

THE MICROWAVE AND FAR-INFRARED SPECTRA OF THE SiH RADICAL¹

J. M. BROWN

Physical Chemistry Laboratory, Oxford, England

R. F. CURL

Department of Chemistry, Rice University, Houston, Texas

AND

K. M. EVENSON

National Bureau of Standards, Boulder, Colorado

Received 1984 July 6; accepted 1984 November 12

ABSTRACT

The frequencies, wavelengths, and line strengths for transitions in the SiH molecule at microwave and far-infrared wavelengths have been calculated from an analysis of its laser magnetic resonance spectrum.

Subject headings: infrared: spectra — interstellar: molecules — line identifications — molecular processes

Astronomers have identified significant concentrations of a number of hydrides in the interstellar gas from the measurement of lines in their rotational spectra. Two of the more abundant free radicals are OH (Weinreb *et al.* 1963) and CH (Rydbeck, Eldér, and Irvine 1973; Turner and Zuckerman 1974). A consideration of the cosmic abundance of silicon leads one to expect that the related molecule SiH might also be detected in extraterrestrial sources. This paper presents transition frequencies which will aid in the astronomical search for this species. The fact that it has not been found so far may be in part due to the lack of good laboratory measurements of the transition frequencies involved.

Some attempts have been made to measure the frequency of the lambda-doubling transition of SiH in its lowest rotational level ($J = \frac{1}{2}$) from lines in its optical spectrum (Douglas and Elliot 1965; Klynning, Lindgren, and Sassenberg 1979). However, such estimates have a limited precision of about 50 MHz, caused mainly by the effects of Doppler broadening at these wavelengths. Much more precise measurements can be provided by the laser magnetic resonance (LMR) spectrum at far-infrared wavelengths. In these experiments, a molecular transition frequency is tuned into coincidence with a fixed-frequency laser by application of a variable magnetic field (0–2 tesla). After a number of unsuccessful attempts, we have recently succeeded in detecting the LMR spectrum of the SiH radical in its ground $^2\Pi$ state. The molecule was generated by the reaction of fluorine atoms with silane, SiH₄. The lines are very weak compared with those of CH, and the failure of previous attempts to detect them is now understood. The subsequent detection by LMR, with large signal-to-noise ratio, of the $^3P_1 \leftarrow ^3P_0$ transition in atomic silicon in the same reaction mixture (Inguscio *et al.* 1984) suggests that the chemical processes involved are similar to those in the F + CH₄ flame, and that concentrations of SiH are similar to those of CH. The much weaker SiH signals imply a smaller dipole moment for SiH than CH. This is supported by recent ab initio calculations which predict a dipole moment of 0.124 debyes (Lewerenz *et al.* 1983).

We have detected Zeeman components of six rotational transitions and have fitted the measurements to a single model Hamiltonian given by Brown *et al.* (1978). An account of the measurements is to be published elsewhere (Brown, Curl, and Evenson 1984), and the transition frequencies and line strengths are in this publication. Zero field frequencies are not measured directly in LMR experiments, but the quality of fit is such that the extrapolation can be performed with an accuracy of about 3 MHz. We have computed the frequencies of individual hyperfine transitions in ²⁸SiH (92% abundance) involving all rotational levels up to $J = 5\frac{1}{2}$. The results are given in Tables 1 and 2. Table 1 contains the lambda-doubling (microwave) frequencies, while Table 2 contains the spin-rotation transition frequencies which fall in the far-infrared region. The results are also summarized in Figure 1, which shows the low-lying energy levels of SiH. We have not been able to characterize the proton hyperfine interactions completely from the experimental measurements, and the remaining parameters have been extracted from those for the corresponding molecule SH (Meerts and Dymanus 1975). We believe that these estimates do not contribute to the uncertainty in our calculated frequencies. We have also failed to detect any fine-structure transitions between the $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ spin components; reference to Table 2 shows that they have much smaller line strengths, by a factor of about 10³. Consequently, we have not been able to determine a value for the spin-orbit coupling constant A and have adopted the value determined from the optical spectrum (Klynning, Lingren, and Sassenberg 1979). The uncertainty in this value (60 MHz, 1 σ) is therefore transmitted directly into our estimates for the frequencies for transitions between the spin components. For transitions within a spin component, we estimate the uncertainty in our frequencies to be 3 MHz.

