NOTE

$g$-Factors of the SH (0–0) Band and SH Upper Limit in Comet P/Brorsen-Metcalf (19890)

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Since H$_2$S was detected in Comets Austin (1989c1) and Levy (1990c) in the microwave range, there has been increasing interest in searching for SH, which is the prime dissociative product of H$_2$S. We present $g$-factors for the $A-X$ (0–0) band of SH as a function of heliocentric velocity at $r = 1.0$ AU. We derive an upper limit production rate, $Q$(SH)[$Q$(H$_2$O) < 0.017, for Comet Brorsen–Metcalf (19890) and calculate a dissociative lifetime of 105 sec at a heliocentric distance, $r = 1.0$ AU, and at a heliocentric velocity, $v(r) = -28.5$ km sec$^{-1}$.

Introduction. Colom et al. (1990) recently reported the first detection of H$_2$S in the millimeter-wavelength range of Comet Austin (1989c1). Subsequently Crovisier et al. (1991) presented production rates of H$_2$S for Comets Austin and Levy (1990c) derived from their microwave data. Marconi et al. (1990) first identified H$_2$S$^+$ in a mass spectrum of Comet Halley obtained with the heavy ion analyzer (PICCA) on board the Giotto spacecraft and attributed its existence to protonation of H$_2$S. It is, therefore, of interest to search for SH, which is the prime dissociative product of H$_2$S. Krishna Swamy and Wallis (1986) and Wallis and Krishna Swamy (1987) tentatively identified the $B-A$ bands of SH in the 1670–1920 Å range in the IUE spectra of faint comets and of Comet Halley, respectively. The suspected features in those spectra are, however, hampered by the typical IUE noise (e.g., Kim and A’Hearn 1991). The recent availability of good, high-resolution, groundbased spectra covering the spectral range including the SH $A-X$ transitions (O’Dell et al. 1990) provides additional stimulus for estimating the expected strength of the emission by SH.

$g$-factors of the SH $A-X$ (0–0) band. The individual lines of the SH $A-X$ (0–0) band have been observed in absorption, and their line positions were presented by Ramsay (1952). We used his line positions in our $g$-factor calculations because the line positions are sufficiently accurate for calculation of the Swings effect, and they are the best available in the literature.

The $A-X$ system is the same type of electronic transition as is the OH $A-X$ system. For the H"{o}nl–London (H–L) factors of this band, we adopted an updated list of the H–L factors for the $^2S^-$ $\rightarrow$ $^2P^1$ system of the OH $A-X$ band presented in Appendix B of Schleicher and A’Hearn (1982).

Friedel et al. (1983) found experimentally that predissociation of SH occurs throughout the rotational levels of the 0–0 band of the $A-X$ system, although previously only the $\nu' \geq 1$ levels of the $A$ state had been thought to predissociate significantly. They found that the predissociative and radiative lifetimes are 3 and 820 nsec, respectively. Senekowski et al. (1985) subsequently revised the radiative lifetime to be 704 nsec. Since most of the radicals predissociate subsequent to their first excitation to the $A$ state, fluorescent equilibrium will not be established and the emission spectrum will be controlled by the Swings effect operating on a ground-state population. The general formula for the $g$-factor ($\gamma'$) for a transition undergoing predissociation can be expressed by

$$g_{ij} = \gamma_{ij} \sum_{k} x_k B_{k'k} \rho_{k'},$$

where the summation is restricted by the selection rule for the rotational transitions, $x_k$ is the fractional population of the $j'$ rotational level in the ground state, $\gamma_{ij}$ is the branching ratio for radiative decay from the $j'$ rotational level of the excited state to the $j$ rotational level of the ground state, $B_{k'k}$ is the Einstein $B$ coefficient, and $\rho_{k'}$ is the solar radiation density. There is major uncertainty as to what should be used for the populations of the ground-state rotational levels, $x_k$. The following is a discussion of the possible population of the ground state and the corresponding temperature of SH.

Hawkins and Houston (1980) conducted laboratory experiments on the photodissociation of H$_2$S and measured the rotational temperatures of SH. They found that the SH radicals are formed a little warmer (about 40 K greater) than their parents when their parents are at room temperature. Hawkins and Houston (1982) performed the same experiment for H$_2$S at 3 K and found that the rotational temperature of the nascent SH is about 150 K. This indicates that if the parents are very cold, the nascent SH becomes much warmer (150 K) than the parents. From the results of Hawkins and Houston, the rotational temperature of the nascent SH seems to be greater than 150 K regardless of the H$_2$S temperature.

