RESONANCE RAMAN STUDY OF THE FIRST ABSORPTION BAND OF H_2S

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Raman spectra of hydrogen sulfide excited at nine wavelengths throughout its first absorption feature in the 180–250 nm region are reported. The spectra are dominated by transitions to S–H stretching overtone states. Several bands corresponding to combinations involving one quantum of the bending vibration are also observed. The intensity pattern varies significantly with excitation energy. These results are interpreted in terms of the nature and number of the excited state potential energy surface(s) in this spectral region.

1. Introduction

A detailed characterization of the electronic structure of small polyatomic molecules is essential to the description of their photochemistry, and is a necessary prerequisite to understanding the excited states of larger molecules. Recent work on the H_2O molecule has greatly increased the understanding of its low lying $\tilde{A}(1\,^1B_1)$ state [1–8]. This state involves the promotion of an electron from an out-of-plane non-bonding b_1 orbital to an a_1 orbital that is of mixed 3s-Rydberg and valence antibonding character [9,10]. Dissociation of the molecule to $OH(^2\Pi)$ and $H(^2S)$ promptly follows optical excitation rendering the relevant absorption band nearly featureless [11,12]. Simulations of the photodissociation have produced results [1–3,7,9] in very good agreement with experimental findings [4–6]. The behavior of the H_2O when optically excited to the $\tilde{A}$ state has become very well characterized. This is possible because of the separation of the $\tilde{A}$ state from nearby potential surfaces, the direct nature of the photodissociation and the involvement of only the two stretching degrees of freedom in the dissociation dynamics.

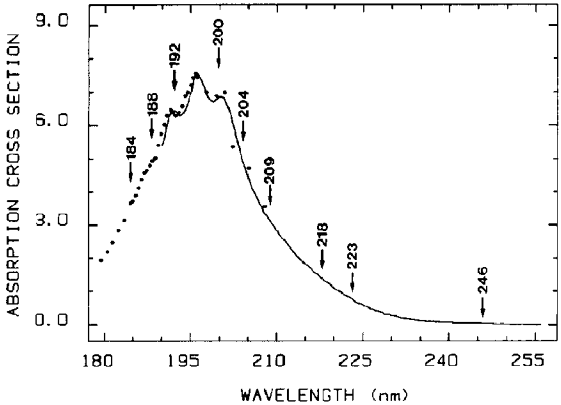

Fig. 1. The absorption spectrum of H_2S. The solid curve was obtained with a room temperature sample using a Varian DMS 300 spectrometer. The dots were obtained from ref. [14].

The situation is much more complex for the isovalent molecule, H_2S. The state of H_2S most analogous to the $\tilde{A}$ state of H_2O is likely to be located in the first absorption band [13–16]. This part of the spectrum, shown in fig. 1, is virtually structureless until about 200 nm, peaks at approximately 196 nm, where a few vibronic features are easily observed, then dies out to shorter wavelengths as the structure once again becomes diffuse. Electronic structure calculations performed so far show that most of the absorption is due to a Rydberg-like $^1B_1$ state which involves excitation of a b_1 electron into a 4s orbital [17–20]. The vibronic structure has been assigned to a bending progression in the allowed $A_1 \rightarrow B_1$ transition [15,16] even though neither the higher Rydberg states nor the ground state of the ion are expected to be distorted in this manner [21]. The large width of the absorption band may be an indication that more than one electronic transition is involved. A $^1A_2$ state giving rise to an $A_1 \rightarrow A_2$ transition (forbidden for C_{2v} symmetric molecules) has been predicted in many calculations to be located near the $^1B_1$ state [17]. However, there is very little experimental evidence for this state and much controversy as to its exact nature [22].

The diffuse character of the first band has long been attributed to predissociation to SH($^2\Pi$) and H(^2S) [23]. Recent determinations of the state distribution of the SH radical after laser photolysis confirmed earlier results [24] which showed that most of the excess energy is channeled into product translation. The vibrational energy distribution for SH has been obtained from measurements of the H atom velocity distribution [25,26]. Detection of SH using the laser-induced fluorescence (LIF) technique has provided the details of the energy partitioning into rotation for the radicals formed in $v=0$ [27–29] and $v=1$ [29]. The models [19,25,30] that have emerged from these results assume that excitation is to a bound $^1B_1$ state that is short-lived due to its coupling to a dissociative $^1A_2$ surface.

