

# Spectroscopy of SH ( $A-X$ ) transition in Ar and Kr matrices: The caging of predissociation

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The  $A(^2\Sigma^+) - X(^2\Pi)$  transition of SH isolated in Ar and Kr matrices is studied by laser induced fluorescence spectroscopy. The (0,0), (1,0), and (2,0) transitions are observed in excitation. These lines are structureless and homogeneously broadened ( $200\text{--}300\text{ cm}^{-1}$ ). The (0,0), (0,1), and (0,2) emission bands, are strongly Stokes shifted and further broadened ( $>1000\text{ cm}^{-1}$ ). The spectra can be successfully interpreted in analogy with OH-Rg pair interactions. The SH( $A$ )-Rg potential is deeply bound ( $\sim 1000\text{ cm}^{-1}$  in Ar and  $\sim 2000\text{ cm}^{-1}$  in Kr) with nearly 1 Å compression along this coordinate. Franck-Condon analysis indicates that the equilibrium bond length of SH( $A$ ) is 0.055 Å longer than in the free radical. The  $A$  state, which is strongly predissociated in the free radical, relaxes radiatively in the matrix:  $\tau=425$  and 770 ns in Ar and Kr, respectively. Predissociation is treated as a two-dimensional tunneling process between two electronic surfaces. Poor Franck-Condon factors along the solvent coordinate, due to differential solvation of electronic states, leads to complete arrest of electronic predissociation.

## I. INTRODUCTION

In the case of open shell, electronegative radicals, charge transfer contributions lead to strong binding with rare gas atoms (Rg). An extreme example is XeF, which in its ground electronic state is bound by 0.15 eV.<sup>1</sup> Given the significant electron affinities of SH and OH, 2.3 and 1.83 eV, respectively, and the fact that they are isoelectronic with halogens, charge transfer is expected to play an important role in their interactions with rare gas atoms. However, in the case of these hydrides, hydrogen bonding contributions need to be taken into account. Based on electron affinities, SH-Rg would be expected to have the stronger interaction. However, due to the smaller electronegativity of S in comparison to O, SH is a much poorer hydrogen donor than OH. Therefore, based on hydrogen binding affinities, OH-Rg would be expected to be more strongly bound. A comparison between the spectroscopies of these radicals in matrices could shed light on this subtle balance of forces.

The SH  $A(^2\Sigma^+) - X(^2\Pi)$  transition has been characterized in the gas phase. It was first studied by high resolution absorption spectroscopy by Ramsay and co-workers.<sup>2,3</sup> In addition to providing molecular parameters, based on observed linewidths of rotationally resolved transitions, it was realized that the vibrationally excited states undergo rapid predissociation. Subsequent laser induced fluorescence (LIF) studies have verified this finding and furthermore established that fluorescence lifetimes are determined by predissociation in  $v'=0$  as well.<sup>4-6</sup> Gas phase photodissociation studies of H<sub>2</sub>S by monitoring LIF from the SH photofragment have been limited by this effect.<sup>7,8</sup> In the direct spectroscopic studies, Franck-Condon factors limit the observations to  $v'=2$ . A rather novel technique, namely, photodissociation studies followed by H atom

photofragment translational spectroscopy, has most recently been applied to H<sub>2</sub>S, and has for the first time yielded a direct observation of the higher lying vibrations of SH( $A$ ).<sup>9</sup>

Ultraviolet and infrared absorption spectra for SH and SD in an Ar matrix were recorded by Aquista and Schoen.<sup>10</sup> They observed a small reduction in electronic origin of the  $A \leftarrow X$  transition in the solid, and only minor perturbation of vibrational frequencies, within 2% of gas phase values, both in the  $A$  and  $X$  states. We have reinvestigated these transitions in Ar and Kr matrices, by laser induced fluorescence spectroscopy. Our spectroscopic observations are in agreement with these earlier measurements. Moreover, we find a direct analogy between the SH and OH spectroscopy in Ar and Kr. Since we intend to draw on this similarity for the interpretation of our results, we first summarize the relevant OH data.

The first observation of matrix isolated OH in Ar and Kr was reported by McCarthy in 1959.<sup>11</sup> The (0,0) transition showed fine structure, which at that time had not been interpreted. Reports of the OH and OD absorption and emission spectra in Ne followed.<sup>12,13</sup> The Ne data show OH rotating almost freely in the matrix, and vibrational frequencies remaining almost identical with those in the gas phase, implying very little interaction between radical and rare gas atoms. A very different picture emerges in heavier rare gases. In 1977, Goodman and Brus obtained LIF spectra for the same transition in Ar, Kr, and Xe.<sup>14</sup> They recorded excitation, as well as dispersed fluorescence spectra. In addition to the OH internal vibrations, a low frequency vibronic progression was observed and assigned to the Rg-OH stretch. In contrast, the emission spectra, were broad, featureless, and markedly redshifted relative to the excitation spectrum. It was concluded that electronic excitation leads to shortening of the Rg-OH bond with substantial binding:  $\sim 700\text{ cm}^{-1}$  in Ar, and greater than  $1000\text{ cm}^{-1}$  in Kr.<sup>14</sup> This work stimulated numerous stud-

