13][14][15]. Hydrogen bonding [16][17] is crucial to all life on Earth. Hydrogen bonds are around twenty times weaker than covalent bonds but strong enough to establish the structure of water ice and play a crucial role in the structure of DNA and passing the genetic code.

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The dissociation energy of the water dimer, defined as D_0 for the fragmentation of $(H_2O)_2$ to yield two isolated water molecules, was measured experimentally to be 1105±10 cm^{-1} (13.2±0.12 kJ/mol)[18]. There have been a number of reports on its sulfur substituted dimer[19][20][21][22][23][24][25]. The microwave spectrum of the H_2S dimer is interesting to examine because of clear structural differences between the condensed phases of H_2O and H_2S. In the most commonly-encountered form of pure, solid, water ice, H_2O is surrounded by four other water molecules. An individual molecule of H_2S is surrounded by twelve H_2S molecules in isomorphs of solid H_2S[26][27] (as shown in Figure 1). Only a sphere could accommodate 12 different neighbours implying that each H_2S molecule interacts with neighbouring molecules through an effectively spherical[28] potential energy surface. The dramatic difference between the condensed phases of water and hydrogen sulfide led Pauling[26] to conclude that the structure of water ice is mediated by anisotropic, hydrogen bonds whereas the structure of solid H_2S is determined by isotropic, van der Waals interactions. Optimized geometries of $(H_2O)_2$ and $(H_2S)_2$ calculated ab initio are similar and both are hydrogen bonded. Experimental studies on the H_2S dimer are fewer in number than those on the H_2O dimer. Matrix isolation studies were not conclusive with respect to the structure of the H_2S dimer in solid N_2[29], O_2[30], Kr[31], Xe[32] and Ar[33] because H_2S readily aggregates at low temperature to form higher oligomers and infrared shifts are much smaller than those observed for H_2O complexes. An experiment that explored the gas phase structure of $(H_2S)_2$ by infrared spectroscopy found that the vibrational stretch of the proton- donating S–H bond is red-shifted by 31 cm^{-1}[25] leading to the proposal that the H_2S dimer is hydrogen bonded. A detailed description of the structure of the H_2S dimer has not yet been provided. Microwave spectroscopy can provide accurate and unambiguous information about the structure of $(H_2S)_2$.

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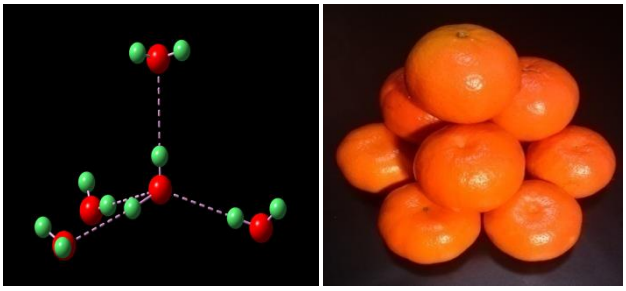

Figure 1. Comparison of the structures of solid ice H_2O (left, close to real) and solid H_2S (right, cartoon).

The rotational spectrum of $(H_2S)_2$ was previously observed using the Balle-Flygare[34] pulsed nozzle FT microwave spectrometers at NIST[35] (around 1988-1991) and IISc[36] (around 2003-2005). For most isotopologues of $(H_2S)_2$, a two state pattern of *a*-type, K_a=0 (K_a is the vector component of rotational angular momentum along the principal axis), transitions only had been observed. Neither the NIST study nor that performed at IISc identified transitions having K_a=1 which implied that the interaction between two H_2S molecules is isotropic, as in solid. With only K_a=0 transitions, the rotational spectrum could yield only average values of $(B_0+C_0)/2$ for upper and lower states (where B_0 and C_0 are rotational constants of the ground vibrational state) and these were found to be 1749.3091(8) MHz and 1748.1090(8) MHz respectively[37][38]. From these, the inferred structure would be that of a pseudo-diatomic molecule in which both H_2S are essentially spherical. This is in agreement with expectations derived from the structure of solid H_2S as modeled in Figure 1.

