AN EXPERIMENTALLY DERIVED TORSIONAL POTENTIAL FUNCTION FOR HSSH

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A variety of milimeter-wave and far-infrared spectral data on the internal rotor HSSH has been used to determine the cis and trans barrier heights to torsional motion. Our values of 2800(90) and 1990(15) cm^{-1} for V_{cis} and V_{trans}, respectively, are in good agreement with the results of ab initio calculations.

1. Introduction

The internal rotors HOOH [1–3] and HSSH [4–7] have proved to be of special interest to spectroscopists. Both of these molecules have their equilibrium geometry in neither the cis nor the trans configuration but with a torsional angle χ in between these two possibilities – 111.5° for HOOH and 90.6° for HSSH, where $\chi=0$ corresponds to the cis configuration. The basic theoretical treatment for the torsional motion of these species has been provided by the IAM (internal axis method) approach of Hunt et al. [1]. Dreizler [8] and later Hougen [9] have shown the utility of appropriate double groups for a deeper understanding of the theoretical results. Although an experimentally derived one-dimensional potential function for the torsional motion in HOOH has been obtained from the far-infrared spectrum [1], no such function has been published for HSSH. For HOOH, the experimentally derived barriers for motion over the cis and trans configurations are $V_{cis}=2460(25)$ cm^{-1} and $V_{trans}=386(4)$ cm^{-1}, where the uncertainties are obtained within the context of a model in which the other degrees of freedom are held rigid at previously determined values. The low trans barrier results in large splittings of the normal end-over-end rotational spectral lines [10] and in a complex far-infrared spectrum [1].

Several high-quality ab initio quantum chemical calculations have recently been undertaken [11,12] for the torsional motion of HSSH. Grein [11] has calculated an equilibrium torsional angle of 90.1° and barrier heights V_{cis} and V_{trans} of 2810 and 1940 cm^{-1}, respectively, whereas Dixon et al. [12] have calculated values of 89.7°, 2870 cm^{-1}, and 1980 cm^{-1} for these same three parameters. The large barriers for tunneling under both the trans and cis configurations should lead to much smaller splittings in the rotational and torsional spectra than is the case for HOOH. Indeed, this has been observed to be the case [4]. Although both theoretical treatments come close to the experimentally determined torsional angle of 90.6°, there is a discrepancy between theory and experiment on the size of the SSH bond angle. The theoretical treatments both obtain 98.4° for this angle whereas the experimental value is 91.3°. It should be mentioned that this experimental value is not the result of a full substitution structure but rather derives from a slight readjustment of an earlier electron diffraction study [13].

It is the purpose of this paper to present for the first time an experimentally determined potential function for the torsional motion of HSSH based on a variety of laboratory spectral studies. As will be discussed below, our values for V_{cis} and V_{trans} of 2800(90) and 1990(15) cm^{-1} are in good agreement with the recent ab initio results but are somewhat dependent on the unknown SSH bond angle. Detailed results of a new investigation of the rotational spectrum of HSSH with the aim of deriving a

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complete substitution structure will be published at a later date.

2. Experimental and analysis

The experimental data used in our analysis are shown in table 1. The two splittings obtained directly from rotational spectra belong to the two lowest torsional states ($v_t=0$, 1) and are measured from doublets in c-type Q-branch transitions [4]. Although the J, K dependence of these doublets is slightly [4] in accord with theory [1,8,9], there is a noticeable variation and we have taken the values associated with the lowest available J, K quantum numbers in each torsional state. The splitting in the lowest torsional state for the Q-branch transitions is sufficiently small that the Lamb dip technique was needed to measure it. The data, which were obtained at Duke University but never before published, are the following c-type $^{R}Q_0(J)$ transition frequencies (MHz): $J=9$, 139817.1460 and 139817.2620; $J=15$, 139701.1344 and 139701.2552; $J=41$, 138536.2840 and 138536.4132. More recent measurements at Cologne of R-branch lines near 60 GHz have also resolved this splitting. The splitting in the $v_t=2$ torsional state was obtained indirectly from doublets observed in a new investigation of the far-infrared spectrum of HSSH carried out using the high-resolution Fourier transform spectrometer at the University of Giessen [14]. The far-infrared doublets, seen in the $v_t=2\leftarrow1$ spectrum, derive from torsional splittings in both of these states. The frequencies for the two torsional band centers used in our analysis ($v_t=1\leftarrow0$ and $v_t=2\leftarrow1$) have recently been measured in the same far-infrared analysis [14]. It is expected that the $v_t=2$ splitting will soon be known more accurately from an analysis of the HSSH rotational spectrum currently being conducted here. In addition, the $v_t=3\leftarrow2$ far-infrared band is currently being analyzed [14].