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ies of the Rg-OH complex in the gas phase.<sup>15-38</sup> The rotationally resolved data of the isolated complex substantiated many of the conclusions derived from the matrix study. The current picture for Ar-OH is one in which the ground state triatomic is linear: bound by  $\sim 100 \text{ cm}^{-1}$  at a bond length of  $3.7 \text{ \AA}$  in the  $\text{Ar} \cdots \text{HO}$  geometry, and showing a secondary minimum at the same distance in the  $\text{Ar} \cdots \text{OH}$  geometry.<sup>30,31</sup> In the excited  ${}^2\Sigma^+$  state, the interaction is substantially stronger: in the Ar-OH geometry the binding energy is  $\sim 1000 \text{ cm}^{-1}$ , and the bond length contracts by as much as  $1.0 \text{ \AA}$ , leading to an Ar-OH vibrational frequency of  $\sim 170 \text{ cm}^{-1}$ . A most recent gas phase study of the Kr-OH molecule presents a very similar picture; a very tightly bound Kr-OH excited state with binding energy close to  $2000 \text{ cm}^{-1}$ , a change in the Kr-OH bond length of  $1.15 \text{ \AA}$ , and an excited state Rg-OH vibrational frequency of  $227 \text{ cm}^{-1}$ .<sup>39</sup>

These results remain in excellent agreement with the original interpretation of the matrix data by Goodman and Brus, who assigned the spectra in the framework of an OH radical interacting with a single Rg atom in the lattice.<sup>14</sup> They correctly concluded that the Rg atom hydrogen bonds to the OH, producing a linear  $\text{Rg} \cdots \text{HO}$  molecule. The original model proposed for the binding remains a valid qualitative description of the interactions. The  $A-X$  transition involves the transfer of a  $\sigma$  bonding electron to a nonbonding  $\pi$  orbital. The  $\text{OH}(A)\text{-Rg}$  binding is then through electron donation by the rare gas into the partially filled  $\sigma$  orbital. This consideration would lead to the expectation of a somewhat weaker binding for  $\text{SH}(A)$  vs  $\text{OH}(A)$ . In the ground state, the binding should be dominated by charge transfer into the  $\pi$  hole on the chalcogen, therefore based on electron affinities, a somewhat stronger binding is to be expected for  $\text{SH}(X)$  vs  $\text{OH}(X)$ . The charge transfer states of OH in Ar and Kr matrices have recently been observed.<sup>40</sup>

In what follows, after a brief experimental section and presentation of results, we discuss the spectroscopy of matrix isolated SH in analogy with the OH-Rg complex; and subsequently discuss the issue of arrested predissociation due to differential solvation of electronic states.

## II. EXPERIMENT

SH is prepared by *in situ* photodissociation of  $\text{H}_2\text{S}$  doped Ar and Kr matrices.<sup>41</sup> The matrices are prepared by pulsed deposition of the premixed gas ( $M/R=10\,000$ ) on a sapphire substrate. The sample is deposited, and most of the data are obtained at  $17.5 \text{ K}$ . The excitation spectra are recorded using an excimer pumped dye laser, after frequency doubling in a BBO crystal (Lambda Physik EMG101/FL2001). The laser power is monitored with a UV photodiode, and used for normalization. Fluorescence is observed through a  $0.75 \text{ m}$  monochromator (Spex 1702), and detected with a photomultiplier tube (Hamamatsu 758). Emission spectra are recorded with  $0.2 \text{ nm}$  resolution. Lifetimes are measured using a digital averaging oscilloscope (Tektronics 2430).