The first hint of a possibility that K_a=1 lines could be observed for $(H_2S)_2$ came during rotational spectroscopic studies of $H_2S\cdots$MI (M=Cu, Ag, Au) complexes[39] by Medcraft et al. using broadband microwave spectrometer at Newcastle University[40][41]. They noted 6 lines which were suspected to be assigned to transitions of the deuterated isotopomers of $(H_2S)_2$. This motivated us to re-examine the rotational spectrum of $(H_2S)_2$. After a short period of time, we observed and assigned several K_a=1 lines for the parent and other deuterated isotopomers of $(H_2S)_2$. The spectrum of $(H_2S)_2$ was observed using the Balle-Flygare[34] pulsed nozzle FT microwave spectrometer at IISc[36]. The complex was formed through supersonic expansion from a pulsed valve where the gaseous sample contained He seeded with 1 to 3 % of H_2S. The microwave pulse was of 1.0 μs duration and the expansion was through a 0.8 mm diameter nozzle with backing pressure ranging from 0.8 bar to 1.2 bar. Further details of the spectrometer employed can be found in Reference [36]. The K_a=0 transitions of the parent species can be observed in our spectrometer with a single shot. Whereas, for transitions having K_a=1, 2000 shots were averaged to obtain a reasonable signal to noise ratio. Transitions having K_a=1 are significantly weaker than those having K_a=0, rationalizing why these were not observed during previous experiments. The reduced intensity of transitions having K_a=1 probably owes to a high A_0 rotational constant of the dimer (calculated *ab initio* to be 95185.7560 MHz or ~3 cm^{-1}) which is slightly smaller than the thermal energy, kT (~2.1 cm^{-1}), at a temperature of 3 K in the molecular beam.

The initial searches for K_a=1 transitions covered the range from 10475 MHz to 10510 MHz where J = 3 – 2 transitions were expected. *Ab initio* calculation at MP2/aug-cc-pVDZ level predicted that the 3_{12}-2_{11} transition is 13 MHz above the corresponding 3_{03}-2_{02} transition. It was observed at 10508.0710 MHz, 13.8 MHz from the observed frequency of the 3_{03}-2_{02} transition (10494.2400 MHz). Similarly,the 3_{13}-2_{12} transition was predicted to be 14.5 MHz below the 3_{03}-2_{02} transition and was found at 10486.7555 MHz. Theory predicts equal intensity of the 3_{12}-2_{11} and 3_{13}-2_{12} transitions but it was experimentally observed that the former is more intense than the latter by a factor of three. The observation of these transitions allowed K_a=1 lines for other J states to be sought and identified thus confirming the initial assignment. Observation and assignment of other K_a=1 lines are unambiguous for the two states (see Tables 1 and Table 2). The rotational constants and distortion constants for the two states of the H_2S dimer are given in Table 3. Transitions from the two states of the dimer were fitted separately using a Watson S-reduced Hamiltonian and the SPFIT program of Pickett[42]. Acceptable fits with rms residuals of the order of 0-5 kHz were obtained only after the inclusion of sextic distortion constants. Given that large amplitude motion can be expected in $(H_2S)_2$, it is quite reasonable to anticipate difficulties in fitting higher K_a lines. The transitions found initially at Newcastle are assigned to transitions of the HSD⋯SDH having K_a=1 (see Supplementary Data Table S17). Since completion of this work, it has been realized that the original data from NIST did have some of the K_a=1 transitions for $(D_2S)_2$ and none for $(H_2S)_2$. The observation of the deutereated dimers must have been the result of the lower A constant, calculated to be 49142.1785 MHz for $(D_2S)_2$ and 72259.3025 MHz for $(HDS)_2$ bringing the energy levels closer to thermal energy in the molecular beam.