The torsional potential function chosen for use in our analysis is that of Hunt et al. [1]:

$$V(\chi)=V_0+V_1\cos\chi+V_2\cos2\chi+V_3\cos3\chi\,, \qquad (1)$$

in which V_0 is not determinable spectroscopically and is added just to make the minimum value of the potential zero. The use of higher-order terms would probably result in an improved potential function but cannot yet be justified in terms of the amount of data to be fitted. The potential is utilized in the one-dimensional torsional eigenvalue equation

$$[F_T P_\chi^2+V(\chi)]\psi(\chi)=\epsilon\psi(\chi)\,, \qquad (2)$$

where P_χ is the torsional angular momentum operator, and F_T is the reduced rotational "constant" for torsional motion, which can be expressed in terms of the molecular geometry and possesses a small dependence on torsional angle [1]. The need for the overall wavefunction (rotation+torsion) to be single-valued for a rotation of either SH group over an angle of 2π leads to two sets of two eigenfunctions

Table 1
Experimental measurements with the results of a typical fit [a]

Measurement	Value	Uncertainty	Residual
$v_t=0$ splitting (MHz)	0.116 [b]	0.008	−0.013
$v_t=1$ splitting (MHz)	15.990 [c]	0.120	0.063
$v_t=2$ splitting (MHz)	780.000 [d]	40.0	−80.321
$v_t=1\leftarrow0$ band center (cm^{-1})	417.476 [e]	0.005	0.000
$v_t=2\leftarrow1$ band center (cm^{-1})	390.410 [e]	0.010	0.000

[a] $F_T=19.616$ cm^{-1} corresponding to the SSH angle=91°. fitted parameters are $V_1=283.4(5.4)$ cm^{-1}, $V_2=1211.4(1.3)$ cm^{-1}, and $V_3=160.1(1.0)$ cm^{-1} leading to $V_{cis}=2870(6)$ cm^{-1}, $V_{trans}=1983(4)$ cm^{-1} and $\chi_{eq}=87.7°$.
[b] Discussed in this work; previously measured unpublished result.
[c] Ref. [4].
[d] This work; estimated from the results of ref. [14]. See discussion in text.
[e] Ref. [14]. The $v_t=2\leftarrow1$ value is the upper component of the split doublet and will be refined somewhat by further analysis.

per torsional state v_t – labelled $\tau=1$, 4 and $\tau=2$, 3, where the order of energy is such that the lower the τ, the lower the energy [1]. The first set appears only if the prolate quantum number K_{-1} is even and the second only if it is odd. In c-type transitions which characterize the rotational and torsional spectrum, the prolate quantum number changes by an odd number and the allowed transitions are $\tau=1\leftrightarrow3$ and $4\leftrightarrow2$, which produce the observed spectral splittings. The average of the energy differences $\tau=1\leftrightarrow4$ and $\tau=2\leftrightarrow3$ is associated with tunneling under the trans barrier whereas the difference between $\tau=1\leftrightarrow4$ and $\tau=2\leftrightarrow3$ is associated with tunneling under the cis barrier [1]. This stems immediately from the zeroth-order analysis of Hougen [9]. If, as is the case for HOOH and HSSH, $V_{cis}\gg V_{trans}$, then the $\tau=1$, 2, and 3, 4 sets of levels are closely spaced pairs separated by a larger energy gap ($\epsilon_{\tau=1}\leqslant\epsilon_{\tau=2}\ll\epsilon_{\tau=3}\leqslant\epsilon_{\tau=4}$).

Eq. (2) has been solved by matrix diagonalization using the exponential basis set $\exp[i(k+\sigma)\chi]$, where $-20\leqslant k\leqslant20$ and $\sigma=0$ for states 1 and 4 and $\sigma=1/2$ for states 2 and 3. The small χ dependence of F_T has been neglected because the expression is based on a rigid framework model which is in conflict with ab initio calculations [11,12] which show the SSH angle to vary during the course of the torsional motion. In a one-dimensional treatment, inclusion of such a variation leads to an average value for F_T. Suitable subtraction of energy levels yields calculated frequencies for both the torsional splittings and band centers in table 1 as functions of the molecular parameters F_T, V_1, V_2, V_3. From the values of the three potential parameters, one can subsequently determine the cis and trans barrier heights and the torsional angle χ_{eq} corresponding to the potential minimum [1]. The data shown in table 1 have been fit by a non-linear least-squares procedure. It was not found possible to vary all of the four parameters due to a strong correlation between F_T and the potential constants. Therefore, V_1, V_2 and V_3 were varied while F_T was held fixed. The parameter F_T is strongly dependent on SSH angle even if one assumes this angle to remain fixed during the torsional motion [1]; the discrepancy between theoretical and experimental determinations of this angle for $\chi=\chi_{eq}$ and its possible variation as χ varies leave an uncertainty for F_T in the range 19.6–20.1 cm^{-1}. The calculations were therefore repeated for different F_T values within this range.