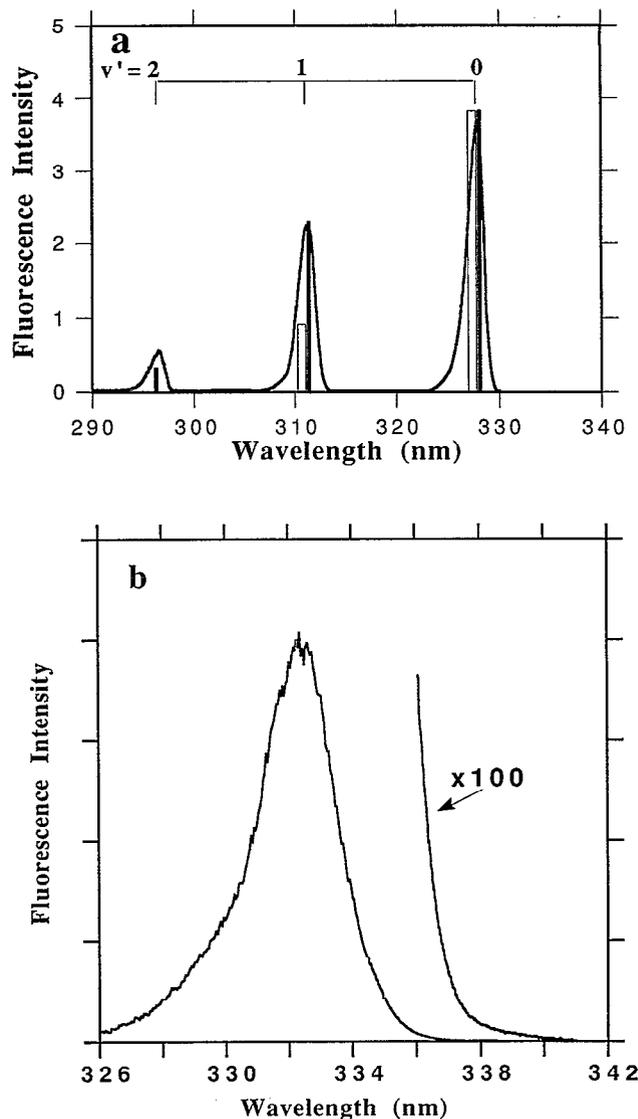


FIG. 1. Excitation spectra of matrix isolated SH: (a) in Ar, (b) in Kr. (a) In addition to the assigned experimental progression F-C factors based on gas phase parameters (open box) are shown. To reproduce the observed relative intensities (solid lines),  $\Delta r_e=0.13$ ,  $\omega_e'=1665.5 \text{ cm}^{-1}$ ,  $\omega_e''=2420.8 \text{ cm}^{-1}$ , are used. (b) The (0,0) excitation band in Kr is shown along with expansion of the red edge. No clear definition of a zero phonon line can be found.

## III. RESULTS

Excitation spectra of SH in Ar and Kr are shown in Fig. 1. Three vibrational bands in the S-H coordinate are observed [see Fig. 1(a)]. The 0-0 transition in Kr and an expanded scale of the red edge showing no observable zero phonon line (ZPL) is shown in Fig. 1(b). The excitation line shapes are broad, FWHM  $\sim 200 \text{ cm}^{-1}$  in Ar and  $\sim 270 \text{ cm}^{-1}$  in Kr, independent of vibrational level accessed. The lines are blue shaded, and homogeneously broadened. The latter is verified by our failure at hole burning. When excited with sufficient laser intensity SH can be made to dissociate by a two-photon process. Excitation spectra obtained after  $\sim 50\%$  dissociation of SH, by tuning

TABLE I. Spectroscopic data for SH(OH) in Ar and Kr.<sup>a</sup>

	Excitation					Emission					
	$\nu'-\nu''$	$\bar{\nu}_{\max}^b$	$\bar{\nu}_{\text{th}}^c$	$\Delta\bar{\nu}^d$	$\Delta T_e^e$	$\Delta G_{1/2}$	$\nu'-\nu''$	$\bar{\nu}_{\max}^b$	$\bar{\nu}_{\text{th}}^c$	$\Delta\bar{\nu}^d$	$\Delta\bar{\nu}_s^f$
Ar	0-0	30 390	30 032	210 (240)	272 (313)		0-0	28 820	30 300	1200 (1700)	1570 (2790)
	1-0	32 092	31 800	185 (210)		1702 [1785]	0-1	26 076		1400	
	2-0	33 740	33 450	200 (230)		[1599]	0-2				
Kr	0-0	30 095	29 545	270	570 (527)		...	23 980	27 780	2500	6115 (3100)
	1-0	31 797		270		1702 [1785]					
	2-0	33 351		300 (400)		1560 [1599]					

<sup>a</sup>All values in  $\text{cm}^{-1}$ . Values in parentheses are for OH. Values in square brackets are for gas phase.

<sup>b</sup>Band maxima.

<sup>c</sup>Estimated red edge.

<sup>d</sup>FWHM.

<sup>e</sup> $\bar{\nu}_{(0,0)\text{gas}} - \bar{\nu}_{\max}$ .

<sup>f</sup>Stokes shift  $\bar{\nu}_{\text{excit}} - \bar{\nu}_{\text{emission}}$ .

the laser to the excitation band tail, are identical to those obtained prior to dissociation. We conclude that the excitation line shapes are homogeneously broadened, as a result of congested F-C envelopes along the Rg-HS coordinate. The observed spectroscopic parameters are collected in Table I, along with relevant parameters from OH matrix data. Based on the excitation maxima of the (0,0) transitions, the observed electronic origins are redshifted relative to the gas phase:  $\Delta T_e = 270$  and  $570 \text{ cm}^{-1}$  in Ar and Kr, respectively. The observed linewidths and shifts are quite comparable to those of OH (see Table I).

Figure 2 shows emission spectra for SH in Ar and Kr. The same emission spectra are obtained independent of which vibration is excited: the emission spectra are strictly from vibrationally relaxed SH(A), and vibrational relaxation is complete within the pulse width of the laser (10 ns). A comparison between excitation and emission spectra shows a significant Stokes shift, and extensive broadening of lines. The Ar data can be assigned to a progression in SH(X) with (0,0), (0,1), and (0,2) transitions. This vibrational progression is barely perceptible in Kr.