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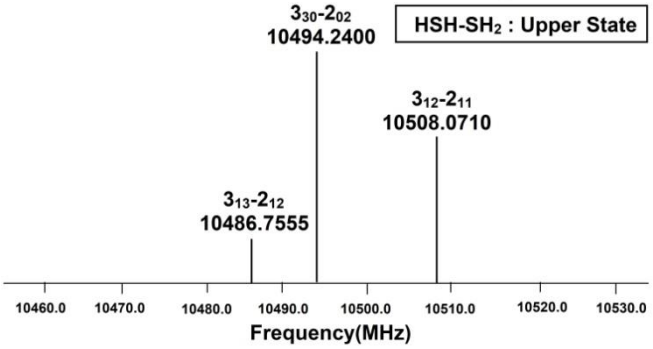

Figure 2. Experimentally-observed 3_{13}-2_{12} and 3_{12}-2_{11}transitions associated with the J = 3 – 2 transition. Intensity not to scale. Intensities of $_a$=1 lines shown on either side have been amplified for clarity.

Table 1. Fitted rotational transitions for parent isotopomer of $(H_2S)_2$ (Upper State).Quantities are in MHz.

J K_a K_c	J K_a K_c	Frequency[a] (MHz)	Residual (MHz)
1 0 1	0 0 0	3498.5605	0.0025
2 1 2	1 1 1	6991.7730	0.0059
2 0 2	1 0 1	6996.7610	0.0035
2 1 1	1 1 0	7006.0220	0.0062
3 1 3	2 1 2	10486.7555	0.0016
3 0 3	2 0 2	10494.2400	0.0001
3 1 2	2 1 1	10508.0710	0.0026
4 1 4	3 1 3	13980.6620	-0.0025
4 0 4	3 0 3	13990.6459	-0.0008
4 1 3	3 1 2	14008.9690	-0.0055
5 1 5	4 1 4	17473.1350	-0.0056
5 0 5	4 0 4	17485.6150	-0.0047
5 1 4	4 1 3	17508.3490	-0.0031
6 1 6	5 1 5	20963.8270	0.0036
6 0 6	5 0 5	20978.8031	0.0028
6 1 5	5 1 4	21005.8220	0.0028

[a] Measurement uncertainty 4 kHz

The experimentally measured centrifugal distortion constants, D_J, for upper and lower states are 14.921(11) kHz and 15.228(11) kHz respectively, which are substantially larger than theoretically-predicted values of 4.38 kHz. For comparison, the centrifugal distortion constants, D_J, of the E_1 and E_2 states of the water dimer were determined to be 49 kHz and -780 kHz respectively[10]. Note that, while the results obtained are sensible, a few of the centrifugal distortion constants determined for the H_2S dimer are negative, suggesting that large amplitude motions are a pervasive feature of the system.

Table 2. Fitted rotational transitions for parent isotopomer of $(H_2S)_2$ (Lower State).Quantities are in MHz.

J K_a K_c	J K_a K_c	Frequency[a] (MHz)	Residual (MHz)
1 0 1	0 0 0	3496.1609	0.0036
2 1 2	1 1 1	6985.1597	-0.0014
2 0 2	1 0 1	6991.9510	0.0025
2 1 1	1 1 0	7001.7420	-0.0054
3 1 3	2 1 2	10479.2300	0.0012
3 0 3	2 0 2	10487.0080	-0.0001
3 1 2	2 1 1	10499.5020	0.0072
4 0 4	3 0 3	13980.9690	-0.0020
4 1 3	3 1 2	13995.6420	-0.0033
5 1 5	4 1 4	17462.5527	-0.0001
5 0 5	4 0 4	17473.4680	-0.0022
5 1 4	4 1 3	17493.2586	0.0005
6 0 6	5 0 5	20964.1353	0.0018

[a] Measurement uncertainty 4 kHz

The results of similar fits of data for the deuterated and partially deuterated species are provided in the supplementary information (see Table S7 to Table S18), which also exhibit harmonic progressions in $B_0 + C_0$, so searches and assignments of various K_a=1 lines followed the same procedure outlined above. K_a=1 transitions for the mono-^{34}S (4% natural abundance) species are not reported in this communication owing to their low signal to noise ratio. To benefit any future investigation of these mono-^{34}S species, we list the K_a=0 transitions and molecular constants in supplementary information (see Table S21). As noted above, no *b*-type transitions were identified in this work and thus, the experimental determination of the A_0 rotational constant is not possible.