The analysis of emission from those few molecules that do not fragment when photoexcited to a repulsive PES may be crucial to the construction of the model for the dissociation [31]. Such a resonance Raman study has been performed by Kleinermanns, Linnebach and Suntz [32] for H_2S excited at 193 nm, but the low resolution and sensitivity of the experiment prevented the extraction of much information. Recently, Butler and coworkers reported a higher resolution measurement of the emission using the same excitation wavelength [33] and presented a detailed analysis of the dynamics of the dissociation at this energy.

In order to use emission spectroscopy to probe a complicated photodissociation process, possibly involving more than one PES, information at more than one excitation energy is essential [#1]. As indicated in our preliminary report of H_2S Raman spectra taken at 184, 200 and 218 nm [34], the intensity pattern changes significantly. The results reported here are for excitation at 184, 188, 192, 200, 204, 209, 218, 223 and 246 nm. These spectra form a coarse excitation profile which allows us to evaluate previous assignments of first absorption band of H_2S.

2. Experimental methods

The experimental apparatus used in this study is essentially the same as detailed previously [35]. The excitation frequencies were generated by stimulated Raman scattering of the harmonics of a JK HY 750 Nd:YAG laser using a high pressure hydrogen cell. The wavelengths used are listed in table 1. The portion of the spectrometer following the input flange of the Raman shifter was enclosed in a N_2 purged system to prevent attenuation of the excitation beam. Hydrogen sulfide gas was used directly from a tank (99.5% minimum purity, Matheson) or (in most of the experiments) was generated in a flow system by the addition of HCl solution to either a Na_2S solution or ZnS solid. The gas flowed through a pipette against a pressure slightly greater than 1 atm into the spectrometer. After passing through the laser beam the gas was exhausted with an aspirator. Traps filled with a saturated $CuSO_4$ solution quantitatively removed the H_2S from the exhaust stream. Emission from H_2S was collected with a backscattering geometry using a curved mirror that imaged the light onto the slits of a 1 m monochromator (McPherson model 225). The light signals were detected with a solar blind photomultiplier, Hamamatsu model 1220 (model 1P28 for the 246 nm spectrum), averaged using a boxcar integrator and stored in a computer.

3. Results

The properties of excited electronic states as probed by the resonance Raman technique are obtained from an analysis of the relative intensities of the scattering to excited vibrational levels of the ground electronic state. The predictions for energies of the vibrational levels of H_2S from the calculations of Halonen and Carrington [36] were used as a guide to previously unobserved vibrational transitions. New vibrational levels seen in the resonance Raman spectra of H_2S and its isotopomers will be reported in a future pub-

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[#1] The results of a preliminary study at 210 nm mentioned in ref. [24] were reported as being similar to those obtained at 193 nm.

Table 1
Vibrational band intensities in the Raman spectra of H_2S

nm^+b	n	Excitation wavelength (nm)							
		223	218	209	204	200	192	188	184
001	1183	0.17	0.12	[b)]	0.64	0.23	0.17	0.17	0.25
002	2355	obscured by nitrogen transition							
100	2614	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
003	3515	c [a)]	b	c	c	a	b	a	a
101	3778	c	0.18	0.45	0.69	0.31	0.27	0.11	b
102	4930	c	b	b	c	b	b	a	a
200	5144	0.50	0.45	0.68	1.17	0.22	0.52	0.52	0.38
110	5243	0.15	0.17	0.32	0.76	0.35	0.16	0.12	0.10
201	6287	0.06	b	0.14	0.30	0.27	0.12	0.07	b
111	6384	b	c	0.09	0.27	0.28	0.13	0.12	0.07
202	7417	b	c	b	0.11	c	0.05	a	b
300	7575	0.16	0.33	0.47	1.05	0.37	0.20	0.50	0.37
210	7754	b	c	0.19	0.31	0.59	0.16	0.13	0.10
301	8697	–	d	0.08	c	0.10	0.04	0.10	b
211	8875	–	c	b	b	0.36	0.06	0.19	0.16
400	9910	–	d	0.23	0.12	0.09	0.08	0.10	0.28
310	10190	–	d	b	b	a	0.05	0.11	c
220	10295	–	d	b	a	0.06	0.03	0.05	c
401	11011	–	–	–	a	a	0.03	a	0.09
311	11290	–	–	–	a	0.03	0.05	0.13	0.16
221	11392	–	–	–	a	0.07	0.03	0.06	c
500	12150	–	–	–	0.11	0.08	0.06	0.15	0.22
410	12526	–	–	–	a	b	b	a	0.13
320	12701	–	–	–	a	0.03	0.05	0.06	c
501	13232	–	–	–	–	a	–	a	b
411	13604	–	–	–	–	a	–	0.04	0.09
321	13779	–	–	–	–	0.05	–	0.06	0.12
600	14278	–	–	–	–	0.06	–	0.08	0.11