In the range of 17–32 K, temperature independent fluorescence decay times of  $425 (\pm 20)$  ns and  $770 (\pm 30)$  ns are observed in Ar and Kr, respectively. If we assume that these lifetimes are determined by radiation, then in order to compare to the gas phase free radical radiative lifetime, two corrections need to be made: a  $\lambda^3$  correction due to the large Stokes shifts, and a correction for the change in the dielectric of the medium.<sup>42</sup> Accordingly,

$$\tau_g = [n(n^2 + 2)^2 / 9] (\lambda_g / \lambda_s)^3 \tau_s \quad (1)$$

in which  $n$  is the index of refraction of the solid, 1.27 for Ar and 1.34 for Kr;  $\tau$  and  $\lambda$  are the radiative lifetimes and emission band centers, respectively. From the measured lifetimes in Ar and Kr, using Eq. (1), gas phase radiative lifetimes of 700 and 800 ns are extrapolated, respectively. Since the gas phase fluorescence lifetimes are determined

by predissociation, the radiative lifetime can only be obtained indirectly. Based on calibrated absolute radical concentrations and laser induced fluorescence yields, Friedl *et al.* have determined a radiative lifetime of  $820 (\pm 240)$  ns.<sup>6</sup> Thus the corrected matrix lifetimes fall within the errors of the known gas phase radiative lifetime of SH(A), and can therefore be safely assumed to be dominated by radiation: Predissociation is absent in the vibrationally relaxed SH(A) state. A comparison of the relative intensities of the vibrational progression observed in the excitation spectra with the earlier absorption spectra obtained in matrices,<sup>10</sup> shows them to be identical within experimental error. This would imply that no predissociation occurs in the vibrationally excited states of SH(A) in the matrix.

## IV. DISCUSSION

### A. The interaction potential

Given the similarity of the spectroscopy of SH and OH in these solids, it would be reasonable to treat the data in the same framework, i.e., in the framework of triatomic SH-Rg. Accordingly, we treat the interaction potentials as a function of two coordinates: the S-H internal coordinate  $q$  and the SH-Rg solvent coordinate  $Q$ . The different electronic surfaces are then designated as  $V^M(q, Q)$  and the Born-Oppenheimer separated wave functions are identified as  $\psi^M(\nu, n)$ , in which  $M = X, A, a$ , is the electronic state of the SH radical. Given the fact that  $\omega(q)/\omega(Q) \gtrsim 10$ , a second Born-Oppenheimer separation between these two motions is in principle possible. Without dwelling into the nature of this separation, we contend that to a good approximation the Hamiltonian is separable along the internal and solvent coordinates:  $V^M(q, Q) = V^M(q) + V^M(Q)$ .

Based on the IR spectra,<sup>10</sup> which show vibrational spacings within 2% of the gas phase, it can be safely assumed that in the ground state,  $V^X(q)$  is well represented by the free radical potential. This is consistent with our