The structure of the complex was determined using two separate methods, one involving substitution analysis by Kraitchman and the other involving Kisiel's fitting program STRFIT[43]. In both cases, the structures of the free monomers were assumed to be unchanged upon complexation and rotational constants from the lowers state were used. Kraitchman equations (see supplementary information) were used to find the R(S – S), donor–acceptor sulphur atoms distance. As a matter of fact, we should keep in mind that hydrogens of $(H_2S)_2$ are affected by large amplitude motions. Thus, the vibrationally averaged geometry is not the same in the deuterated structure because deuterium will undergo smaller motions than will the hydrogen atoms.

Table 3. Fitted rotational constants (Upper State and Lower State) of $(H_2S)_2$.

Constants	Theory[a]	Upper State[b]	Lower State[b]
A_0/MHz	95185.7560	-	-
B_0/MHz	1774.9376	1752.8788(11)	1753.1019(28)
C_0/MHz	1765.7506	1745.7388(11)	1743.1163(28)
$(D_J)_0$/kHz	4.383	14.921(11)	15.227(11)
$(D_{JK})_0$/kHz	130.92	-537.46(80)	-363.46(88)
$(d_1)_0$/kHz	-0.0221	-0.4887(87)	-59.83(10)
$(H_{JK})_0$/Hz	-	-508.(14)	1590.(19)
$(h_1)_0$/Hz	-	-	1068.6(22)
σ/kHz		4	3
# transitions		16	13

[a] Theoretical value calculated at MP2/aug-cc-pVDZ

[b] Uncertainties are one standard deviation

Kisiel's STRFIT program[43] was implemented to find the three parameters (1) r(H···S), the hydrogen bond distance, (2) θ(S-H···S), the angle between the S–H donor and acceptor sulfur atom and (3) φ, the angle between the symmetry axis of the proton-accepting H_2S with respect to intermolecular bond. The dihedral angle between the planes of the two H_2S molecules was kept at 90˚ initially. The fitted parameters are further verified using the SFQ3 program, written by Schwendeman[44], which fits the internal co-ordinates like Kisiel's program. Both fits are in close agreement with each other. The fitted parameters from STRFIT are listed in Table 4 along with the *ab initio* results. The hydrogen bond distance in H_2S dimer is found out to be 2.777(9) Å which is less than the sum of van der Waals radii of the H and S atoms (3.0 Å)[45]. Angle between (S-H···S) is 176(7)˚, which suggests hydrogen bond is almost linear. Dyke and co-workers[6] had found the water dimer structure, using molecular beam electric resonance spectroscopy, with an oxygen-oxygen distance R(O-O) of 2.98(1) Å. The proton-accepting water axis is 58(6)˚ with respect to R(O-O) and the proton-donating water axis at -51(6)˚ with respect to R(O-O). In H_2S dimer, the tilt between the acceptor H_2S moiety and the intermolecular axis is found out to be φ = 78(4)˚. The structure of both $(H_2O)_2$ and $(H_2S)_2$ are given for comparison (Figure 3 and Figure 4). As noted in the title of this communication, the goal of this work was to determine whether H_2S dimer is hydrogen bonded or not. It can be concluded that H_2S dimer qualifies for all the criteria recommended by IUPAC to be hydrogen bonded[16][17] and its structure is similar to that of the water dimer.