The line strengths of the transitions are also given in Tables 1 and 2. The line strength $S_{F'F''}$ can be used to assess the relative intensity of an individual transition. It is defined by

$$S_{F'F''} = |\langle \gamma' F' \| D_q^{(1)}(\omega) \| \gamma'' F'' \rangle|^2, \quad (1)$$

where $D_q^{(1)}(\omega)$ is the reduced matrix element of the rotation matrix (Brink and Satchler 1968), γ stands for subsidiary quantum numbers, F is the total angular momentum, and ω

¹ Work supported in part by NASA contract W-15,047.

TABLE 1
CALCULATED LAMBDA-DOUBLING TRANSITION FREQUENCIES FOR THE SiH RADICAL IN ITS GROUND STATE

TRANSITION ^a			FREQUENCY (MHz)		LINE STRENGTH ^b	TRANSITION ^a			FREQUENCY (MHz)		LINE STRENGTH ^b
F_i	J	$F'-F''$	(± 3 MHz) ^c			F_i	J	$F'-F''$	(± 3 MHz) ^c		
${}^2\Pi_{1/2}$	$\frac{1}{2}$	$0^- - 1^+$	2969.7	0.3334	${}^2\Pi_{3/2}$	$1\frac{1}{2}$	$2^- - 1^+$	220.2	0.2961		
		$1^- - 1^+$	3004.6	0.6666			$1^- - 1^+$	228.8	1.4806		
		$1^- - 0^+$	3015.6	0.3334			$2^- - 2^+$	229.0	2.6650		
${}^2\Pi_{1/2}$	$1\frac{1}{2}$	$1^+ - 1^-$	5752.5	0.1733	${}^2\Pi_{3/2}$	$2\frac{1}{2}$	$3^+ - 2^-$	872.2	0.8290×10^{-1}		
		$1^+ - 2^-$	5757.2	0.3464×10^{-1}			$2^+ - 2^-$	882.1	1.1607		
		$2^+ - 1^-$	5766.6	0.3464×10^{-1}			$3^+ - 3^-$	882.6	1.6581		
		$2^+ - 2^-$	5771.4	0.3118			$2^+ - 3^-$	892.5	0.8291×10^{-1}		
${}^2\Pi_{1/2}$	$2\frac{1}{2}$	$2^- - 2^+$	8086.9	0.1469	${}^2\Pi_{3/2}$	$3\frac{1}{2}$	$4^- - 3^+$	2090.1	0.3367×10^{-1}		
		$3^- - 2^+$	8094.3	0.1049×10^{-1}			$3^- - 3^+$	2101.5	0.9090		
		$3^- - 2^+$	8097.3	0.1049×10^{-1}			$4^- - 4^+$	2102.3	1.1783		
		$3^- - 3^+$	8104.8	0.2098			$3^- - 4^+$	2113.8	0.3367×10^{-1}		
${}^2\Pi_{1/2}$	$3\frac{1}{2}$	$3^+ - 3^-$	9842.4	0.1267	${}^2\Pi_{3/2}$	$4\frac{1}{2}$	$5^+ - 4^-$	3957.7	0.1665×10^{-1}		
		$4^+ - 3^-$	9845.6	0.4689×10^{-2}			$4^+ - 4^-$	3970.6	0.7324		
		$3^+ - 4^-$	9856.5	0.4692×10^{-2}			$5^+ - 5^-$	3971.8	0.8988		
		$4^+ - 4^-$	9859.7	0.1642			$4^+ - 5^-$	3984.7	0.1665×10^{-1}		
${}^2\Pi_{1/2}$	$4\frac{1}{2}$	$4^- - 4^+$	10931.8	0.1134	${}^2\Pi_{3/2}$	$5\frac{1}{2}$	$6^- - 5^+$	6509.7	0.9308×10^{-2}		
		$5^- - 4^+$	10931.8	0.2576×10^{-2}			$5^- - 5^+$	6523.9	0.6051		
		$4^- - 5^+$	10948.6	0.2580×10^{-2}			$6^- - 6^+$	6525.6	0.7168		
		$5^- - 5^+$	10948.6	0.1392			$5^- - 6^+$	6539.7	0.9310×10^{-2}		

^a Quantum numbers for the upper and lower states are denoted by single and double primes respectively. The superscript on the F quantum number values indicate the parities of the states involved in accordance with the definition in Brown *et al.* 1978.

^b For definition, see eq. (1).

^c Estimated uncertainty (1σ).