[a)] Noise limits for the indicated peaks. a: <0.02, b: <0.05, c: <0.1, d: <0.2. [b)] Region obscured by spurious laser line.

lication. The nature of the motion in the vibrational eigenstates is however not trivial to characterize. The normal to local mode transition (in description) for hydride stretching vibrations occurs at fairly low energy [37] and is also observed within the manifold of states that have the same overall number of stretching quanta [38]. From previous calculations [37,40] and our recent studies of HSD we expect H_2S bond vibrations to be best described in the local mode basis and thus use the corresponding labeling convention throughout this paper [#2].

The transitions observed in the Raman spectra obtained with excitation in the first absorption band of H_2S are summarized in table 1, where the band intensities and average vibrational energies are listed. All bands had widths corresponding to the resolution limit of the monochromator (ranging from 20 to 40 cm^{-1}) and were assumed to be the Q branches of the rovibronic transitions. Significant rotational side bands were observed, but not analyzed. Peak heights were taken as a measure of band intensity and normalized to the peak height of the 10^+0 transition for each spectrum. The entries have been corrected for the variation of instrument sensitivity [6] and resolution.

As can be seen from the table, the spectra are dominated by progressions in the stretching modes of the molecule and combination bands involving excita-

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[#2] The vibrational states, written as nm^+b, denote the symmetric combination of n quanta in one S–H oscillator and m quanta in the other plus b quanta in the bending mode.

tion of stretching modes along with one quantum of the bending mode. The activity observed for the bending fundamental is probably due to resonance with the first absorption band, since a spectrum obtained with 246 nm excitation contains only the 10^+0 band. The noise level in the region of the 00^+1 band is less than 10% of the 10^+0 signal intensity.

We cannot be certain of the presence or absence of the 00^+2 band in any of the spectra since it is expected at 2355 cm^{-1} and this region is obscured by scattering from the N_2 in our system. The most intense signal for a combination involving two quanta of the bend is seen at 20^+2 in the 204 nm spectrum. As shown in fig. 2, this feature is at the base of an intense 30^+0 band whose rotational structure may have perturbed the baseline. It is also possible that the 20^+2 band acquires intensity through a Fermi resonance interaction with 30^+0.

The nature of the Raman scattering changes drastically as one tunes through the H_2S absorption band. This is highlighted in fig. 2 where a portion of the overtone and combination region of each spectrum is shown. At 223 nm the spectrum shows significant activity in the 20^+0 and 30^+0 bands, along with a small peak due to the 11^+0 band. No bending or other stretching activity is observed. The 218 nm spectrum exhibits some intensity in 10^+1 and 11^+0. By 209 nm the 10^+1 activity is quite apparent concomitant with an increase in 11^+0 and 21^+0 intensity. The spectra at 204 and 200 nm show a considerable variation in the relative intensities of the contributions to the pure stretching states and substantial intensity in bend fundamental-plus-stretch combinations. The spectra from 192 to 184 nm show a decrease in this latter type of activity and a change in the nature of the stretching overtones so that at 184 nm, the spectrum looks very much like that seen with excitation near 220 nm with only 20^+0 and 30^+0 being observed.

As can be seen in table 1, consideration of the higher lying overtones observed in this study also reveals some interesting features. For example, note the development of activity in combination bands involving the bending vibration for the spectra taken at 184 nm. There is very little intensity at 10^+1 and the scattering to 20^+1 and 11^+1 is weak. However 21^+1, 31^+1 and 32^+1 make significant contributions to the spectrum. It is also fascinating that the 204 nm spectrum, which exhibits in the 10^+1 band the most intense bend–stretch combination relative to 10^+0, shows no activity in the bending vibration above 11^+1 level.

It must be mentioned that trends discussed above are based on normalization to the 10^+0 band which depends on excitation energy in an unknown manner. However there is no doubt that significant conclusions of a qualitative nature can be drawn from the data. Note also the similarity between the data obtained by Butler and coworkers at 193 nm [33] and our results at 192 nm. Our spectra were obtained with higher resolution but do not extend to as large frequency shifts.

4. Discussion

The resonance Raman spectra of water obtained with excitation throughout its first absorption band [5] are characterized by stretching activity exclusively. The progressions observed reflect a symmetric extension of the OH bonds as the molecule begins to dissociate. The spectra are quantitatively independent of excitation wavelength in the $\tilde{A}$ state region and show no activity in the bending mode until the excitation reaches the $\tilde{B}$ state at much higher energy.

