Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Material

Insights into the non-covalent interactions of hydrogen sulfide with fenchol and fenchone from a gas-phase rotational study

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Contents

Experimental setup

The rotational spectra were recorded using a pulsed Fabry–Pérot Fourier transform microwave (FP-FTMW) spectrometer coupled to supersonic expansion, available in the PhLAM laboratory in Lille, and operating in the frequency range 2-20 GHz[1].

Fenchol (1,3,3-Trimethylbicyclo [2.2.1] heptan-2-ol, $C_{10}H_{18}O$, ≥ 99 %, with endo-fenchol labeled as EF) and Fenchone (1,3,3-Trimethylbicyclo [2.2.1] heptan-2-o, $C_{10}H_{16}O$, ≥ 99 %, labeled as FEN) were purchased from Sigma-Aldrich and used without any further purification. The H_2S (dihydrogen sulfide, ≥ 99.5 %) was purchased in the form of a 15 bar gas cylinder from Air Liquide and used as it is without any further purification.

A premixture of H_2S and Neon as carrier gas was prepared in a 500 mL sampling cylinder (Swagelok). The mixture contained 50 mbar of H_2S and excess of Neon to reach 3.5 bar (≈1.5% dilution). The mixture was then seeded into an injector containing fenchol or fenchone and supersonically expanded into the vacuum chamber through a 1 mm pinhole. The injector was heated to 348 K to enhance the molecular signal-to-noise ratio. The rotational temperature of the molecules in the jet is in the order of a few Kelvins. Microwave power pulses of 2 µs duration were used to polarize the molecules in the optical cavity. The Free Induction Decay (FID) molecular signals were recorded by a 14-bit digitizer card operating at 120 MSa/s. Between 500 and 3000 FIDs were averaged, in high-resolution mode (frequency step between 0.96 and 3.68 kHz) to achieve a reasonable signal-to-noise ratio. A fast Fourier transform (FFT) was applied to the FID time-domain signals to obtain the frequency domain signals. The signals in the cavity are recorded as Doppler doublets and the experimental frequency considered is the central frequency obtained by the arithmetic averaging of the two Doppler components. Figures S1 and S2 show transitions recorded using the high-resolution mode for the **EF-H2S** and **FEN-H_2S** complexes, respectively.

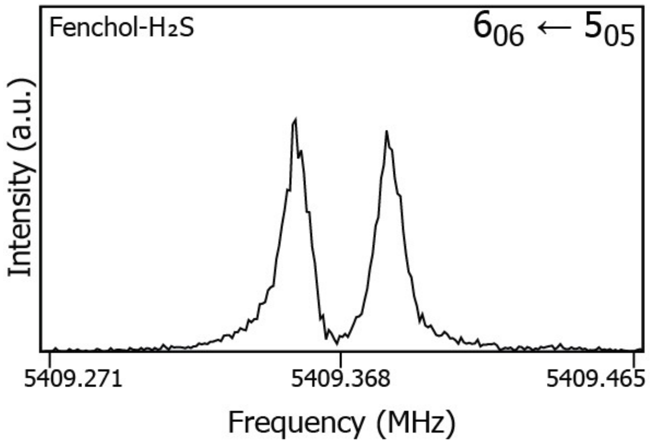


Figure S1. Observed transition at high resolution of the endo fenchol-H_2S complex. The signal is the result of 2800 averages. The transition appears as a doublet due to the coaxial alignment of the exciting radiation and molecular beam. The assignment is indicated in the top right corner.

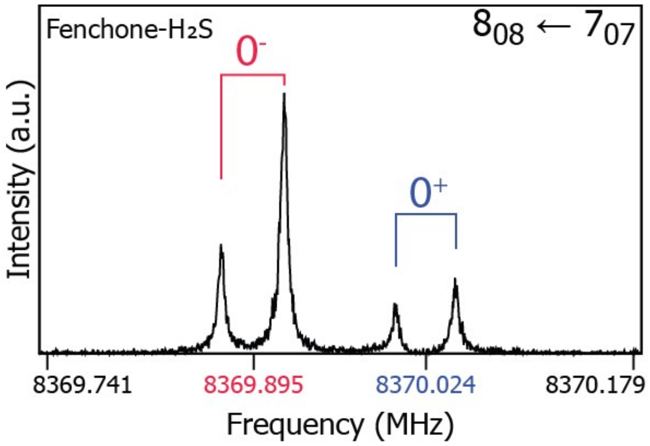


Figure S2. Observed transition at high resolution of the fenchone-H_2S complex. The signal is the result of 1000 averages. The transitions appear as doublets due to the coaxial alignment of the exciting radiation and molecular beam. The splitting due to a large amplitude motion of H_2S are labelled as 0^+ and 0^-. The assignment is indicated in the top right corner.

Theoretical calculations

Quantum chemical calculations facilitate the identification of the observed conformers and the assignment of the experimental spectrum. *Ab initio* and density-functional theory (DFT) calculations were used to predict the most stable conformers. Calculations were performed using the Gaussian 16[2] software available on the high-performance computing cluster of PhLAM. The methods used were Møller-Plesset second-order perturbation theory (MP2)[3], and the DFT ωB97X-D[4] and B3LYP[5,6] functionals. Pople split-valence triple-zeta basis set, augmented with diffuse and polarization functions on all atoms (6-311++G(d,p)) basis set[7] was used with the MP2 and ωB97X-D methods, while Ahlrichs split-valence and triple zeta basis set with polarization (def2TZVP)[8,9], with empirical dispersion correction (D3 version of Grimme's dispersion with Becke-Johnson damping), was used with the B3LYP method. First, geometry optimization of the conformers was done to obtain the rotational constants A, B and C. Second, harmonic frequencies calculations were performed to obtain the centrifugal distortion parameters Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_k, as well as the energy ordering of the different conformers. Relative energy ordering is important to have an idea about what to predict in the spectrum and to have an idea about the relaxations taking place in the jet. Four stable conformers were predicted for the EF-H2S complex, labeled using Roman numerals I_{EF}, II_{EF}, III_{EF} and IV_{EF}, following the energy order. Similarly, six stable conformers were predicted for the FEN-H_2S complex, and they were labeled as I_{FEN}, II_{FEN}, III_{FEN}, IV_{FEN}, V_{FEN} and VI_{FEN}, according to the increasing order of their relative energies. The calculations also gave the dipole moments values of each conformer. The calculated dipole moments were used to optimize the polarizing power, and for the identification of the observed conformers. The calculated constants for the different conformers, and at different levels of theory, are summarized in Tables S1 through S4 for the EF-H2S complex and in the Tables S5 through S10 for the FEN-H_2S complex.

Furthermore, analysis of the natural bonding orbitals (NBOs) involved in the intermolecular charge transfer, which stabilizes the complexes with Sulfur, was carried out at the MP2/6-311++G(d,p) level of theory. The output of the MP2/6-311++G(d,p) optimization was also used to perform non-covalent interaction (NCI) calculations, using NCIplot[10], that permits to plot the isosurface of the interactions occurring between the different atoms, thus helping to understand the different forces that stabilize the complex. In addition, Symmetry-adapted perturbation theory (SAPT),[11] which calculates the total noncovalent energy, and decomposes it into electrostatic, exchange, induction and dispersion terms, was used to compare the contribution of the different interaction terms in the observed complexes. The SAPT energy was calculated at the $SAPT_{2+3}$ level using the PSI4 code.[12,13]

Optimized geometries of the endo fenchol-H_2S complex conformers

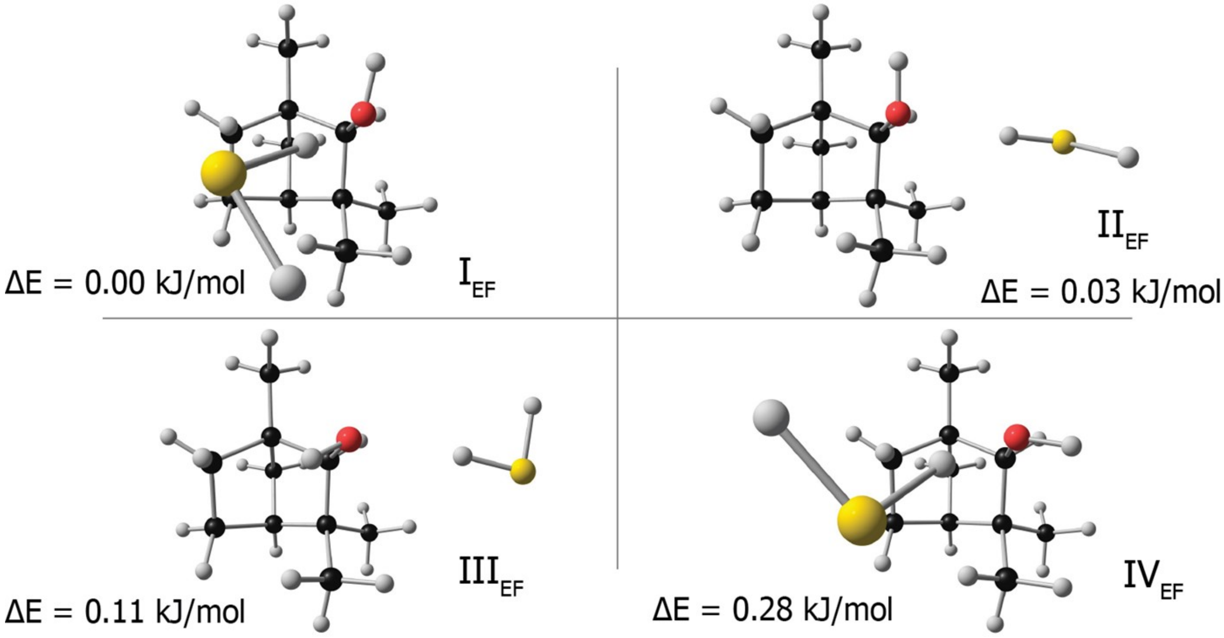


Figure S3. Calculated structures for the conformers of the fenchol-H_2S complex at the MP2/6-311++G(d,p) level of theory.