In summary, though the microwave spectrum of H_2S dimer had been investigated 3 decades ago, with only K_a=0 lines very little structural information could be obtained[37][38]. With only K_a=0 lines identified, one had to assume H_2S to be a sphere and model the dimer geometry as pseudo-diatomic. The observation and assignment of K_a=1 lines are extremely important in proving that H_2S dimer is hydrogen bonded and the interaction between individually-isolated H_2S molecules is not isotropic. The disparity of behavior of H_2S in solids and in our experimental conditions can be understood, in the light of the criterion proposed by Goswami and Arunan[46]. In solids, the thermal energy along a coordinate that can break the hydrogen bond is greater than the barrier along that coordinate, leading to an average spherical shape for H_2S. When the temperature reduces significantly, the thermal motion becomes restrained, leading to the observation of a hydrogen bonded geometry in our case. Hence, though H_2S remains in gaseous form at room temperature and each H_2S has 12 neighbors when frozen at -60˚C; at lower temperatures, the H_2S dimer exhibits hydrogen bonding. In fact, Loveday *et al.*[27] have showed earlier that, even in crystals, at low temperature and high pressure, D_2S exhibits anisotropic packing and hydrogen bonded. They used D_2S which has significantly shorter oscillations due to thermal vibrations compared to H_2S. They concluded that H_2S is an excellent model system, where we can literally jingle with the hydrogen bond strength from "absent or very weak to structurally significant". Microwave spectrum of the H_2S dimer reported in this Communication provides the first unambiguous confirmation that H_2S dimer is hydrogen bonded.

Table 4. Structural parameters of $(H_2S)_2$ along with the theoretically predicted values.

	R(S – S) Å	r(H···S) Å	θ(S-H···S)˚	φ˚
Ab-initio[a]	4.096	2.743	173	85
Experiment	4.112(1)[b]	2.777(9)	176(7)	78(4)

[a] *Ab initio* values calculated at MP2/aug-cc-pVDZ[47] [b] Evaluated using Kraitchman analysis.

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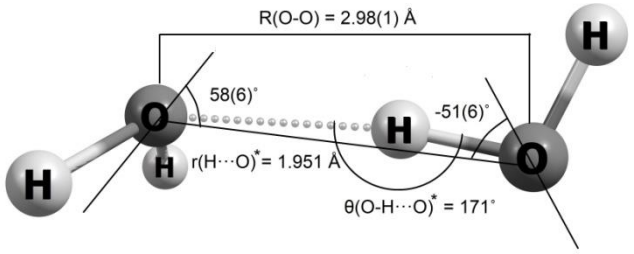

Figure 3: Structure of the H_2O dimer obtained from the molecular beam electric resonance spectroscopy[6]. * *ab initio* (MP2/aug-cc-pVDZ) values.

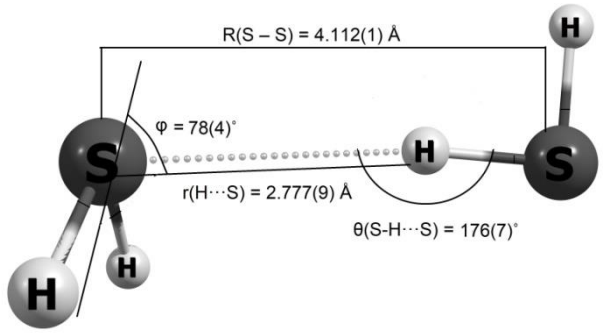

Figure 4: Structure of the H_2S dimer obtained from the experiment.

Water dimer undergoes several tunnelling motions that permit each of the four hydrogens to participate in the H-bonding[10]. The ground vibrational level of water dimer is eight-fold degenerate and it splits into six levels as a result of tunnelling. Two of them are doubly degenerate (E_1 and E_2 states) and the remaining four are non-degenerate (A_1, B_1, A_2, B_2). Only the doubly degenerate states give rigid rotor spectra. The other four give tunneling spectra having lines displaced from rigid rotor predictions by very large tunneling splitting. H_2S dimer microwave spectra should also be affected by the large amplitude tunneling motions. If we assume that H_2S dimer would exhibit tunneling motions similar to those of water dimer, then the two states reported here could be labeled as E_1 and E_2 states. There is evidence for another progression of transitions and more are likely to be found. Further studies of the dimer, with a detailed analysis of the tunnelling levels will be published in future.