TABLE 2
SPIN-ROTATION TRANSITION FREQUENCIES FOR THE SiH RADICAL IN ITS GROUND STATE

TRANSITION ^a			FREQUENCY (GHz)		VACUUM WAVELENGTH (μm)		LINE STRENGTH ^b	TRANSITION ^a			FREQUENCY (GHz)		VACUUM WAVELENGTH (μm)		LINE STRENGTH ^b
$F_i - F_i'$	$J' - J''$	$F' - F''$	(± 3 MHz) ^c					$F_i - F_i'$	$J' - J''$	$F' - F''$	(± 3 MHz) ^c				
$F_1 - F_1$	$1\frac{1}{2} - \frac{1}{2}$	$2^- - 1^+$	624.9201	479.7292	1.6505	$F_2 - F_2$	$2\frac{1}{2} - 1\frac{1}{2}$	$2^+ - 2^-$	1168.8814	256.4787	0.1338				
		$1^- - 1^+$	624.9248	479.7256	0.3301			$2^+ - 1^-$	1168.8900	256.4762	1.2042				
		$1^- - 0^+$	624.9358	479.7172	0.6602			$3^+ - 2^-$	1168.8912	256.4759	1.8732				
		$1^+ - 1^-$	627.6727	477.6254	0.3301			$2^- - 2^+$	1169.5345	256.3349	0.1338				
		$2^+ - 1^-$	627.6869	477.6146	1.6504			$2^- - 1^+$	1169.5433	256.3329	1.2042				
		$1^+ - 0^-$	627.7076	477.5989	0.6601			$3^- - 2^+$	1169.5448	256.3326	1.8732				
$F_1 - F_1$	$2\frac{1}{2} - 1\frac{1}{2}$	$3^+ - 2^-$	1043.9127	287.1815	2.7744	$F_2 - F_2$	$3\frac{1}{2} - 2\frac{1}{2}$	$3^- - 3^+$	1631.9865	183.6979	0.1195				
		$2^+ - 1^-$	1043.9184	287.1800	1.7835			$3^- - 2^+$	1631.9964	183.6968	2.3894				
		$2^+ - 2^-$	1043.9231	287.1787	0.1982			$4^- - 3^+$	1631.9980	183.6966	3.2257				
		$2^- - 2^+$	1046.2386	286.5431	0.1982			$3^+ - 3^-$	1633.2054	183.5608	0.1195				
		$3^- - 2^+$	1046.2461	286.5411	2.7741			$3^+ - 2^-$	1633.2158	183.5596	2.3894				
		$2^- - 1^+$	1046.2528	286.5392	1.7834			$4^+ - 3^-$	1633.2177	183.5594	3.2257				
$F_1 - F_1$	$3\frac{1}{2} - 2\frac{1}{2}$	$4^- - 3^+$	1464.5142	204.7044	3.8248	$F_2 - F_2$	$4\frac{1}{2} - 3\frac{1}{2}$	$4^+ - 4^-$	2091.3915	143.3459	0.1004				
		$3^- - 2^+$	1464.5179	204.7038	2.8332			$4^+ - 3^-$	2091.4030	143.3451	3.5124				
		$3^- - 3^+$	1464.5284	204.7024	0.1417			$5^+ - 4^-$	2091.4044	143.3450	4.4156				
		$3^+ - 3^-$	1466.2659	204.4598	0.1416			$4^- - 4^+$	2093.2598	143.2180	0.1004				
		$4^+ - 3^-$	1466.2692	204.4594	3.8243			$4^- - 3^+$	2093.2720	143.2171	3.5125				
		$3^+ - 2^-$	1466.2734	204.4588	2.8328			$5^- - 4^+$	2093.2739	143.2170	4.4157				
$F_1 - F_1$	$4\frac{1}{2} - 3\frac{1}{2}$	$5^+ - 4^-$	1886.8023	158.8892	4.8519	$F_2 - F_2$	$5\frac{1}{2} - 4\frac{1}{2}$	$5^- - 5^+$	2546.7418	117.7161	0.8514×10^{-1}				
		$4^+ - 3^-$	1886.8050	158.8889	3.8594			$5^- - 4^+$	2546.7547	117.7155	4.5978				
		$4^+ - 4^-$	1886.8191	158.8878	0.1103			$6^- - 5^+$	2546.7560	117.7154	5.5344				
		$5^- - 4^+$	1887.8912	158.7975	4.8512			$5^+ - 5^-$	2549.2939	117.5982	0.8515×10^{-1}				
		$4^- - 4^+$	1887.8912	158.7975	0.1103			$5^+ - 4^-$	2549.3080	117.5976	4.5980				
		$4^- - 3^+$	1887.8944	158.7973	3.8589			$6^+ - 5^-$	2549.3097	117.5975	5.5346				