Crovisier et al. (1991) measured a rotational temperature of 40 K for H$_2$S in Comet Austin at about 1 AU heliocentric distance. Although the rotational temperature was not measured, we expect a low rotational temperature for this molecule in Comet B–M because rotationally excited H$_2$S relaxes rapidly (D. Buckee-Morvan, private communication, 1991). From these arguments, we can say that the temperature of the nascent SH is greater than 150 K and is likely to be less than 400 K because of the probably low excitation temperature of H$_2$S.

In order to estimate the changes in the rotational populations of SH expected after formation but prior to fluorescence, we roughly calculated rotational transition probabilities of SH as follows. The OH and SH
ground states have the same transition types, and therefore the only
major differences are the frequency and dipole moment. The radiative
transition probability is proportional to the square of the dipole moment
and the cube of the frequency. The dipole moments of SH and OH are
0.7580 and 1.6676 D, respectively, and the rotational B constants are
9.46 and 18.5 cm⁻¹, respectively. Burdyszha and Varshalovich (1973)
presented Einstein A coefficients for the hyperfine transitions of OH.
We scale down these values using the ratios of the dipole moments and
the frequencies of SH and OH. The resultant radiative lifetimes for the
lowest lines in the R branch are about 200 sec. which are greater than
the SH lifetime of ~100 sec as discussed in the next section. The radiative
lifetime decreases as rotational quantum number J increases, and it
approaches 1 sec at around J = 25. The radiative lifetimes for lines in
other satellite branches are much greater than the SH lifetime. We
conclude that the lower rotational levels of the SH radicals do not
undergo significant rotational deexcitation (or cooling) before they are
destroyed by photodissociation.

Since the SH is formed where densities in the coma are moderately
high, collisions can also affect the distribution of populations. The recent
model of Ciffo (1991) predicts kinetic temperatures near 200 K at a
distance of 4000 km from the nucleus, the mean distance at which H₂S
photodissociates to produce the SH. Thus collisions, which would tend
to produce rotational distributions in equilibrium with the kinetic tempera-
ture, will tend to produce a rotational excitation characterized by a
temperature near 200 K. We therefore will assume that the rotational
distribution in the ground state can be characterized by temperatures
between 150 and 400 K. This range leads to about a 15% variation in the
g-factor for the entire 0-0 band and about a 50% variation for the
R₁ + R₂, branch lines clustered near 3238 Å. These variations are still smaller
than the variation caused by the Swings effect. The variation for individ-
ual lines within the band, however, is greater than that caused by the
Swings effect.

The other parameters needed to solve Eq. (1) are much better deter-
dined. The branching ratio, γᵣ, can be expressed in terms of the Ein-
stein A coefficients for the downward transitions coupled with the disso-
ciative lifetime of the upper state as follows:

\[
γᵣ' = \frac{Aᵣ'}{(1/τ₀) + Aᵣ' + Aᵣ'+1 + Aᵣ'+1}
\]

(2)

Here Aᵣ' is the Einstein A coefficient and τ₀ is the dissociative lifetime
of the ν' = 0 state in the A state. The equation is written for a Q-branch
line, and the subscripts in the denominator differ for P and R branches.
In all cases, the branching ratio can be approximated as Aᵣ/τ₀ because
1/τ₀ dominates the term in the denominator.

Bᵣ is the Einstein coefficient for radiative absorption in a given
transition and can be expressed in terms of A(0-0), the Einstein coeffi-
cient for spontaneous emission in the entire band, as follows:

\[
Bᵣ = \frac{\text{A}(0-0) \ \text{H-L}}{8\pi \hbar v \omega₀(2v' + 1)}
\]

(3)

where h is Planck's constant, ω₀ is the frequency of the band head in
units of cm⁻¹, and H-L is the Hön-London factor for the transition
taken as noted above, from Schleicher and A'Hearn (1982).

The radiation density at each transition, Bᵣ, is taken directly from
A'Hearn et al. (1983) with allowance for the Swings effect.

Using the above equations, g-factors for Comet 1989A (1989a) have
been calculated for a heliocentric distance, r = 1.0 AU, and for a
heliocentric velocity, \( v(r) = -28.5 \ \text{km sec}^{-1} \). A model spectrum made
from these g-factors with a 1-Å spectral resolution is presented in Fig.