3. Results and discussion

Table 1 shows the residuals (measured – calculated frequencies) for a typical analysis. It is seen that the variation of three potential parameters can fit the five data points to approximately within their uncertainties. The fit shown in table 1 is not unique since different values of F_T can be used. Table 2 shows the values of V_{cis}, V_{trans}, and χ_{eq} calculated from the derived potential parameters V_1, V_2, and V_3 obtained with F_T held fixed at various values in the range 19.6–20.1 cm^{-1}. The uncertainty in F_T affects V_{cis} significantly more than V_{trans}. Assuming F_T to be totally unknown within the 19.6–20.1 cm^{-1} range, our measured values and uncertainties for V_{cis} and V_{trans} are 2800(90) and 1990(15) cm^{-1}, respectively, in good agreement with the theoretical values, as can be seen in table 3. For comparison with these values, one must remember that the one-dimensional potential utilized in eqs. (1) and (2) is at best an effective potential incorporating the averaging of

Table 2
Least-squares determinations of V_{cis}, V_{trans} and χ_{eq} as functions of the rotational constant F_T. Numbers in parentheses represent one standard deviation

F_T (cm^{-1})	V_{cis} (cm^{-1})	V_{trans} (cm^{-1})	χ_{eq} (deg)
19.6	2876(6)	1982(4)	87.7
19.7	2842(6)	1987(4)	87.6
19.8	2809(6)	1991(4)	87.5
19.9	2777(6)	1995(4)	87.4
20.0	2746(6)	1999(4)	87.3
20.1	2714(6)	2003(4)	87.1

Table 3
Comparison of experimental and theoretical determinations of V_{cis} and V_{trans}

Ref.	V_{cis} (cm^{-1})	V_{trans} (cm^{-1})
this work, exp.	2800(90)	1990(15)
[10], theor.	2810	1940
[11], theor.	2870	1980
[11], theor. [a]	2840	1950

[a] Corrected for zero-point effects. See text.

other vibrational degrees of freedom since these other degrees are not rigorously independent of the torsional mode. Even if the other degrees of freedom were independent, one should add their zero-point motions to the ab initio potential at the equilibrium, cis, and trans positions. Performing this task on the results of Dixon et al. [12] leads to a slight diminution of the cis barrier height by $\approx 34\ cm^{-1}$ and the trans barrier height by $\approx 26\ cm^{-1}$. These small changes do not change the agreement between ab initio calculation and our results. However, if the torsional degree of freedom is not even approximately separable from other degrees of freedom, one can expect larger effects. In this context, it should be noted that the observed torsional splitting in the first excited S–S stretching state is much larger than that observed in the ground state despite the fact that the torsional motion is not excited [4]. One explanation is a diminution of the torsional barrier height when the S–S bond distance differs significantly from its equilibrium value. Another explanation is a Fermi resonance-type coupling between the first excited torsional and stretching states. Further work on understanding this effect is planned.

The potential utilized in this work has been truncated at the V_3 term because of a present shortage of spectral frequencies to which potential parameters could be fitted. The inadequacy of this potential can be seen from the relatively large size of the V_3 term compared with the V_1 term in a typical fit (table 1) and the derived equilibrium torsional angles. These vary in the range 87.1–87.7° depending on the value of F_T chosen but are all on the wrong side of 90° compared with experiment. Still, with the potential form chosen we have been able to fit five spectral frequencies close to or within their measured uncertainties by varying only three parameters and to determine the cis and trans barrier heights to within a reasonable degree of uncertainty. Future work in this laboratory will include a full measurement of the substitution structure of HSSH allowing a precise determination of the SSH bond angle and a refinement in the current uncertainty in the parameter F_T. This will permit a significant reduction in the uncertainty of the cis barrier height. An IAM analysis of the complete rotational–torsional spectrum rather than the limited data used here is also a possibility although the high values of J for which spectral data have been obtained will require the use of supercomputers for such an analysis.

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