TABLE 2—Continued

TRANSITION ^a			FREQUENCY (GHz) (± 6 MHz) ^c	VACUUM WAVELENGTH (μm)	LINE STRENGTH ^b	TRANSITION ^a			FREQUENCY (GHz) (± 6 MHz) ^c	VACUUM WAVELENGTH (μm)	LINE STRENGTH ^b
$F'_i-F'_i$	$J'-J''$	$F'-F''$				$F'_i-F'_i$	$J'-J''$	$F'-F''$			
F_2-F_1	$1\frac{1}{2}-\frac{1}{2}$	1^+-1^-	4540.651	66.0241	0.3264×10^{-2}	F_2-F_1	$3\frac{1}{2}-3\frac{1}{2}$	3^--4^+	4201.107	71.3603	0.6719×10^{-3}
		2^+-1^-	4540.660	66.0240	0.1632×10^{-1}			3^--3^+	4201.110	71.3603	0.1813×10^{-1}
	1^+-0^-	4540.686	66.0236	0.6527×10^{-2}	4^--4^+		4201.118	71.3601	0.2351×10^{-1}		
	$1^- -1^+$	4543.427	65.9838	0.3240×10^{-2}	4^--3^+		4201.122	71.3601	0.6713×10^{-3}		
	$2^- -1^+$	4543.436	65.9836	0.1620×10^{-1}	3^+-3^-		4213.054	71.1580	0.1764×10^{-1}		
	$1^- -0^+$	4543.438	65.9836	0.6479×10^{-2}	4^+-3^-		4213.066	71.1578	0.6529×10^{-3}		
F_2-F_1	$2\frac{1}{2}-1\frac{1}{2}$	$2^- -2^+$	5082.508	58.9851	0.1195×10^{-2}	F_2-F_1	$4\frac{1}{2}-4\frac{1}{2}$	4^+-4^-	4404.619	68.0632	0.2190×10^{-1}
		$3^- -2^+$	5082.518	58.9850	0.1673×10^{-1}			4^+-5^-	4404.619	68.0632	0.4979×10^{-3}
	$2^- -1^+$	5082.522	58.9850	0.1076×10^{-1}	5^+-4^-		4404.631	68.0630	0.4973×10^{-3}		
	2^+-1^-	5087.392	58.9285	0.1061×10^{-1}	5^+-5^-		4404.632	68.0630	0.2688×10^{-1}		
	2^+-2^-	5087.397	58.9285	0.1179×10^{-2}	4^--4^+		4419.521	67.8337	0.2119×10^{-1}		
	3^+-2^-	5087.407	58.9283	0.1650×10^{-1}	$5^- -4^+$		4419.535	67.8335	0.4811×10^{-3}		
F_2-F_1	$3\frac{1}{2}-2\frac{1}{2}$	3^+-3^-	5669.478	52.8783	0.6233×10^{-3}	F_2-F_1	$1\frac{1}{2}-2\frac{1}{2}$	1^+-2^-	2866.726	104.5766	0.1680×10^{-2}
		3^+-2^-	5669.485	52.8783	0.1247×10^{-1}			2^+-3^-	2866.727	104.5766	0.2614×10^{-2}
	4^+-3^-	5669.490	52.8782	0.1683×10^{-1}	2^+-2^-		2866.735	104.5763	0.1868×10^{-3}		
	$3^- -2^+$	5675.470	52.8225	0.1222×10^{-1}	$1^- -2^+$		2874.584	104.2907	0.1645×10^{-2}		
	$3^- -3^+$	5675.481	52.8224	0.6113×10^{-3}	$2^- -2^+$		2874.593	104.2904	0.1828×10^{-3}		
	$4^- -3^+$	5675.492	52.8223	0.1650×10^{-1}	$2^- -3^+$		2874.603	104.2900	0.2558×10^{-2}		
F_2-F_1	$4\frac{1}{2}-3\frac{1}{2}$	$4^- -4^+$	6296.480	47.6127	0.3689×10^{-3}	F_2-F_1	$2\frac{1}{2}-3\frac{1}{2}$	$2^- -3^+$	2569.996	116.6510	0.3415×10^{-2}
		$4^- -3^+$	6296.484	47.6127	0.1291×10^{-1}			$3^- -4^+$	2570.003	116.6506	0.4610×10^{-2}
	$5^- -4^+$	6296.495	47.6126	0.1623×10^{-1}	$3^- -3^+$		2570.006	116.6505	0.1709×10^{-3}		
	4^+-3^-	6302.355	47.5683	0.1261×10^{-1}	2^+-3^-		2578.956	116.2457	0.3325×10^{-2}		
	4^+-4^-	6302.370	47.5683	0.3603×10^{-3}	3^+-3^-		2578.966	116.2452	0.1664×10^{-3}		
	5^+-4^-	6302.382	47.5681	0.1585×10^{-1}	3^+-4^-		2578.980	116.2446	0.4489×10^{-2}		
F_2-F_1	$1\frac{1}{2}-1\frac{1}{2}$	$1^- -2^+$	3912.736	76.6197	0.1298×10^{-2}	F_2-F_1	$3\frac{1}{2}-4\frac{1}{2}$	3^+-4^-	2315.317	129.4822	0.4601×10^{-2}
		$2^- -2^+$	3912.744	76.6195	0.1168×10^{-1}			4^+-4^-	2315.329	129.4816	0.1316×10^{-3}
	$1^- -1^+$	3912.750	76.6194	0.6487×10^{-2}	4^+-5^-		2315.329	129.4816	0.5784×10^{-2}		
	$2^- -1^+$	3912.759	76.6192	0.1298×10^{-2}	$3^- -4^+$		2324.147	128.9903	0.4463×10^{-2}		
	1^+-1^-	3918.731	76.5024	0.6391×10^{-2}	$4^- -4^+$		2324.159	128.9897	0.1276×10^{-3}		
	1^+-2^-	3918.736	76.5023	0.1279×10^{-2}	$4^- -5^+$		2324.176	128.9887	0.5610×10^{-2}		
F_2-F_1	$2\frac{1}{2}-2\frac{1}{2}$	2^+-1^-	3918.740	76.5023	0.1278×10^{-2}	F_2-F_1	$4\frac{1}{2}-5\frac{1}{2}$	$4^- -5^+$	2097.642	142.9188	0.5194×10^{-2}
		2^+-2^-	3918.745	76.5022	0.1151×10^{-1}			$5^- -5^+$	2097.657	142.9178	0.9631×10^{-4}
	2^+-3^-	4035.380	74.2910	0.9313×10^{-3}	$5^- -6^+$		2097.659	142.9176	0.6252×10^{-2}		
	2^+-2^-	4035.387	74.2909	0.1303×10^{-1}	4^+-5^-		2104.988	142.4200	0.5024×10^{-2}		
	3^+-3^-	4035.389	74.2908	0.1862×10^{-1}	5^+-5^-		2105.001	142.4191	0.9314×10^{-4}		
	3^+-2^-	4035.397	74.2907	0.9308×10^{-3}	5^+-6^-		2105.020	142.4178	0.6047×10^{-2}		