Tables S1-S2. Experimental vs calculated constants for the different conformers of endo fenchol-H_2S

Table S1

		EF-H_2S					
		I_{EF}			II_{EF}		
Constants	Experimental	MP2/ 6-311++G(d,p)	ωB97X-D/ 6-311++G(d,p)	B3LYP/ def2TZVP	MP2/ 6-311++G(d,p)	WB97XD/ 6-311++G(d,p)	B3LYP/ def2TZVP
A (MHz)	1161.2329(32)	992.1	996.6	994.4	1187.5	1201.7	1193.0
B (MHz)	494.21434(11)	564.6	550.3	551.2	510.2	494.7	496.8
C (MHz)	430.006772(86)	491.9	479.5	479.7	445.3	434.4	435.7
Δ_J (kHz)	0.20603(35)	0.0867	0.0911	0.1337	0.1213	0.0552	0.0728
Δ_{JK} (kHz)	0.8615(31)	0.3675	0.2997	0.4271	0.1910	0.1425	0.2224
Δ_K (kHz)	-0.4525	-0.4211	-0.3497	-0.5187	0.0580	-0.0600	-0.0828
δ_J (kHz)	0.03287(22)	0.0111	0.0110	0.0163	0.0208	0.0070	0.0101
δ_K (kHz)	0.231(12)	0.1317	0.1346	0.1797	0.1466	0.0444	0.0773
|μa|(D)	observed	2.1	2.5	2.1	1.6	2.3	2.0
|μb|(D)	Not observed	0.07	0.01	0.1	0.8	0.5	0.6
|μc|(D)	Not observed	0.9	1.0	1.0	0.2	0.1	0.1
ΔE^a		0.14	0.96	1.47	0.00	0.61	0.49
ΔE_{ZPE} ^{b}		0.00	0.54	1.38	0.03	1.22	0.86
ΔG_{348} ^{c}		1.37	1.42	1.71	0.00	3.37	2.23
No. of lines	56						
RMS (kHz)	1.44						

a Electronic relative energies corresponding to the global minima corresponding to the method/basis set.

b Electronic relative energies including ZPE correction corresponding to the global minima corresponding to the method/basis set.

c Gibbs energies corresponding to the global minima corresponding to the method/basis set.

Table S2

		EF-H2S					
		III_{EF}			IV_{EF}		
Constants	Experimental	MP2/ 6-311++G(d,p)	ωB97X-D/ 6-311++G(d,p)	B3LYP/ def2TZVP	MP2/ 6-311++G(d,p)	WB97XD/ 6-311++G(d,p)	B3LYP/ def2TZVP
A (MHz)	1161.2329(32)	1182.5	1187.5	1192.7	993.9	995.7	995.5
B (MHz)	494.21434(11)	505.8	498.4	497.4	566.5	553.8	553.9
C (MHz)	430.006772(86)	439.5	434.8	434.9	492.6	481.8	481.3
Δ_J (kHz)	0.20603(35)	0.0553	0.0546	0.0605	0.0761	0.0930	0.1143
Δ_{JK} (kHz)	0.8615(31)	0.7496	0.5767	0.4782	0.5718	0.4246	0.4798
Δ_K (kHz)	-0.4525	-0.4525	-0.3646	-0.2790	-0.6174	-0.4852	-0.5599
δ_J (kHz)	0.03287(22)	0.0076	0.0071	0.0074	0.0095	0.0107	0.0135
δ_K (kHz)	0.231(12)	0.2892	0.1999	0.1653	0.2354	0.1898	0.1942
|μa|(D)	observed	2.7	3.0	2.5	2.0	2.3	1.9
|μb|(D)	Not observed	0.02	0.2	0.1	0.03	0.04	0.1
|μc|(D)	Not observed	0.1	0.1	0.1	0.7	0.9	0.9
ΔE^a		0.29	0.00	0.00	0.53	1.64	1.48
ΔE_{ZPE}^b		0.11	0.00	0.00	0.28	1.22	1.39
ΔG_{348} ^{c}		0.40	0.00	0.00	1.02	1.27	1.82
No. of lines	56						
RMS (kHz)	1.44						

[a] Electronic relative energies corresponding to the global minima corresponding to the method/basis set.

[b] Electronic relative energies including ZPE correction corresponding to the global minima corresponding to the method/basis set.

[c] Gibbs free energies (348 K) corresponding to the method/basis set.

Differences (in %) between observed and calculated rotational constants

Table S3

		III_{EF}		
Constants	Experimental	MP2/6-311++G(d,p) [a]	ωB97X-D/6-311++G(d,p) [a]	B3LYP/def2TZVP [a]
A (MHz)	1161.2329(32)	1.8	2.3	2.7
B (MHz)	494.21434(11)	2.3	0.8	0.6
C (MHz)	430.006772(86)	2.2	1.1	1.1
Δ_J (kHz)	0.20603(35)	73.2	73.5	70.6
Δ_{JK} (kHz)	0.8615(31)	13.0	33.1	44.5
Δ_K (kHz)	-0.4525	-	-	-
δ_J (kHz)	0.03287(22)	97.7	97.8	97.8
δ_K (kHz)	0.231(12)	25.2	13.5	28.4

[a] The % has been calculated using the formula: ($\Delta = \frac{observed - calcualted}{observed}$)

Measured rotational transitions for the observed conformer of endo fenchol-H_2S complex

Table S4

J	K_a	K_c	J'	K_a'	K_c'	ν_{EXP} (MHz)	$\Delta\nu_{EXP}$ (MHz) *
3	0	3	2	0	2	2755.1185	0.0010
4	1	4	3	1	3	3560.1331	-0.0005
4	0	4	3	0	3	3653.8855	0.0004
5	2	3	4	2	2	4693.7287	-0.0012
5	1	4	4	1	3	4760.1133	-0.0021
6	1	6	5	1	5	5322.1969	0.0006
6	0	6	5	0	5	5409.3682	0.0000
6	2	5	5	2	4	5525.3124	0.0007
6	1	5	5	1	4	5696.9547	0.0041
7	1	7	6	1	6	6197.5214	-0.0005
7	0	7	6	0	6	6270.2349	0.0011
7	2	6	6	2	5	6435.1684	0.0000
7	4	4	6	4	3	6490.7416	-0.0002
7	4	3	6	4	2	6491.5472	-0.0011
7	3	5	6	3	4	6494.9286	0.0000
7	3	4	6	3	3	6517.9149	0.0006
7	1	6	6	1	5	6623.8815	0.0007
7	2	5	6	2	4	6633.3928	-0.0002
8	1	8	7	1	7	7069.3239	-0.0001
8	0	8	7	0	7	7125.4661	0.0002
8	2	7	7	2	6	7340.1844	0.0029
8	4	5	7	4	4	7423.2486	0.0018
8	3	6	7	3	5	7425.0992	-0.0016
8	4	4	7	4	3	7425.4432	-0.0010
8	3	5	7	3	4	7469.5995	-0.0039
8	1	7	7	1	6	7538.2905	-0.0018
8	2	6	7	2	5	7605.8638	-0.0007
9	1	9	8	1	8	7938.0568	0.0008
9	0	9	8	0	8	7978.8205	-0.0012
9	3	7	8	3	6	8353.8626	0.0005
9	4	6	8	4	5	8357.3959	0.0006
9	2	7	8	2	6	8573.2939	-0.0010
10	1	10	9	1	9	8804.2585	-0.0015
10	0	10	9	0	9	8832.505	0.0017
10	3	8	9	3	7	9280.1342	0.0002
10	4	7	9	4	6	9292.9756	0.0010
10	4	6	9	4	5	9304.0275	-0.0016
10	1	9	9	1	8	9321.5323	-0.0009
10	3	7	9	3	6	9404.2328	-0.0017
10	2	8	9	2	7	9531.9971	-0.0005
11	1	11	10	1	10	9668.4842	-0.0005
11	0	11	10	0	10	9687.3703	-0.0021
11	2	10	10	2	9	10022.8814	-0.0015
11	1	10	10	1	9	10190.1427	-0.0012
11	3	9	10	3	8	10202.8627	0.0000
11	4	8	10	4	7	10229.5622	0.0005
11	4	7	10	4	6	10251.0814	0.0012
11	3	8	10	3	7	10386.0615	-0.0015
11	2	9	10	2	8	10479.3008	0.0021
12	1	12	11	1	11	10531.2279	0.0023
12	0	12	11	0	11	10543.5221	-0.0008
12	2	11	11	2	10	10906.2358	0.0005
12	1	11	11	1	10	11046.9143	-0.0014
12	3	10	11	3	9	11121.0994	-0.0003
12	4	8	11	4	7	11205.3872	-0.0022
13	2	12	12	2	11	11784.6293	0.0021