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Keywords: Hydrogen bonding • van der Waals interactions• Molecular Beam• Water• Weakly bound complexes

[1] T. R. Dyke, J. S. Muenter, *The Journal of Chemical Physics* **1974**, *60*, 2929–2930.

[2] L. H. Coudert, F. J. Lovas, R. D. Suenram, J. T. Hougen, *The Journal of Chemical Physics* **1987**, *87*, 6290–6299.

[3] J. A. Odutola, T. A. Hu, D. Prinslow, S. E. O'Dell, T. R. Dyke, *The Journal of Chemical Physics* **1988**, *88*, 5352–5361.

[4] K. L. Busarow, R. C. Cohen, G. A. Blake, K. B. Laughlin, Y. T. Lee, R. J. Saykally, *The Journal of Chemical Physics* **1989**, *90*, 3937–3943.

[5] R. D. Suenram, G. T. Fraser, F. J. Lovas, *Journal of Molecular Spectroscopy* **1989**, *138*, 440–449.

[6] T. R. Dyke, K. M. Mack, J. S. Muenter, *The Journal of Chemical Physics* **1977**, *66*, 498–510.

[7] F. N. Keutsch, N. Goldman, H. A. Harker, C. Leforestier, R. J. Saykally, *Molecular Physics* **2003**, *101*, 3477–3492.

[8] T. R. Dyke, *The Journal of Chemical Physics* **1977**, *66*, 492–497.

[9] L. H. Coudert, J. T. Hougen, *Journal of Molecular Spectroscopy* **1988**, *130*, 86–119.

[10] G. T. Fraser, *International Review in Physical Chemistry* **1991**, *10*, 189–206.

[11] R. S. Fellers, C. Leforestier, L. B. Braly, M. G. Brown, R. J. Saykally, *Science* **1999**, *284*, 945–948.

[12] N. Goldman, R. S. Fellers, M. G. Brown, L. B. Braly, C. J. Keoshian, C. Leforestier, R. J. Saykally, *The Journal of Chemical Physics* **2002**, *116*, 10148–10163.

[13] Y. Watanabe, T. Taketsugufoot, D. J. Wales, *The Journal of Chemical Physics* **2004**, *120*, 5993–5999.

[14] S. Scheiner, *Annual Review of Physical Chemistry* **1994**, *45*, 23–56.

[15] L. B. Braly, J. D. Cruzan, K. Liu, R. S. Fellers, R. J. Saykally, *The Journal of Chemical Physics* **2000**, *112*, 10293-10313.

[16] E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci, and D. J. Nesbitt, *Pure and Applied Chemistry* **2011**, *83*, 1637–1641.

[17] E. Arunan, G. R. Desiraju, R. A. Klein, J. Sadlej, S. Scheiner, I. Alkorta, D. C. Clary, R. H. Crabtree, J. J. Dannenberg, P. Hobza, H. G. Kjaergaard, A. C. Legon, B. Mennucci, and D. J. Nesbitt, *Pure and Applied Chemistry* **2011**, *83*, 1619–1636.

[18] B. E. Rocher-Casterline, L. C. Chng, A. K. Mollner, H. Reisler, *The Journal of Chemical Physics* **2011**, *134*, 211101.

[19] P. Kollman, J. McKelvey, A. Johansson, S. Rothenberg, *Journal of the American Chemical Society* **1975**, *97*, 955–965.