^a Quantum numbers for the upper and lower states are denoted by single and double primes respectively. The superscripts on the F quantum number values indicate the parities of the states involved in accordance with the definition in Brown *et al.* 1978.

^b For definition, see eq. (1).

^c These are 1 σ estimates of the uncertainty. Note: The spacings between the different hyperfine components for a given rotational transition are much more reliably estimated.

represents the Euler angles. The relative intensity of a line in absorption can be obtained by multiplying the line strength by the square of the dipole moment (0.124 debyes; Lewerenz *et al.* 1983), by the transition frequency, and by the population factor for the lower level. The Einstein A -coefficients for spontaneous emission from state i to j can also be calculated from the line strengths by use of

$$A_{i \rightarrow j} = (16\pi^3 v_{ij} / 3\epsilon_0 hc^3) (2F_i + 1)^{-1} S_{ij} \mu^2. \quad (2)$$

It is hoped that the frequencies in Tables 1 and 2 will be useful to laboratory spectroscopists and astrophysicists alike. It should be noted that the lambda-doubling frequencies are significantly different from those predicted from the optical spectrum (Klyning, Lindgren, and Sassenberg 1979), which have been used in all searches for the radio spectrum to date. Although the small dipole moment of the molecule may make it more difficult to detect, the large optical path length in the interstellar clouds may compensate for this.