At first glance the resonance Raman spectra of hydrogen sulfide are significantly different from that for water. The band intensities clearly vary with excitation wavelength and there is considerable bending activity. In the long wavelength tail of the absorption spectrum (223 and 218 nm) the Raman spectra contain only a progression in the stretching sequence $n0^+0$. The rather large intensity in the $n=2$ and 3 levels identifies this activity as being dominated by resonance with the electronic state responsible for the absorption. At shorter wavelengths, where there is some structure in the absorption spectrum, new bands appear in the Raman spectra. Activity is seen both in transitions involving one quantum of bending motion and in the nm^+0 levels with $m\neq0$. At still shorter wavelengths, as the structure in the absorption spectrum appears to die off, these bands decrease in relative intensity in the first overtone region but retain intensity in the higher overtone region.

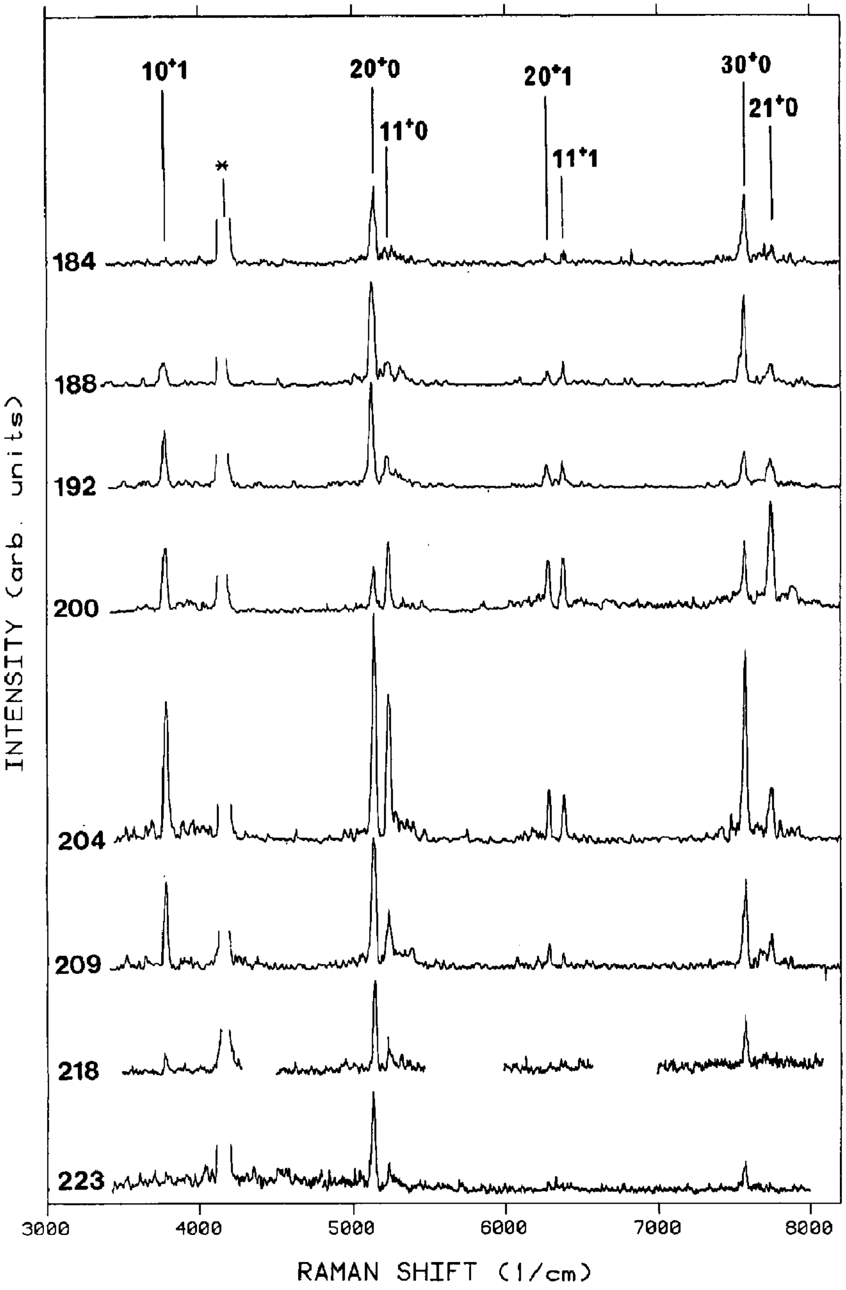

Fig. 2. The low overtone region of the resonance Raman spectra at the indicated excitation energies. Local mode labelling of the bands is used (see footnote 2). The spurious lower-order line from the Raman shifter has been removed and this region denoted with an asterisk.