* $\Delta\nu = \nu_{CALC} - \nu_{EXP}$

MP2/6-311++G(d,p) cartesian coordinates of the calculated structures of endo fenchol-H_2S

Table S5

	I_{EF}			II_{EF}			III_{EF}			IV_{EF}		
	E= 864.705888 Hartree			E= 864.705943 Hartree			E= 864.705834 Hartree			E= 864.705739 Hartree		
Element	X	Y	Z	X	Y	Z	X	Y	Z	X	Y	Z
C	1.021351	-1.222370	-0.163763	1.445694	0.981386	0.222467	1.418933	1.009223	0.218733	-0.938743	1.255171	-0.178520
C	0.020031	-1.321922	1.008062	2.192642	0.524655	-1.051134	2.199744	0.559056	-1.038594	0.091140	1.310837	0.973125
C	0.435609	-0.161940	1.956490	2.390302	-1.003587	-0.840455	2.432058	-0.963735	-0.818757	-0.361097	0.179864	1.940264
C	1.504557	0.577436	1.132650	1.572748	-1.273406	0.434200	1.610385	-1.245272	0.451109	-1.506740	-0.491625	1.161065
C	2.258374	-0.624333	0.530258	1.949453	-0.031973	1.264873	1.946749	0.016433	1.269440	-2.191192	0.751868	0.561345
C	0.867265	1.230411	-0.126194	0.057269	-1.046882	0.169133	0.091195	-1.063134	0.178560	-0.959557	-1.203352	-0.107010
C	0.630652	-0.015841	-1.039033	-0.019362	0.514272	0.117949	-0.032668	0.502297	0.114549	-0.637654	0.020213	-1.038832
C	-0.415792	2.008718	0.172665	-0.443040	-1.717723	-1.113337	-0.390846	-1.751851	-1.099961	0.260580	-2.084970	0.164102
C	1.864018	2.188986	-0.789204	-0.765876	-1.586453	1.345830	-0.725720	-1.615226	1.353192	-2.053162	-2.074178	-0.737717
C	1.209096	-2.511609	-0.942685	1.597857	2.456228	0.549713	1.520931	2.490082	0.531063	-1.059446	2.539085	-0.978008
O	-0.706645	-0.048537	-1.548274	-0.704268	0.967041	-1.054000	-0.777428	1.032325	-0.979992	0.699944	0.089320	-1.542532
H	-1.012113	-1.227286	0.661659	1.613282	0.753064	-1.951057	1.662091	0.778988	-1.970184	1.111659	1.169221	0.612533
H	0.118596	-2.296727	1.499935	3.153286	1.047159	-1.127372	3.147740	1.105547	-1.098112	0.041799	2.293044	1.457841
H	-0.404083	0.469189	2.255375	2.072601	-1.602256	-1.696903	2.142812	-1.577530	-1.675036	0.447388	-0.504232	2.207817
H	0.893354	-0.554535	2.871662	3.444619	-1.234895	-0.650404	3.490391	-1.164009	-0.617734	-0.756524	0.600025	2.871981
H	2.103717	1.286729	1.714997	1.774189	-2.247592	0.893987	1.840549	-2.207538	0.922416	-2.135399	-1.148644	1.773397
H	2.673356	-1.292379	1.294922	3.028798	0.050736	1.442606	3.022390	0.129553	1.452784	-2.531308	1.459199	1.327500
H	3.052711	-0.353613	-0.174696	1.423471	0.047839	2.222802	1.413272	0.092128	2.223217	-3.025574	0.530680	-0.113484
H	1.325525	0.028724	-1.893371	-0.562396	0.880594	1.005812	-0.583684	0.856530	0.995251	-1.331483	0.018994	-1.894869
H	-1.223072	1.368939	0.530729	-0.042787	-1.252286	-2.016129	0.057144	-1.342438	-2.011483	1.133710	-1.510758	0.477358
H	-0.210396	2.768863	0.936498	-0.156478	-2.776526	-1.104409	-0.138894	-2.818400	-1.063680	0.022952	-2.813930	0.948355
H	-0.769640	2.516059	-0.731066	-1.534996	-1.664823	-1.168532	-1.478064	-1.663339	-1.193845	0.536334	-2.648594	-0.736072
H	2.019840	3.072798	-0.159302	-0.712860	-2.681604	1.371854	-0.652015	-2.709064	1.388966	-2.277218	-2.933482	-0.094582
H	1.477956	2.524975	-1.759205	-1.817741	-1.299824	1.241904	-1.781049	-1.341549	1.248647	-1.723538	-2.458646	-1.711565
H	2.836520	1.714174	-0.956607	-0.399925	-1.206882	2.305863	-0.368570	-1.220739	2.310408	-2.981337	-1.515332	-0.894871
H	0.261441	-2.848200	-1.382949	1.215722	3.087545	-0.263781	1.069577	3.085655	-0.270209	-0.111927	2.770241	-1.476812
H	1.565541	-3.313432	-0.286458	2.653110	2.715697	0.690049	2.568155	2.795036	0.639535	-1.317822	3.379248	-0.323391
H	1.937897	-2.381408	-1.752357	1.054891	2.714342	1.467054	0.994773	2.725903	1.463665	-1.836801	2.449971	-1.746571
S	-3.746500	-0.150466	0.130995	-3.898273	0.449671	0.111308	-3.957842	0.346430	0.001828	3.742430	-0.112300	0.106759
H	-0.723548	-0.718820	-2.239893	-0.681036	1.930569	-1.026885	-0.332489	0.772126	-1.793089	0.778165	-0.572452	-2.237431
H	-2.648551	-0.000215	-0.621609	-2.757916	0.586534	-0.581209	-2.804409	0.699756	-0.584223	2.634393	0.105827	-0.613822
H	-4.048856	1.146695	0.046518	-4.627439	0.322449	-0.999615	-4.149389	1.574671	0.487391	3.979315	1.194387	0.239914