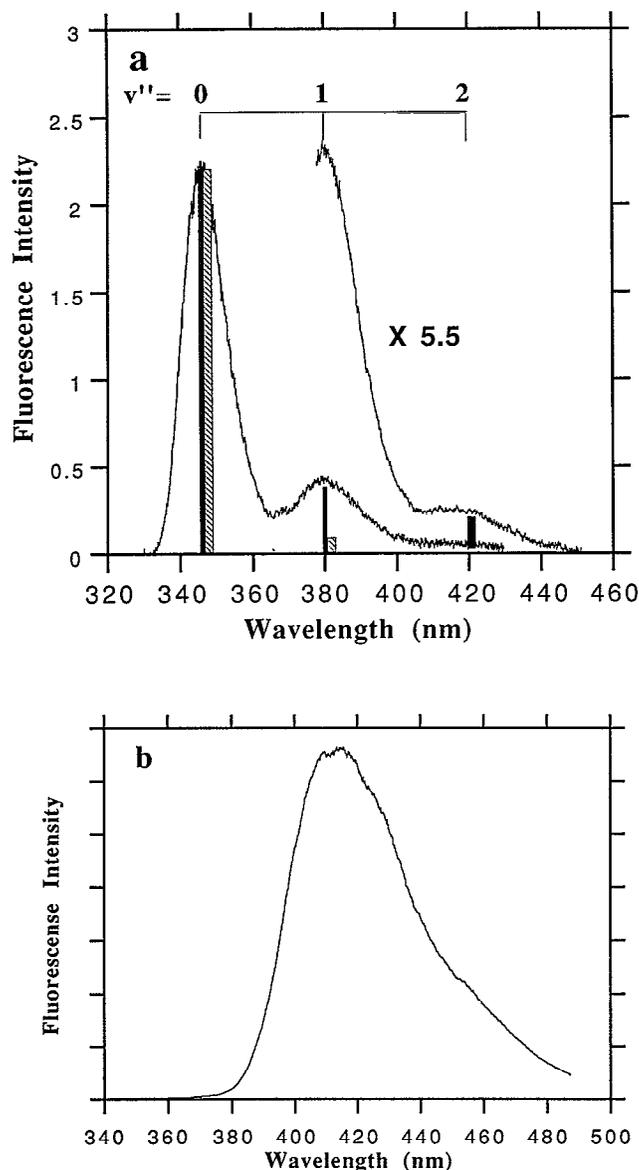


FIG. 2. Emission spectra of matrix isolated SH: (a) in Ar, (b) in Kr. (a) In Ar a clear progression of three vibrations in the SH coordinate can be seen. Their intensities can be reproduced with the parameters derived from the excitation spectrum (see Fig. 1 and text); which are shown by the solid stick spectrum. The gas phase F-C factors are also shown (shaded boxes). (b) The emission spectrum in Kr is broadened such that a vibrational progression cannot be discerned.

notions of binding in the ground state. Along the  $\text{SH} \cdots \text{Rg}$  coordinate, due to the poorer hydrogen binding of SH, a well depth less than that of  $\text{OH-Rg}$  of  $\sim 100 \text{ cm}^{-1}$  is to be expected. Along the  $\text{HS} \cdots \text{Rg}$  coordinate, due to the 1 eV smaller electron affinity of SH, a well depth less than that of the isoelectronic  $\text{Cl-Rg}$  potential of  $\sim 100 \text{ cm}^{-1}$  is to be expected.<sup>20,40</sup> We therefore expect SH to be subject to a nearly isotropic potential in substitutional trapping sites. Whether  $\text{SH}(X)$  is a free or hindered rotor cannot be established based on existing IR spectra.

Given the fact that only three broadened vibrational transitions are observed in excitation, accurate potential

parameters for  $V^A(q)$  cannot be obtained. It can however be stated that  $\Delta G_{1/2}(q)$  values in the  $A$  state are  $\sim 5\%$  smaller than in the gas phase (see Table I). The intensities of the observed transitions are more informative. The relative intensities of the vibronic bands are assumed to be given by the Franck-Condon factors  $\langle \psi^X(q) | \psi^A(q) \rangle$ . A stick spectrum based on gas phase harmonic wave functions is shown in Fig. 1(a) to deviate significantly from that observed in solid Ar. To fit the intensity pattern of the solid state excitation spectrum, a difference in equilibrium bond lengths between the  $A$  and  $X$  states of  $|\Delta q_e| = 0.13 \text{ \AA}$ , instead of the gas phase value of  $0.0448 \text{ \AA}$ , has to be assumed. The synthesized stick spectrum using this displacement is also shown in Fig. 1(a). The same parameters reproduce the observed relative intensities in the emission spectrum in Ar [see Fig. 2(a)]. Although the analysis does not yield the sign of  $\Delta q_e$ , we expect the major perturbation to occur in the  $A$  state. An increase in the  $\text{SH}(A)$  bond length by  $0.055 \text{ \AA}$  relative to the gas phase would be consistent with the intensity pattern, and also the reduction in  $\Delta G_{1/2}$  values. We conclude that the  $\text{Rg-HS}$  interactions weaken the  $\text{S-H}$  bond in the excited state.

The dramatic difference in emission and excitation spectra can be entirely attributed to differences in potentials along the  $\text{SH-Rg}$  solvent coordinate in the ground and electronically excited states, namely: due to differences in  $V^A(Q)$  and  $V^X(Q)$ . The excitation line shapes should then represent the envelope of F-C factors along this coordinate:

$$\sum_n \langle \psi_0^X(Q) | \psi_n^A(Q) \rangle \delta(E_{v,n} - h\nu). \quad (2)$$

While in the present only broad profiles are observed, in the case of OH in Ar and Kr, clear progressions in  $V^A(Q)$  are seen.<sup>14</sup> In Ar, these progressions are fit with Morse parameters of  $\omega_e(Q) = 203 \text{ cm}^{-1}$ , and  $\omega_e x_e(Q) = 13.1 \text{ cm}^{-1}$ . The F-C envelope along this coordinate peaks at  $n = 4-5$ , resulting in an overall width of order 2–2.5 nm. In Kr, a similar analysis yields  $\omega_e(Q) = 230 \text{ cm}^{-1}$  and  $\omega_e x_e(Q) = 8.2 \text{ cm}^{-1}$  for the  $\text{OH-Kr}$  vibration in the  $A$  state. The F-C envelope for this system peaks at  $n = 7-8$  quanta,<sup>39</sup> yielding an overall linewidth of  $\sim 3 \text{ nm}$ . Comparison of the  $\text{SH-Rg}$  line shapes and linewidths with  $\text{OH-Rg}$  overall envelopes shows them to be quite similar (see Table I). Note, in both SH and OH, the observed F-C envelopes are nearly independent of the particular  $v$  state accessed, implying a weak coupling between  $q$  and  $Q$  coordinates. The absence of structure in SH can be rationalized. If one assumes a similar interaction potential for  $\text{Rg-HS}$  and  $\text{Rg-HO}$ , due to the larger SH mass, a reduction in  $\omega_e$  by a factor of 1.4 in Kr, and 1.23 in Ar is to be expected. Thus near the F-C maximum, the spacings in this local mode are within a factor of 2 of the Debye limit of the solid. Efficient coupling to bulk phonons, or a local mode other than the optically active coordinate, would lead to lifetime broadening, and would therefore be expected to blend the phonon structure in the SH spectra. A lifetime broadening of order  $100 \text{ cm}^{-1}$  is required for this argu-