The most straightforward explanation for this pattern of Raman spectra and of the absorption spectrum is that there are two overlapping states: a dissociative B_1 state directly analogous to the $\tilde{A}$ state of water and, slightly higher in energy at the vertical geometry, a state of A_2 symmetry giving rise to a forbidden transition to a bound or "quasi-bound" surface. We further hypothesize that the B_1 state has essentially the same bond angle as that for the ground state (again analogous to the $\tilde{A}$ state of water) while the A_2 state has a slightly different bond angle from the ground state value. Both states would be expected to differ from the ground state in terms of the equilibrium bond lengths.

In order to contribute to the Raman activity, the A_2 state must borrow intensity from the B_1 state via vibronic coupling, involving the asymmetric stretch coordinate in both the upward and downward transitions. For a normal mode molecule this would result in intensity in the two-quantum transition to the level $2\nu_a$. But for a local mode molecule such as H_2S, what would be a normal mode antisymmetric overtone level can be functionally described as an approximately equal admixture of the 20^+0 and 11^+0 levels plus components from other polyads of the same symmetry. Thus vibronic activity is revealed in the Raman spectrum as intensity in many of the nm^+0 levels. In our spectra the resonance with the A_2 state results in a large increase in the relative intensities of the 11^+0 and 21^+0 transitions. Due to the multimode nature of the vibrational overlap factors, the vibronically induced intensity will also result in activity in any modes that have geometry changes in the A_2 state. By hypothesis this includes the bending mode, leading to intensity in the 11^+1 and 20^+1 band. The vibronic mechanism also results in intensity in the 00^+1 and 10^+1 bands via compensating $\Delta v=+1$ and $\Delta v=-1$ vibronic transitions in the promoting mode. The most persuasive argument in favor of this proposal is that all of these expected bands appear to be enhanced in the same excitation region. The postulated domination of the Raman spectrum by contributions from the forbidden transition (even though it is superimposed on an allowed transition) can be explained on the basis of strong vibronic coupling and compensating lifetime factors resulting in a relative depression of the contribution from the dissociative allowed transition.

It might be possible to formulate a potential for a single excited state surface that describes the observed absorption and emission spectra. In considering such a possibility it should be remembered that the combination of the 20^+0 and 11^+0 levels (and their higher dyadic components) represents both the antisymmetric and the symmetric normal mode overtone. Thus an alternative explanation for (or description of) the nature of the motion observed with excitation in the 200 nm region is that it is primarily normal-mode-like rather than being motion best characterized as mostly local mode, as is the case at lower excitation energy. However, based on the present results, it seems more natural to describe the behavior observed for the resonance Raman spectra as a function of excitation in terms of two overlapping electronic state potential energy surfaces.

In any case, the dependence of the Raman spectra on the excitation wavelength is indicative of recurrences in the dissociation dynamics following excitation. Because of this it is not possible to associate the higher-order overtone and combination band intensity with the later part of the dissociation dynamics on a one-to-one basis as was assumed by Butler and coworkers [33]. This situation is further complicated by the fact that the excited state motion is revealed in these experiments in terms of ground state vibrational wavefunctions. Emission to high-lying overtones and combinations, which is indicative of motion in the exit channel for a direct dissociation, may contain contributions due to bound-like motion for H_2S in the excited state. Hence, the assumption made by Butler and coworkers [33] which correlates the highest $n0^+0$ bands with dissociation of the molecule must be tested by calculation and emission data in this region using other excitation wavelengths.

Our explanation in disagreement with the model that has been used to explain the final state distributions from H_2S photolysis [19,25,30], but provides a better explanation of the absorption spectrum. A model proposed by Valentini and coworkers [29] involves considerable bending motion in the excited state, consistent with the interpretation of the vibronic progression in the absorption spectrum [15,16]. However, an excited state PES with sufficient displacement along the bending coordinate to account for the progression would give rise to much more intensity in the mn^+2 bands in the resonance Raman spectra. The present work as well as the results of Butler and coworkers [33] demonstrate that this is not the case. This difference in the form of the potential that appears to be needed to explain the final state distribution and the emission data may be a reflection of the emphasis of the emission process on the bound character of the photoexcitation process.

Acknowledgement

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