Optimized geometries of the fenchone-H_2S complex conformers

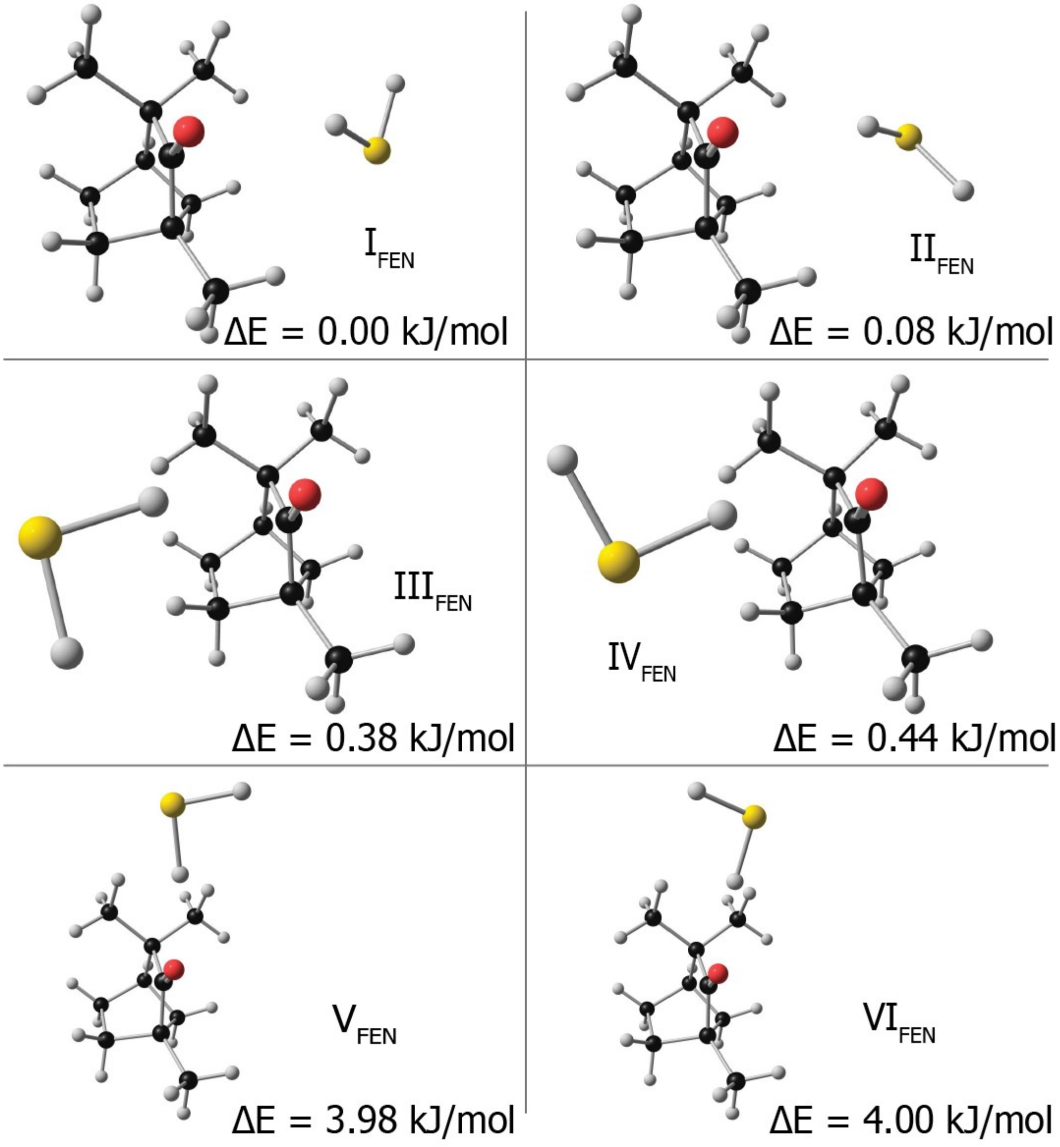


Figure S4. Calculated conformers of the FEN-H_2S complex at the MP2/6-311++G(d,p) level of theory.

Tables S6-S8 Experimental vs calculated constants for the different conformers of fenchone-H_2S

Table S6

FEN-H_2S								
			I_{FEN}			II_{FEN}		
Constants	Experimental		MP2/ 6-311++G(d,p)	ωB97X-D/ 6-311++G(d,p)	B3LYP/ def2TZVP	MP2/ 6-11++G(d,p)	WB97XD/ 6-311++G(d,p)	B3LYP/ def2TZVP
	0+	0-						
A (MHz)	983.41497(21)	983.40341(13)	1092.9	1103.7	1099.5	1091.5	1101.6	1095.5
B (MHz)	582.232474(64)	582.241521(34)	610.7	596.0	595.5	610.4	597.7	603.9
C (MHz)	511.016389(44)	511.007220(30)	507.2	493.8	493.5	506.6	495.5	500.3
Δ_J (kHz)	0.18499(14)		0.1136	0.0957	0.1604	0.1288	0.1354	0.1261
Δ_{JK} (kHz)	1.4868(14)		0.0192	0.0656	-0.0570	0.1082	0.0969	0.0947
Δ_K (kHz)	-1.6012(59)		-0.0363	-0.0613	0.0258	-0.1155	-0.1040	-0.1195
δ_J (kHz)	0.015727(80)		0.0146	0.0127	0.0190	0.0157	0.0165	0.0162
δ_K (kHz)	0.7361(24)		0.0758	0.0793	0.0799	0.1124	0.1330	0.1306
$\lvert\mu a\rvert$(D)	observed		2.0	2.9	2.6	1.9	2.5	2.1
$\lvert\mu b\rvert$(D)	observed		0.5	0.5	0.4	0.9	1.0	0.9
$\lvert\mu c\rvert$(D)	observed		1.8	1.8	1.8	1.4	1.5	1.5
ΔE[a]			0.00	0.92	0.79	0.60	1.09	0.45
ΔE_{ZPE}[b]			0.00	0.69	0.66	0.08	0.49	0.54
ΔG_{348}[c]			3.22	3.97	1.68	1.64	2.11	2.91
No. of lines	70	99						
RMS (kHz)	1.72							

[a] Electronic relative energies corresponding to the global minima corresponding to the method/basis set.

[b] Electronic relative energies including ZPE correction corresponding to the global minima corresponding to the method/basis set.

[c] Gibbs free energies (348 K) corresponding to the method/basis set.

Table S7

FEN-H_2S								
			III_{FEN}			IV_{FEN}		
Constants	Experimental		MP2/ 6-311++G(d,p)	ωB97X-D/ 6-311++G(d,p)	B3LYP/ def2TZVP	MP2/ 6-311++G(d,p)	WB97XD/ 6-311++G(d,p)	B3LYP/ def2TZVP
	0+	0-						
A (MHz)	983.41497(21)	983.40341(13)	984.2	982.9	974.8	985.1	987.8	978.0
B (MHz)	582.232474(64)	582.241521(34)	597.2	594.6	602.1	599.0	592.7	595.5
C (MHz)	511.016389(44)	511.007220(30)	525.1	521.5	528.5	526.9	520.0	522.8
Δ_J (kHz)	0.18499(14)		0.1214	0.1123	0.0995	0.1091	0.0959	0.1017
Δ_{JK} (kHz)	1.4868(14)		1.4238	0.9362	0.7129	0.6980	1.1162	1.2980
Δ_K (kHz)	-1.6012(59)		-1.3961	-1.0025	-0.7733	-0.7291	-1.1260	-1.3375
δ_J (kHz)	0.015727(80)		0.0136	0.0099	0.0095	0.0101	0.0091	0.0099
δ_K (kHz)	0.7361(24)		0.6329	0.4385	0.3172	0.3034	0.4632	0.5222
$\lvert\mu a\rvert$(D)	observed		2.7	3.0	2.5	2.5	3.3	2.9
$\lvert\mu b\rvert$(D)	observed		1.1	0.9	0.8	0.4	0.4	0.4
$\lvert\mu c\rvert$(D)	observed		1.3	1.3	1.4	1.5	1.5	1.6
ΔE[a]			0.83	0.86	0.22	0.52	0.71	0.39
ΔE_{ZPE}[b]			0.38	0.00	0.05	0.44	0.47	0.0
ΔG_{348}[c]			0.00	0.00	1.17	2.00	1.65	0.0
No. of lines	70	99						
RMS (kHz)	1.72							

[a] Electronic relative energies corresponding to the global minima corresponding to the method/basis set.

[b] Electronic relative energies including ZPE correction corresponding to the global minima corresponding to the method/basis set.

[c] Gibbs free energies (348 K) corresponding to the method/basis set.

Table S8

	FEN-H_2S							
			V_{FEN}			VI_{FEN}		
Constants	Experimental		MP2/ 6-311++G(d,p)	ωB97X-D/ 6-311++G(d,p)	B3LYP/ def2TZVP	MP2/ 6-311++G(d,p)	WB97XD/ 6-311++G(d,p)	B3LYP/ def2TZVP
	0+	0-						
A (MHz)	983.41497(21)	983.40341(13)	1261.9	1266.7	1269.5	1275.8	1265.7	1270.9
B (MHz)	582.232474(64)	582.241521(34)	473.1	476.4	474.4	474.4	476.8	475.0
C (MHz)	511.016389(44)	511.007220(30)	417.4	417.7	416.6	415.0	418.0	416.6
Δ_J (kHz)	0.18499(14)		0.0445	0.0397	0.0416	0.0464	0.0427	0.0421
Δ_{JK} (kHz)	1.4868(14)		0.3936	0.2611	0.2203	0.8164	0.2743	0.2319
Δ_K (kHz)	-1.6012(59)		-0.0736	-0.1377	-0.1120	-0.7087	-0.1563	-0.1281
δ_J (kHz)	0.015727(80)		0.0047	0.0043	0.0047	0.0037	0.0040	0.0048
δ_K (kHz)	0.7361(24)		-0.0249	0.0448	0.0441	0.1435	0.0652	0.0503
$\vert\mu a\vert$(D)	Observed		3.3	4.0	3.7	3.4	4.0	3.6
$\vert\mu b\vert$(D)	Observed		1.2	1.7	1.7	1.6	1.3	1.3
$\vert\mu c\vert$(D)	Observed		1.1	0.5	0.3	0.4	1.2	1.1
ΔE[a]			3.91	0.06	0.01	3.89	0.00	0.00
ΔE_{ZPE}[b]			3.98	0.22	0.42	4.00	0.12	0.36
ΔG_{348}[c]			4.89	2.94	2.51	4.27	2.84	2.25
No. of lines	70	99						
RMS (kHz)	1.72							

[a] Electronic relative energies corresponding to the global minima corresponding to the method/basis set.

[b] Electronic relative energies including ZPE correction corresponding to the global minima corresponding to the method/basis set.

[c] Gibbs free energies (348 K) corresponding to the method/basis set.