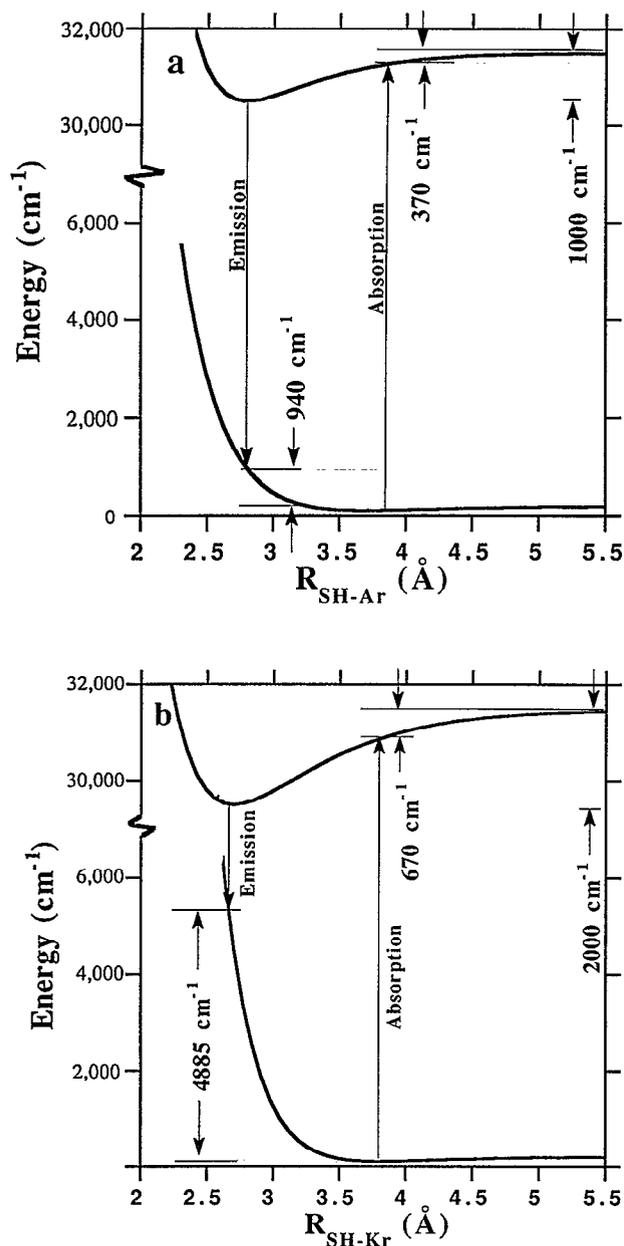


FIG. 3. Interaction potentials  $V(Q)$  for SH-Rg: (a) Rg=Ar, (b) Rg=Kr.

ment to hold, and therefore a relaxation time of order  $10^{-13}$ – $10^{-12}$  s is implied.

The above spectral interpretations, can be summarized by the construction of qualitative potentials for the SH-Rg interactions:  $V^A(Q)$  and  $V^X(Q)$ . These are shown in Fig. 3. To establish the overall energy scale we assume ground state Rg-SH binding of  $100 \text{ cm}^{-1}$  consistent with the known Ar-HO( $X$ ) state. Since the interactions in the  $A$  state are so much larger, this number is not critical in the model. The shift in electronic origin relative to the gas phase can only be estimated since ZPL's are not apparent. The peak of the 0,0 excitation band gives the SH( $A$ ) energy for  $v'=0$  in SH and the Rg atoms at the ground electronic state equilibrium geometry. These are redshifted relative to the gas phase 0,0 transition by 272 and 570

$\text{cm}^{-1}$  for Ar and Kr, respectively. To find the minimum in  $V^A(Q)$ , we search for the red edge in the excitation spectra [see Fig. 1(b)]. This gives a lower limit for the binding energy:  $D_e^A(Q) > 730$  and  $1220 \text{ cm}^{-1}$  for Ar and Kr, respectively. A more realistic binding energy can be obtained by comparing the SH line shapes to those of OH. Based on the similarity in linewidth we can estimate the ZPL positions. This procedure yields binding energies of  $\sim 1000$  and  $\sim 1900 \text{ cm}^{-1}$  for  $V^A(Q)$  in Ar and Kr, respectively. This analysis implies that the center of the SH absorption band corresponds to excitation of  $n=6$  in Ar and  $n=10$  in Kr. The relatively narrow absorption lines are due to the fact that absorption occurs to the attractive part of the excited state potential where forces are weak. Given the binding energies in  $V^A(Q)$ , from the difference in excitation and emission maxima of the (0,0) lines, the energy of  $V^X(Q)$  at the excited state minimum can be obtained: 940 and  $4885 \text{ cm}^{-1}$  for Ar and Kr, respectively. The breadth of the emission lines is then due to access of the steep repulsive wall of  $V^X(Q)$ .