1. The \( R₁ + \ \text{Q} ) \) branch occurs at 3238 Å, consisting of about 15
individual lines. In Fig. 2 we present g-factors for this branch as a
function of heliocentric velocity at r = 1 AU. The g-factor for this
branch is \( 6.2 \times 10^{-4} \ \text{sec}^{-1} \) for \( v(r) = 0 \ \text{km sec}^{-1} \) and \( 7.8 \times 10^{-4} \ \text{sec}^{-1} \)
for \( v(r) = -28.5 \ \text{km sec}^{-1} \). The g-factor of the entire 0-0 band ranges
from 2.5 × 10⁻⁴ to 4.1 × 10⁻⁴ sec⁻¹ for the heliocentric velocity between
-80 and 80 km sec⁻¹ at a constant temperature of 200 K. The total g-
factor also varies between 3.4 × 10⁻⁴ and 4.4 × 10⁻⁴ sec⁻¹ for the
temperature range of 50–400 K at a heliocentric velocity of 0.0 km sec⁻¹.
Our values are significantly lower than the value (3.2 × 10⁻³ sec⁻¹)
derived by Krishna Swamy and Wallis (1988), who apparently did not
consider predissociation in the A-X band.

Krishna Swamy and Wallis (1986) and Wallis and Krishna Swamy
(1987) tentatively identified the B-X band of SH in the 1670–1920 Å
range in the IUE spectra of certain comets. Krishna Swamy and Wallis
(1988) derived the g-factors of the B-X bands to be less than 5 × 10⁻⁸
sec⁻¹, which is so low that the presence of the band in the noisy IUE
spectra is doubtful. They also did not consider possible predissociation
in the B-X band. According to the absorption spectrum of the B-X band
presented in Fig. 1 of Morrison (1966), the absorption linewidths (~0.8
cm⁻¹) are wider than the uncertainty (~±0.1 cm⁻¹) in the line positions.
This suggests that predissociation occurs through these lines, and the
predissociation will lower the derived g-factors even more, rendering
the tentative detection even more doubtful.

**Upper limits of SH in Comet P/Brosen-Metzlaff and lifetimes of SH.** In order to calculate the upper limits of SH in comets, the lifetimes
of H₂S and SH are required. Crovisier et al. (1991) estimated an H₂S
lifetime of 4000 sec at 1 AU using an absorption spectrum of Lee et al.
(1997).

The dissociation rate of SH through the 0-0 transitions can be easily
derived from Eq. (1) and is given by

\[
Dᵣ(0-0) = \sum Bᵣ γᵣ
\]

(4)

Here we have used the lifetimes given previously to assume that the
branching ratio for dissociation is nearly unity. The total dissociation
rate through the 0-0, 1-0, and 2-0 bands is the sum of \( Dᵣ(0-0), Dᵣ(1-0),\)
and \( Dᵣ(2-0) \). The dissociation at 0-0 at 1 AU is \( 8.20 \times 10^{-8} \ \text{sec}^{-1} \) for \( v(r) = -28.5 \ \text{km sec}^{-1} \) and \( 5.78 \times 10^{-8} \ \text{sec}^{-1} \) for \( v(r) = 0 \ \text{km sec}^{-1} \). According to
the F-C factor calculations by Nicholls et al. (1960), which, although old, is the only available source, the F-C factors of the
0-0, 1-0, and 2-0 transitions are 0.74, 0.20, and 0.04, respectively. The
branching ratio for dissociation is nearly unity. The total dissociation
rate through the 0-0, 1-0, and 2-0 bands is the sum of

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\sum Bᵣ γᵣ (0-0)
\]

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where \( M(\text{SH per slt}) \) is the instantaneous number of SH molecules
in a slt, \( \Delta F` \) is the energy of the transition, \( g \) is the g-factor, and \( ν \) is the

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in a slt, \( \Delta F` \) is the energy of the transition, \( g \) is the g-factor, and \( ν \) is the
frequency. Using the H$_2$S lifetime of 4000 sec and the SH lifetime of 105 sec, and a H$_2$S model (Haser 1957) with $v = 1$ km sec$^{-1}$ for SH and H$_2$S, we obtain a production rate of SH, $Q$(SH), which is less than $6.7 \times 10^{-7}$ sec$^{-1}$. Using the OH (0-0) observations of Comet B-M by O'Dell et al., we determined $Q$(H$_2$O) to be about $4.0 \times 10^{-6}$ sec$^{-1}$ using a H$_2$S model with $v = 1$ km sec$^{-1}$. We derive that $Q$(SH)/$Q$(H$_2$O) is about <0.017.

Crovisier et al. (1991) reported a production rate of H$_2$S, $Q$(H$_2$S)/$Q$(H$_2$O) = $2 \times 10^{-7}$, for both Comets Austin and Levy (1990c) using their microwave observations. Our upper limit for Comet B-M is thus consistent with the results of Crovisier et al., for Comets Austin and Levy. Detection of SH, which should require an order of magnitude greater sensitivity, would be valuable in testing the models used to interpret the observations of H$_2$S.

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REFERENCES