Differences (in %) between observed and calculated rotational constants

Table S9

				IV_{FEN}	
Constants	Experimental		MP2/6-311++G(d,p)[a]	ωB97X-D/6-311++G(d,p)[a]	B3LYP/def2TZVP[a]
A (MHz)	983.41497(21)	983.40341(13)	0.2	0.4	0.6
B (MHz)	582.232474(64)	582.241521(34)	2.9	1.8	2.3
C (MHz)	511.016389(44)	511.007220(30)	3.1	1.8	2.3
Δ_J (kHz)	0.18499(14)		41.1	48.2	45.0
Δ_{JK} (kHz)	1.4868(14)		53.1	24.9	12.7
Δ_K (kHz)	-1.6012(59)		54.5	29.7	16.5
δ_J (kHz)	0.015727(80)		35.6	41.9	37.4
δ_K (kHz)	0.7361(24)		58.8	37.1	29.1

[a] The % has been calculated using the formula: ($\Delta = \frac{observed - calcualted}{observed}$)

Measured rotational transitions for the observed conformer of fenchone-H_2S complex

Table S10

0^- state

J	Ka	Kc	J'	Ka'	Kc'	obs. (MHz)	obs - calc (MHz) *
3	0	3	2	0	2	3245.871	-0.0002
4	1	4	3	1	3	4214.963	0.0007
4	0	4	3	0	3	4293.025	-0.0002
4	1	4	3	0	3	4475.436	0.0012
4	1	3	3	1	2	4495.926	-0.0018
5	1	5	4	1	4	5256.432	-0.0002
5	0	5	4	0	4	5321.597	-0.0016
5	3	3	4	3	2	5489.483	0.0013
5	3	2	4	3	1	5503.023	0.0004
5	2	3	4	2	2	5591.082	0.0006
5	1	4	4	1	3	5599.03	0.0008
6	0	6	5	1	5	6222.178	-0.0002
6	1	6	5	1	5	6292.456	0.0004
6	0	6	5	0	5	6339.421	-0.0009
6	1	6	5	0	5	6409.699	0.0002
5	2	4	4	1	3	6419.479	0.0002
5	1	4	4	0	4	6489.12	-0.0026
6	2	5	5	2	4	6520.677	0.0001
6	4	3	5	4	2	6588.052	0.0001
6	4	2	5	4	1	6589.546	-0.0008
6	3	4	5	3	3	6590.567	0.0005
6	3	3	5	3	2	6625.255	0.0003
6	1	5	5	1	4	6685.105	0.0002
5	2	3	4	1	3	6686.1	0.0007
6	2	4	5	2	3	6739.093	0.0000
7	1	6	6	2	5	7093.495	0.0016
5	2	4	4	1	4	7127.163	0.0004
7	0	7	6	1	6	7283.909	0.0005
7	1	7	6	1	6	7323.882	0.0000
7	0	7	6	0	6	7354.186	-0.0002
7	1	7	6	0	6	7394.159	-0.0001
4	4	0	3	3	0	7431.381	-0.0009
4	4	1	3	3	1	7432.005	-0.0005
7	2	6	6	2	5	7586.683	-0.0001
5	3	2	4	2	2	7596.487	0.0007
7	3	5	6	3	4	7689.677	-0.0003
7	4	4	6	4	3	7693.489	0.0004
7	4	3	6	4	2	7698.377	0.0007
5	3	3	4	2	3	7700.733	0.0011
7	1	6	6	1	5	7749.515	-0.0003
7	3	4	6	3	3	7762.489	-0.0006
6	2	4	5	1	4	7826.162	-0.0013
7	2	5	6	2	4	7880.094	-0.0002
8	1	7	7	2	6	8297.39	0.0006
8	0	8	7	1	7	8329.921	-0.0005
8	1	8	7	1	7	8351.802	0.0002
8	0	8	7	0	7	8369.895	-0.0001
8	1	8	7	0	7	8391.775	0.0000
6	3	3	5	2	3	8630.659	0.0002
8	2	7	7	2	6	8644.449	-0.0008
8	1	7	7	1	6	8790.579	0.0000
8	4	5	7	4	4	8800.993	0.0004
8	4	4	7	4	3	8814.033	0.0001
6	3	4	5	2	4	8844.436	0.0028
8	2	6	7	2	5	9007.115	0.0000
7	2	5	6	1	5	9021.154	0.0011
9	1	9	8	1	8	9377.271	-0.0002
9	0	9	8	0	8	9387.511	0.0000
6	4	2	5	3	2	9611.075	0.0000
6	4	3	5	3	3	9627.361	0.0002
7	3	4	6	2	4	9654.054	-0.0005
9	2	8	8	2	7	9694.105	-0.0006
9	1	8	8	1	7	9812.118	0.0002
9	4	6	8	4	5	9909.543	0.0002
9	4	5	8	4	4	9939.417	0.0002
7	3	5	6	2	5	10013.43	-0.0016
9	2	7	8	2	6	10115.37	-0.0001
8	2	6	7	1	6	10278.75	-0.0028
10	1	10	9	1	9	10401.15	0.0001
10	0	10	9	0	9	10406.73	-0.0003
7	4	4	6	3	3	10677.43	-0.0010
7	4	3	6	3	3	10684.2	0.0004
8	3	5	7	2	5	10689.12	-0.0003
7	4	4	6	3	4	10730.28	-0.0001
10	2	9	9	2	8	10736.35	0.0000
7	4	3	6	3	4	10737.04	0.0002
10	1	9	9	1	8	10822.49	-0.0002
10	3	8	9	3	7	10954.67	-0.0003
10	4	7	9	4	6	11017.55	-0.0003
10	4	6	9	4	5	11077.93	-0.0001
10	2	8	9	2	7	11200.81	0.0000
8	3	6	7	2	6	11211.43	0.0004
10	3	7	9	3	6	11240.98	0.0002
11	1	11	10	1	10	11424.05	0.0008
11	0	11	10	0	10	11427.01	-0.0003
9	3	6	8	2	6	11760.04	-0.0006
11	2	10	10	2	9	11772.3	0.0007
8	4	5	7	3	5	11841.6	0.0006
11	3	9	10	3	8	12026.94	0.0000
11	4	8	10	4	7	12123.01	-0.0004
11	4	7	10	4	6	12232.09	0.0001
11	2	9	10	2	8	12260.42	-0.0003
11	3	8	10	3	7	12393.38	0.0000
12	2	11	11	2	10	12803.32	0.0000
12	3	10	11	3	9	13089.87	-0.0001
12	4	9	11	4	8	13223.73	-0.0004
12	2	10	11	2	9	13294.34	0.0001
12	4	8	11	4	7	13401.02	0.0005
12	3	9	11	3	8	13527.43	0.0006

* $\Delta\nu = \nu_{CALC} - \nu_{EXP}$

Table S11

0^+ state

J	K_a	K_c	J'	K_a'	K_c'	obs (MHz)	obs -calc (MHz) *
5	1	5	4	1	4	5256.495	0.0007
5	0	5	4	0	4	5321.666	0.0008
5	1	4	4	1	3	5599.012	-0.0005
6	0	6	5	1	5	6222.224	0.0011
6	1	6	5	1	5	6292.536	-0.0003
6	0	6	5	0	5	6339.512	0.0000
6	1	6	5	0	5	6409.826	0.0005
6	2	5	5	2	4	6520.698	-0.0007
6	2	4	5	2	3	6739.029	0.0001
7	1	6	6	2	5	7093.356	-0.0004
7	0	7	6	1	6	7283.984	-0.0001
7	1	7	6	1	6	7323.982	-0.0002
7	0	7	6	0	6	7354.297	-0.0001
4	4	0	3	3	0	7431.471	0.0016
4	4	1	3	3	1	7432.089	-0.0023
7	2	6	6	2	5	7586.718	-0.0010
5	3	2	4	2	2	7596.565	-0.0014
7	4	4	6	4	3	7693.464	0.0000
7	4	3	6	4	2	7698.346	-0.0006
5	3	3	4	2	3	7700.766	-0.0002
7	3	4	6	3	3	7762.424	0.0001
6	2	4	5	1	4	7826.115	-0.0006
7	2	5	6	2	4	7880.029	0.0009
8	0	8	7	1	7	8330.026	0.0004
8	1	8	7	1	7	8351.922	0.0000
8	0	8	7	0	7	8370.024	0.0004
6	3	3	5	2	3	8630.75	-0.0026
8	2	7	7	2	6	8644.5	-0.0023
8	1	7	7	1	6	8790.642	-0.0004
8	4	5	7	4	4	8800.961	-0.0011
8	4	4	7	4	3	8813.989	0.0003
6	3	4	5	2	4	8844.442	-0.0009
7	2	5	6	1	5	9021.04	0.0012
9	1	9	8	1	8	9377.411	0.0000
9	0	9	8	0	8	9387.657	-0.0001
6	4	2	5	3	2	9611.162	-0.0004
6	4	3	5	3	3	9627.435	0.0000
7	3	4	6	2	4	9654.15	0.0018
9	2	8	8	2	7	9694.179	0.0000
9	1	8	8	1	7	9812.216	-0.0002
9	4	6	8	4	5	9909.506	-0.0013
7	3	5	6	2	5	10013.41	-0.0007
9	2	7	8	2	6	10115.33	0.0001
8	2	6	7	1	6	10278.55	0.0008
10	1	10	9	1	9	10401.31	-0.0006
10	0	10	9	0	9	10406.89	0.0000
7	4	4	6	3	3	10677.54	-0.0004
7	4	3	6	3	3	10684.3	0.0010
8	3	5	7	2	5	10689.19	0.0019
7	4	4	6	3	4	10730.35	0.0008
10	2	9	9	2	8	10736.44	0.0008
10	1	9	9	1	8	10822.62	0.0009
10	3	8	9	3	7	10954.69	0.0021
10	2	9	9	1	8	10965.63	-0.0001
10	4	7	9	4	6	11017.51	0.0000
10	4	6	9	4	5	11077.83	-0.0002
10	2	8	9	2	7	11200.81	0.0003
11	1	11	10	1	10	11424.23	0.0009
11	0	11	10	0	10	11427.19	-0.0006
9	3	6	8	2	6	11760.05	0.0012
11	2	10	10	2	9	11772.42	0.0011
11	3	9	10	3	8	12026.97	0.0001
11	4	8	10	4	7	12122.97	0.0005
11	4	7	10	4	6	12231.95	-0.0026
11	2	9	10	2	8	12260.46	0.0019
11	3	8	10	3	7	12393.26	0.0003
12	3	10	11	3	9	13089.93	0.0006
12	4	9	11	4	8	13223.7	-0.0017
12	2	10	11	2	9	13294.43	-0.0008
12	3	9	11	3	8	13527.33	-0.0001