The potentials illustrated in Fig. 3 should be considered only as schematic representations. While the energy scale is fairly quantitative the displacement axes are based on the known OH parameters. Note, the matrix data do not directly determine to which end of the SH molecule the Rg atom binds. The choice of the SH  $\cdots$  Rg configuration, is based on the expectation that in the excited state the binding proceeds mainly by electron donation to the  $\sigma$  hole in SH. Thus very similar pictures emerge for OH and SH interactions with Ar and Kr. The difference in electron affinities are manifest in the larger redshift and Stokes shift of SH in Kr (see Table I), which may be interpreted as an indication of larger charge transfer contributions. Although a smaller effect, this situation is reversed in the case of Ar. Both the redshift in excitation, and the Stokes shift in the case of SH-Ar are smaller than that of OH-Ar. This may be interpreted as an indication that the binding in  $V^A(Q)$  in Ar is strictly due to the three center hydrogen bond, in which case a better overlap is to be expected for species in the same row of the periodic table.

## B. Predissociation

In the gas phase vibrationally excited states of SH predissociate on a time scale of 10–100 ps,<sup>2</sup> while the  $v'=0$  level predissociates on a timescale of 0.2 ns (Ref. 6) to  $3(\pm 2)$  ns.<sup>4</sup> An accurate value for the dissociation energy of SH( $X$ ),  $D_0=3.62(\pm 0.03)$  eV, has been obtained recently.<sup>43</sup> Using the gas phase (0,0) transition energy of  $30\,662.4 \text{ cm}^{-1}$ , it can be established that SH( $A$ ,  $v=0$ ) is  $1463 \text{ cm}^{-1}$  above the dissociation limit of SH( $X$ ). A fluorescence lifetime of 230 ns is observed for SD( $A$ ,  $v=0$ ) in the gas phase, implying a predissociation rate 2–3 orders of magnitude smaller than SH.<sup>6</sup> It would therefore appear that the electronic state responsible for predissociation crosses the attractive part of the  $A$  state above  $v=0$ . The isotope effect is twofold: First, increase in mass slows tunneling rates; second,  $v=0$  in the heavier isotope is  $\sim 500 \text{ cm}^{-1}$  farther below the crossing. *Ab initio* calculations show three repulsive states  ${}^2\Sigma^-$ ,  ${}^4\Sigma^-$ ,  ${}^4\Pi$ , to cross SH( $A$ )

above  $v=0$ , the lowest of which is the  $a^4\Sigma^-$  state.<sup>44</sup> Although both spin and symmetry forbidden, this state is presumed to be responsible for the predissociation of  $v=0$ . The same states were used to explain predissociation in the low vibrational levels of the OH( $A$ ).<sup>45</sup> In OH predissociation rates are 2–3 orders of magnitude slower, and were shown to be rotational level dependent. The larger rates in SH are a reflection of the stronger electronic mixing.

Based on the absence of resolved resonances, solvation of SH( $A$ ), relaxation in  $V^A(Q)$ , was estimated to proceed on a subpicosecond time scale. Therefore, this process could well compete with predissociation. As such, predissociation from only ( $v=0,1,2; n=0$ ) states need be considered. In Kr, the ( $v=0, n=0$ ) state cannot undergo predissociation, since its energy falls  $\sim 600\text{ cm}^{-1}$  below the  $S(^3P) + H(^2S)$  dissociation limit. In Ar, while this state is lowered in energy relative to the crossing point, it remains  $\sim 750\text{ cm}^{-1}$  above the dissociation limit. Based on this energetic argument alone, a reduction in predissociation rate of the ( $v=0, n=0$ ) state in Ar is to be expected. However, a complete arrest of the process would be difficult to justify.

No predissociation is observed from the vibrationally excited states of SH( $A$ ), for which the energetic argument is not applicable. A special consideration of these states would be obviated if they were to relax on a time scale shorter than 10 ps, i.e., shorter than the gas phase predissociation lifetimes of these states. In fact, it is known that in the gas phase OH–Rg complex, vibrational relaxation in the  $A$  state proceeds on a timescale of 10–100 ps.<sup>34,39</sup> While this may be the case in the matrix, a careful consideration of the potential energy surfaces that arise from differential solvation of electronic states, leads to a more general mechanism for blocking of predissociation, a mechanism that would be operative even if vibrational relaxation were not fast.