[20] R. C. Kerns, L. C. Allen, *Journal of the American Chemical*

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*Society***1978**, *100*, 6587–6594.
[21] G. de Oliveira, C. E. Dykstra, *Chemical Physics Letters***1995**, *243*, 158–164.
[22] R. D. Amos, *Chemical Physics***1986**, *104*, 145–151.
[23] K. H. Lemke, *The Journal of Chemical Physics***2017**, *146*, 234301.
[24] T. Pradeep, C. N. R. Rao, *Chemical Physics Letters***1991**, *185*, 496–500.
[25] A. Bhattacherjee, Y. Matsuda, A. Fujii, S. Wategaonkar, *ChemPhysChem***2013**, *14*, 905–914.
[26] L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals,* Cornell University Press,**1939**.
[27] J. S. Loveday, R. J. Nelmes, S. Klotz, J. M. Besson, G. Hamel, *Physical Review Letters***2000**, *85*, 1024–1027.
[28] E. Arunan, D. Mani, *Faraday Discussions***2015**, *177*, 51–64.
[29] A. J. Tursi, E. R. Nixon, *The Journal of Chemical Physics***1970**, *53*, 518–521.
[30] E. L. Woodbridge, T. L. Tso, M. P. McGrath, W. J. Hehre, E. K. C. Lee, *The Journal of Chemical Physics***1986**, *85*, 6991–6994.
[31] H. Tsujii, K. Takizawa, S. Koda, *Chemical Physics***2002**, *285*, 319–326.
[32] K. Koga, A. Takami, S. Koda, *Chemical Physics Letters***1998**, *293*, 180–184.
[33] J. Pacansky, V. Calder, *The Journal of Chemical Physics***1970**, *53*, 4519–4524.
[34] T. J. Balle, W. H. Flygare, *Review of Scientific Instruments***1981**, *52*, 33–45.
[35] F. J. Lovas, R. D. Suenram, *The Journal of Chemical Physics***1987**, *87*, 2010–2020.
[36] E. Arunan, A. P. Tiwari, P. K. Mandal, P. C. Mathias, *Current Science***2002**, *82*, 533–540.
[37] F. J. Lovas, R. D. Suenram, L. H. Coudert, *43 Int. Symp. On Molecular Spectroscopy***1988**.
[38] P. K. Mandal, *Ph.D. Dissertation Indian Institute of Science***2005**.
[39] C.Medcraft, D. M. Bittner, D. P. Tew, N. R. Walker, A. C. Legon, *Journal of Chemical Physics***2016**, *145*, 194306.
[40] S. L. Stephens, N. R. Walker, *Journal of Molecular Spectroscopy***2010**, *263*, 27–33.
[41] D. P. Zaleski, S. L. Stephens, N. R. Walker, *Physical Chemistry Chemical Physics***2014**, *16*, 25221–25228.
[42] H. M. Pickett, *Journal of Molecular Spectroscopy***1991**, *148*, 371–377.
[43] Z. Kisiel, *Journal of Molecular Spectroscopy***2003**, *218*, 58–67.
[44] R.H. Schwendeman, in: D.R. LideJr., M.A. Paul (Eds.), Critical Evaluation of Chemical and Physical Structural Information, National Academy of Sciences-National Research Council, Washington, DC, **1974**, pp. 94–115.
[45] S. S. Batsanov, *Inorganic Materials Translated from Neorganicheskie Materialy Original Russian Text***2001**, *37*, 871–885.
[46] M. Goswami, E. Arunan, *Physical Chemistry Chemical Physics***2009**, *11*, 8974-8983.
[47] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

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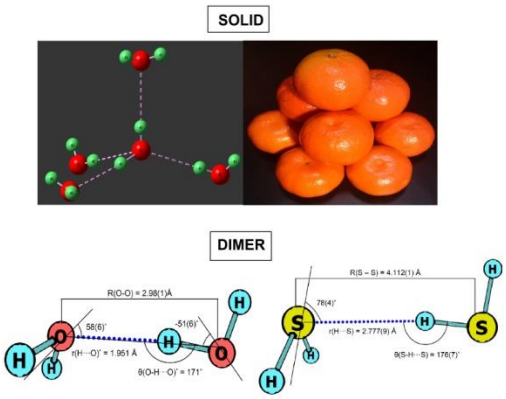

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