* $\Delta\nu = \nu_{CALC} - \nu_{EXP}$

MP2/6-311++G(d,p) cartesian coordinates of the calculated structures I_{FEN}, II_{FEN} and III_{FEN}

Table S12

	I_{FEN}			II_{FEN}			III_{FEN}		
	E= 863.519314 Hartree			E= 863.519087 Hartree			E= 863.518998 Hartree		
Element	X	Y	Z	X	Y	Z	X	Y	Z
C	-0.086208	0.083348	0.762925	0.079483	-0.041715	0.758447	0.188927	-0.06139	-0.81717
C	-0.823662	1.177205	-0.024888	0.747625	-1.191090	-0.011029	1.004145	-1.14024	-0.09122
C	-0.367086	-1.244458	0.078859	0.447988	1.256352	0.059451	0.618367	1.288931	-0.26996
C	-1.498756	0.329139	-1.132524	1.489986	-0.402004	-1.118890	1.848314	-0.2643	0.869685
C	-2.637855	-0.518888	-0.536735	2.674161	0.378108	-0.517352	0.954436	0.333386	1.973004
C	-1.873451	-1.513531	0.383148	1.964782	1.434656	0.377926	0.037422	1.306734	1.17828
C	-0.443793	-0.769374	-1.386422	0.512351	0.759407	-1.399079	2.10485	0.997992	0.017944
C	0.191718	2.163536	-0.621313	-0.328227	-2.110221	-0.609759	1.892405	-1.87911	-1.10418
C	-1.769104	1.947391	0.901459	1.628336	-2.017223	0.930575	0.069627	-2.15332	0.575715
C	0.569326	-2.373164	0.450611	-0.425546	2.442113	0.405315	0.238138	2.473303	-1.13059
O	0.587118	0.266358	1.763461	-0.607814	-0.167642	1.758438	-0.66061	-0.26948	-1.66777
H	0.861216	1.686672	-1.341994	-0.954148	-1.596791	-1.344791	2.616598	-1.21597	-1.58627
H	0.800448	2.598631	0.179024	-0.973854	-2.497854	0.185871	1.269781	-2.32993	-1.88376
H	-0.344821	2.974405	-1.127876	0.155805	-2.960132	-1.104974	2.443651	-2.67645	-0.5923
H	-1.181101	2.535394	1.613345	0.994341	-2.558160	1.640248	-0.45454	-2.72748	-0.19557
H	-2.397829	2.631438	0.319071	2.214182	-2.747143	0.359326	0.647138	-2.85072	1.194231
H	-2.418959	1.283348	1.478568	2.316464	-1.394936	1.509839	-0.68683	-1.67342	1.202329
H	-1.791026	0.925662	-2.003605	1.754284	-1.026551	-1.979166	2.739078	-0.78103	1.243046
H	-3.387900	0.071231	-0.005071	3.375984	-0.252378	0.033436	0.396433	-0.41828	2.535823
H	-3.152323	-1.055586	-1.341010	3.234233	0.867844	-1.321109	1.576113	0.883737	2.687389
H	-2.099716	-2.555433	0.129114	2.259603	2.455730	0.109878	0.100533	2.330177	1.566267
H	-2.100116	-1.376218	1.446656	2.170869	1.300618	1.446013	-1.01507	1.005672	1.194759
H	-0.811710	-1.558489	-2.053497	0.939958	1.515075	-2.069323	2.574811	1.804509	0.593586
H	0.516266	-0.400658	-1.760038	-0.463878	0.449899	-1.784104	2.689336	0.821	-0.89061
H	1.599598	-2.141512	0.164302	-1.461518	2.259105	0.104360	0.679923	2.390477	-2.12906
H	0.549879	-2.545712	1.531921	-0.412013	2.624901	1.485097	-0.84926	2.522041	-1.25169
H	0.270913	-3.297784	-0.055690	-0.066903	3.342349	-0.105843	0.579958	3.407247	-0.67132
S	3.507997	0.045809	-0.301899	-3.503258	-0.140545	-0.334262	-3.58933	-0.27408	0.236739
H	2.757951	0.373035	0.754730	-2.760397	-0.188664	0.775829	-2.7315	-0.41675	-0.77902
H	3.937561	1.300561	-0.455969	-4.154004	0.946630	0.086461	-3.60181	1.054417	0.107357

MP2/6-311++G(d,p) cartesian coordinates of the calculated structures $IV_{FEN,}$ V_{FEN} and VI_{FEN}

Table S13

	IV_{FEN}			V_{FEN}			VI_{FEN}		
	E= 863.519117 Hartree			E= 863.517825 Hartree			E= 863.517831 Hartree		
Element	X	Y	Z	X	Y	Z	X	Y	Z
C	0.192599	-0.059738	-0.820105	-0.15606	0.559208	0.072415	-0.142661	0.538750	-0.059014
C	0.993968	-1.146717	-0.089979	-0.06385	-0.95956	0.277419	-0.065399	-0.969870	0.214240
C	0.630698	1.285880	-0.269386	-1.62716	0.939539	0.078377	-1.593022	0.964695	0.096001
C	1.841304	-0.279185	0.875812	-1.56798	-1.32913	0.340336	-1.562146	-1.290440	0.458898
C	0.948138	0.327063	1.974995	-2.2151	-1.16697	-1.04876	-2.356112	-1.171490	-0.856581
C	0.042014	1.307329	1.176113	-2.15961	0.371958	-1.27326	-2.289757	0.353787	-1.158564
C	2.113152	0.980901	0.025556	-2.17406	-0.10988	1.066387	-2.052316	-0.021709	1.187789
C	1.880104	-1.894491	-1.098081	0.641673	-1.2619	1.609628	0.774232	-1.229187	1.476384
C	0.044154	-2.149635	0.570438	0.732018	-1.61575	-0.85568	0.585524	-1.702984	-0.963072
C	0.267087	2.475636	-1.129945	-1.90456	2.407282	0.317388	-1.802539	2.449790	0.293220
O	-0.654208	-0.261465	-1.675049	0.786186	1.317406	-0.0896	0.791924	1.257674	-0.373226
H	2.612093	-1.237963	-1.577397	0.107325	-0.84905	2.470257	0.355573	-0.747607	2.364770
H	1.257206	-2.340390	-1.880316	1.654164	-0.84682	1.59834	1.794016	-0.861877	1.329589
H	2.422259	-2.696152	-0.583192	0.716498	-2.34782	1.74005	0.821710	-2.308814	1.661553
H	-0.488902	-2.709927	-0.205147	1.793087	-1.37272	-0.75062	1.655882	-1.478071	-0.989822
H	0.610027	-2.860092	1.184865	0.622861	-2.70598	-0.80847	0.464613	-2.786444	-0.844379
H	-0.704267	-1.660777	1.199841	0.405415	-1.27695	-1.84331	0.155689	-1.408836	-1.925115
H	2.725575	-0.804286	1.253051	-1.74384	-2.30433	0.807037	-1.709492	-2.237595	0.988889
H	0.382239	-0.418933	2.537569	-1.70788	-1.73492	-1.8319	-1.953141	-1.788020	-1.663291
H	1.572231	0.872945	2.690724	-3.25313	-1.51414	-1.01135	-3.391402	-1.486778	-0.688718
H	0.111037	2.330170	1.564348	-3.15556	0.790171	-1.45933	-3.290244	0.792138	-1.249980
H	-1.013290	1.015945	1.187486	-1.51682	0.661469	-2.11226	-1.740555	0.587513	-2.077644
H	2.587594	1.782934	0.603703	-3.27057	-0.12836	1.076879	-3.140957	-0.006271	1.319788
H	2.700442	0.798940	-0.880252	-1.81057	0.035607	2.088464	-1.573655	0.158374	2.155312
H	0.709642	2.387603	-2.127663	-1.50724	2.726857	1.286421	-1.288329	2.799999	1.194277
H	-0.819281	2.540464	-1.251861	-1.42663	3.017318	-0.45595	-1.400087	3.008635	-0.557853
H	0.621337	3.404089	-0.668960	-2.98263	2.600962	0.299687	-2.870011	2.676765	0.388225
S	-3.571509	-0.104501	0.221774	4.141585	0.37074	-0.28869	4.151146	0.405678	-0.053655
H	-2.721434	-0.328720	-0.785728	4.558702	0.843934	0.88711	4.454349	0.156277	-1.328937
H	-3.906003	-1.394360	0.298432	2.930112	0.924885	-0.15065	2.927485	0.850318	-0.368181