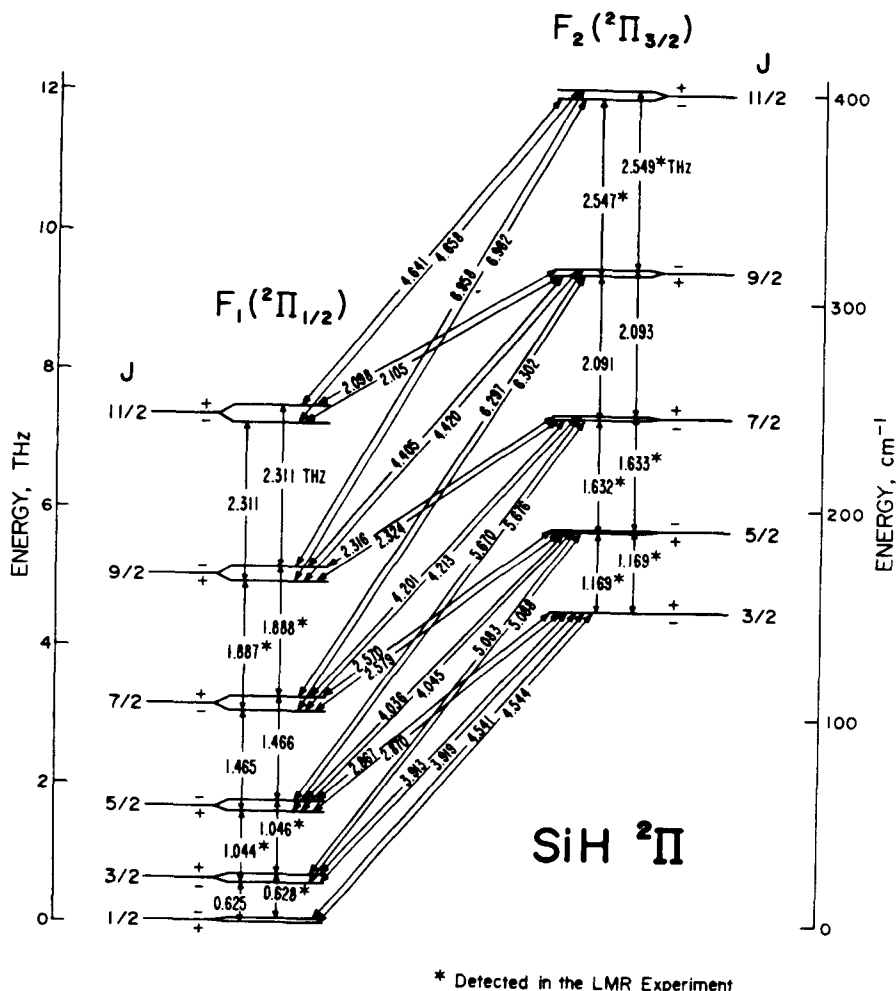


FIG. 1.—The low-lying energy levels of the SiH radical, connected by electric dipole transitions (+ ↔ -) in the microwave and far-infrared regions. The parity doubling (lambda-doubling) has been exaggerated by a factor of 20 for the sake of clarity. The transition frequencies are given in THz. The observations observed in the LMR experiment are marked with an asterisk.

REFERENCES

Brink, D. M., and Satchler, G. R. 1968, *Angular Momentum* (Oxford: Oxford University Press).
 Brown, J. M., Curl, R. F., and Evenson, K. M. 1984, *J. Chem. Phys.*, **81**, 2884.
 Brown, J. M., Kaise, M., Kerr, C. M. L., and Milton, D. J. 1978, *Molec. Phys.*, **36**, 553.
 Douglas, A. E., and Elliot, G. A. 1965, *Canadian J. Phys.*, **43**, 496.
 Inguscio, M., Evenson, K. M., Betrán-Lopez, V., and Ley-Koo, E. 1984, *Ap. J. (Letters)*, **278**, L127.
 Klynning, L., Lindgren, B., and Sassenberg, U. 1979, *Phys. Scripta*, **20**, 617.
 Lewerenz, M., Bruna, P. J., Peyerimhoff, S. D., and Brienker, R. J. 1983, *Molec. Phys.*, **49**, 1.
 Meerts, W. L., and Dymanus, A. 1975, *Canadian J. Phys.*, **53**, 2123.
 Rydbeck, O. E. H., Eldér, J., and Irvine, W. M. 1973, *Nature*, **246**, 466.
 Turner, B. E., and Zuckerman, B. 1974, *Ap. J. (Letters)*, **187**, L59.
 Weinreb, S., Barrett, A. H., Meeks, M. L., and Henry, J. C. 1963, *Nature*, **200**, 829.

J. M. BROWN: Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QE, England, UK

R. F. CURL: Department of Chemistry, Rice University, Houston, TX 77001

K. M. EVENSON: National Bureau of Standards, Boulder, CO 80303