Natural bonding orbitals representation for endo fenchol-H_2S

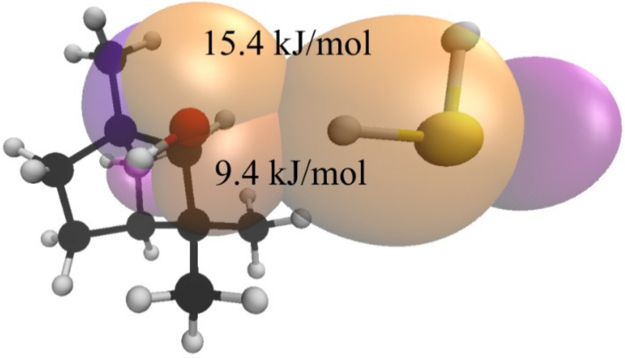


Figure S5. The iso-surface of the natural bond orbitals involved in the hydrogen bonding in the EF-H_2S complex: the two lone pairs of oxygen and SH sigma antibonding. The orange and purple colors represent the positive and negative lobes, respectively. The numbers represent the magnitude of the stabilizing energy of the interaction involved.

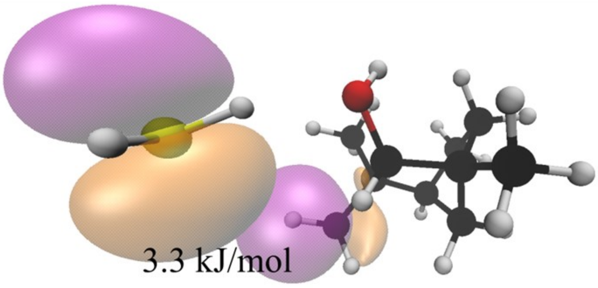


Figure S6. The iso-surface of the natural bond orbitals contributing to the dispersive forces in the EF-H_2S complex: one lone pair of sulfur and the nearest CH sigma antibonding. The orange and purple colors represent the positive and negative lobes, respectively. The numbers represent the magnitude of the stabilizing energy of the interaction involved.

Natural bonding orbitals representation for fenchone-H_2S

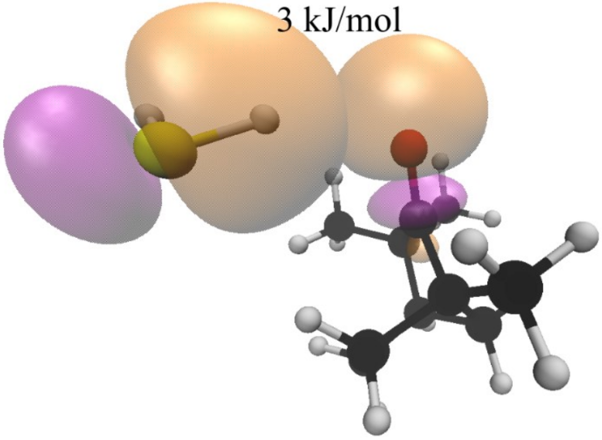


Figure S7. The iso-surface of the natural bond orbitals involved in the hydrogen bonding in the FEN-H_2S complex: one lone pair of oxygen and SH sigma antibonding. The orange and purple colors represent the positive and negative lobes, respectively. The numbers represent the magnitude of the stabilizing energy of the interaction involved.

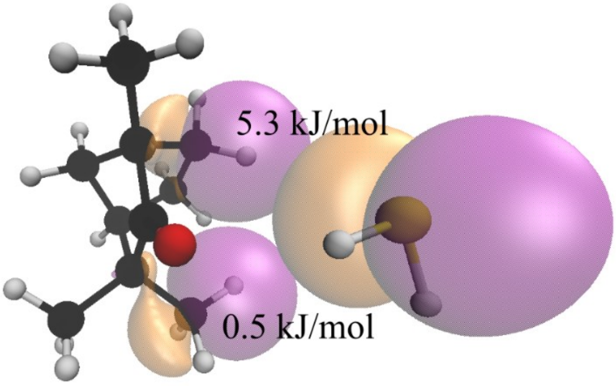


Figure S8. The iso-surface of the natural bond orbitals contributing to the dispersive forces in the FEN-H_2S complex: one lone pair of S and sigma antibonding of SH of the two nearest CH. The orange and purple colors represent the positive and negative lobes, respectively. The numbers represent the magnitude of the stabilizing energy of the interaction involved.

Comparison between the calculated structures of endo fenchol-H_2O and endo fenchol-H_2S complexes

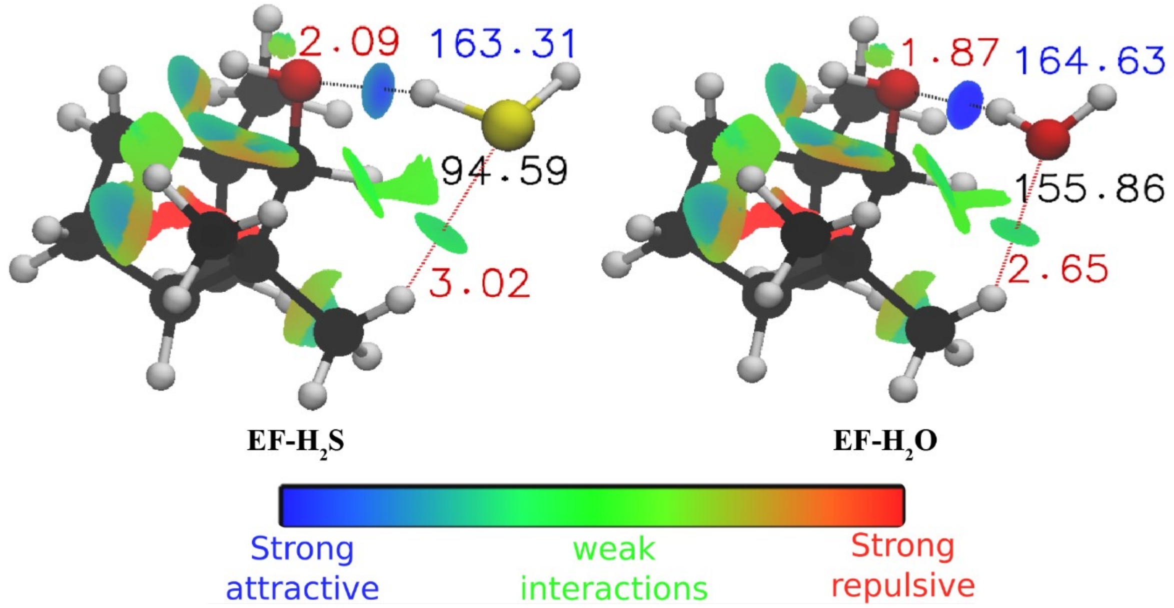
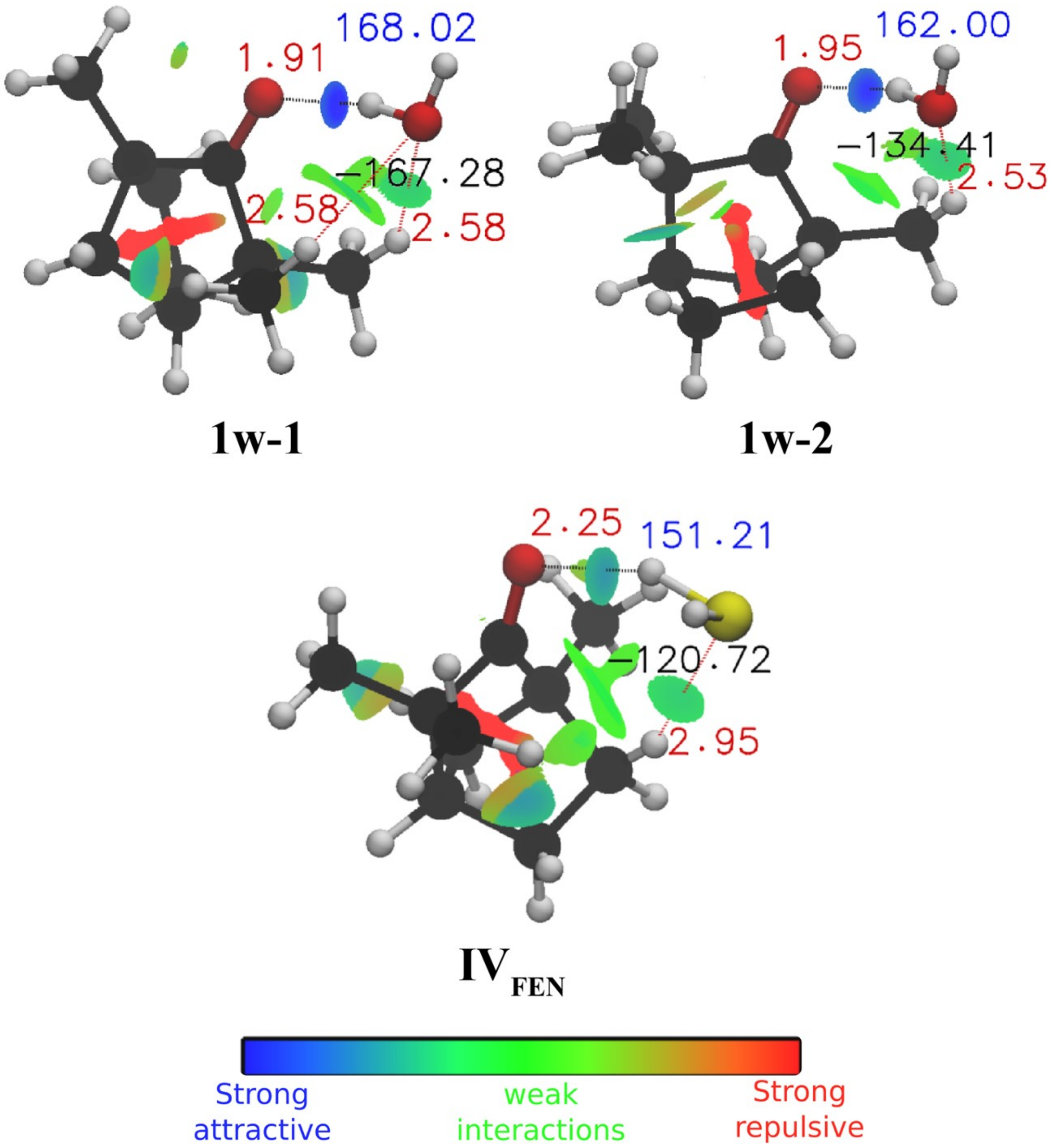


Figure S9 Comparison between the observed endo-fenchol-H_2O[12] and the endo-fenchol-H_2S complexes. Distances (Å) are shown in red. The OHS and the OHSH angles values are indicated in blue and in black, respectively.

In the EF-H_2S complex is a hydrogen bond to the fenchol in a similar way the monohydrate does. It also seems to alter the orientation of the hydroxy group in the molecule, in the same way the H_2O does.

Comparison between the calculated structures of FEN-H_2O and FEN-H_2S complexes



1w-1 **1w-2**

IV$_{FEN}$

Figure S10. Comparison between the calculated structures of Fenchone-H2O[11] and Fenchone-H2S complexes. Distances (Å) are shown in red. The OHS and the OHSH angles values are indicated in blue and in black, respectively.

The structure of the observed FEN-H_2S complex cannot be compared to that of the monohydrate[14], as H_2S is hydrogen-bonded to fenchone from a different side of the ring.

SAPT analysis

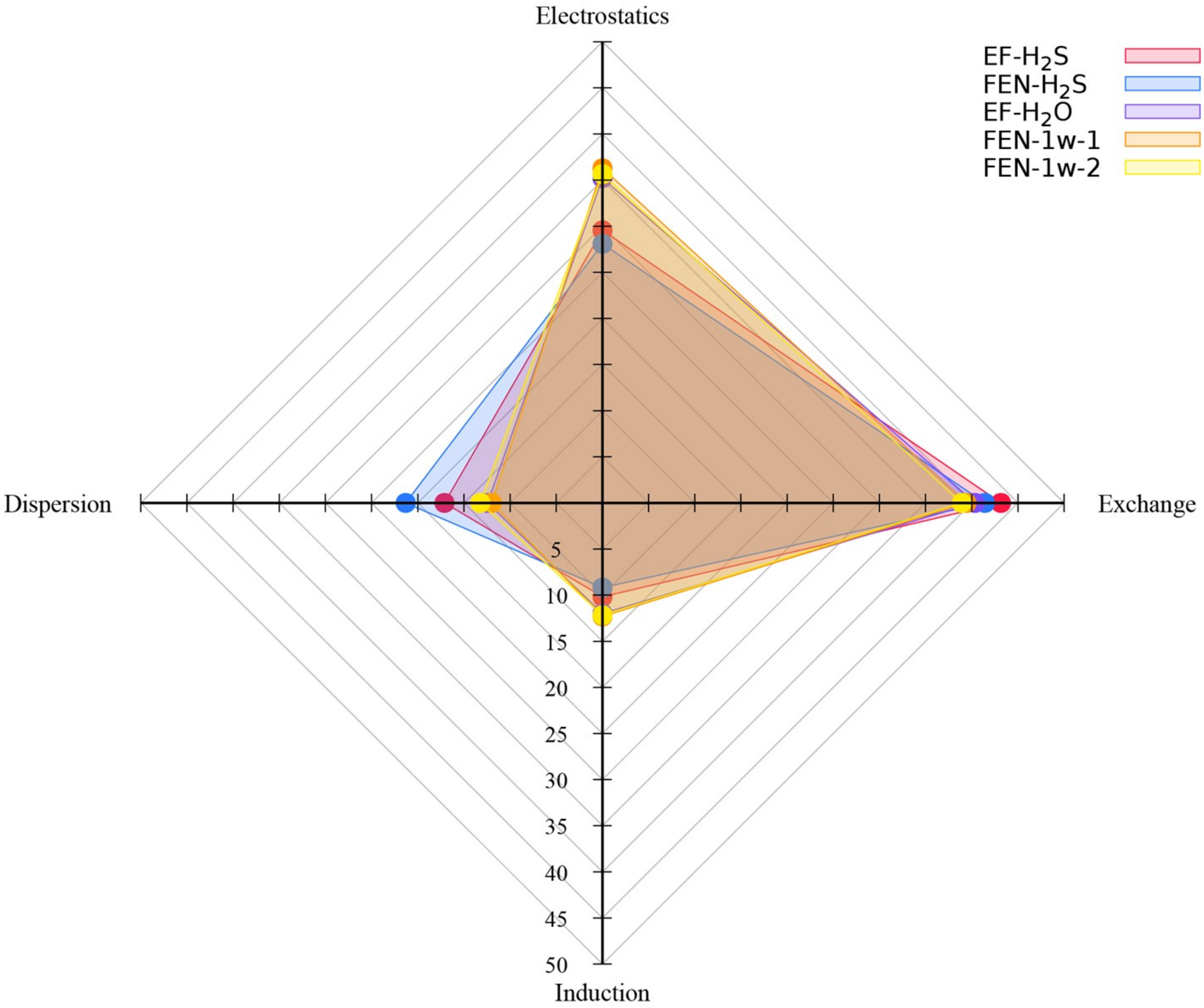


Figure S11. Contribution of the different terms (in%) to the total SAPT energy. The values are derived from $SAPT_{2+3}$ level. The calculations for the water complexes were performed starting from the geometries reported in the corresponding articles.

Barrier height for the rotation of H_2S around its C_2 axis in the fenchone-H_2S complex

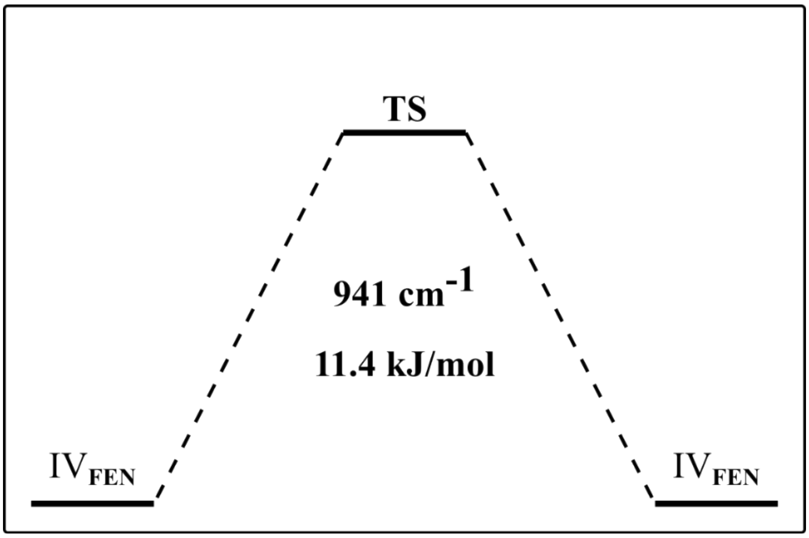


Figure S12. The transition state (TS) and the barrier height of the rotation of H_2S around its C_2 axis in the FEN-H_2S complex

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Figure S7 shows the barrier height for the proton exchange in H_2S, which explains the experimental splitting observed due to tunneling. The transition state is obtained by rotating the H_2S molecule around its C_2 axis of symmetry. The barrier height extracted from the scan was calculated to be 941 cm^{-1}. The proton exchange gives two isoenergetic structures.

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