We consider the two-dimensional surfaces  $V(q,Q)$  involved in the intersystem crossing. The final electronic state responsible for the predissociation is assumed to be the purely repulsive  $^4\Sigma^-$  state, given by the *ab initio* calculations.<sup>44</sup> The synthesis of  $V^A(q,Q)$  is direct, it consists of the SH( $A$ ) Morse function along  $q$ , and the potential curves extracted in Fig. 3 along  $Q$ :  $V^A(q,Q) = V^A(q) + V^A(Q)$ . In the case of the  $a^4\Sigma^-$  state, which correlates with the same dissociation limit as SH( $X$ ), it is reasonable to assume that the potential along  $Q$  is similar to  $V^X(Q)$ . Accordingly, we assume  $V^a(q,Q) = V^a(q) + V^X(Q)$ . The resulting surface is given in Fig. 4. The predissociation rate between these two surfaces can be given in a golden rule formulation as

$$\Gamma_{A \rightarrow a} = \frac{4\pi^2}{\hbar} |\langle H_{so} \rangle|^2 \sum_{v',n'} |\langle \psi_v^A(q) | \psi_{v'}^a(q) \rangle|^2 \times |\langle \psi_0^A(Q) | \psi_{n'}^a(Q) \rangle|^2 \delta(E_{v,0} - E_{v',n'}), \quad (3)$$

$v',n'$  states in this case belong to the  $a$  state continuum, and the summation can be replaced by integration over the equipotential surface subject to the energy conservation implied by the delta function. Only  $n=0$  states are consid-

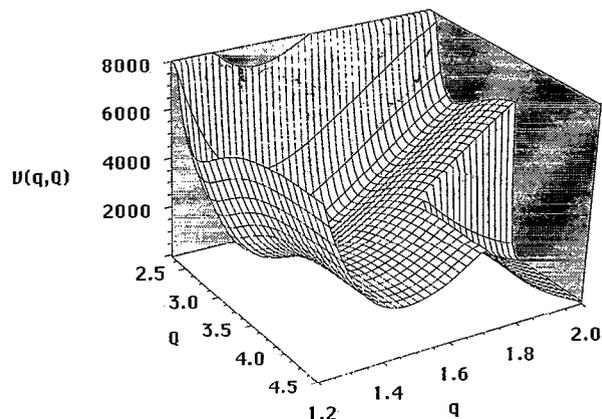


FIG. 4. Minimum energy surface showing the crossing between  $V^A(q,Q)$  and  $V^a(q,Q)$ . The potential minimum in  $V^A$  occurs at  $Q=2.7\text{ \AA}$ ,  $q=1.45\text{ \AA}$ .  $V^a$  remains purely repulsive and is the minimum energy surface in the quadrant  $q > 1.8\text{ \AA}$  and  $Q > 3.5\text{ \AA}$ . Tunneling along  $q$  alone is not possible for  $n=0$  states.

ered, since as argued above relaxation along  $Q$  is believed to be much faster than intersystem crossing. The electronic mixing between these two states is assumed to be dominated by spin–orbit mixing  $|\langle H_{so} \rangle|$  the magnitude of which would not be expected to change significantly between gas and matrix. The first F–C factor in Eq. (3) is the same as the operative term in the gas phase. The second F–C factor, and the double summation (surface integral) are due to introduction of the rare gas coordinate. We note that now for  $n=0$  states predissociation along  $q$  alone is not possible. In the case of the  $v=0, n=0$  state, a cut along  $Q=2.7\text{ \AA}$  (i.e., at the solvated geometry), would show that this state is  $\sim 5000\text{ cm}^{-1}$  below  $V^a$  in the asymptotic limit in  $q$ . Predissociation now requires tunneling between the two-dimensional surfaces, along trajectories that simultaneously involve  $q$  and  $Q$ . Along any such coordinate, the crossing point is significantly removed and the barrier height significantly increased, as compared to the crossing in the  $Q=0$  plane, i.e., in the unsolvated configuration. The F–C factors along the SH–Rg coordinate are poor, corresponding to tunneling of a particle with the reduced mass of SH–Rg, along a barrier which is more than  $1\text{ \AA}$  in width. In effect, predissociation of the complex requires favorable F–C factors along both coordinates, and the expected poor overlap along  $Q$  alone arrests the entire process.

## V. CONCLUSIONS

The  $A(^2\Sigma^+) - X(^2\Pi)$  spectra of SH isolated in Ar and Kr matrices is rather similar to those of OH isolated in the same media, and therefore yield themselves to similar interpretations of interaction potentials. Among the quantitative differences between these two systems are: larger redshifts in the case of SH–Kr, consistent with the expected larger contribution of charge transfer in this case; smaller redshifts in the case of SH–Ar, attributed to the poorer overlap of the Ar valence electrons with the  $\sigma$  hole

in SH as compared to OH. While the SH(A) state is strongly solvated, the SH(X) interactions with the host are mainly repulsive.

Electronic predissociation of SH(A) is completely arrested in both Ar and Kr matrices. Solvation could lead to this effect by one of two possible mechanisms. The first is somewhat trivial, and can be operative only for excited vibrational levels: if vibrational energy transfer to the solvent is efficient, relaxation may compete with predissociation. The lowering of the  $\nu=0$  level relative to the surface crossing can then lead to reduction of predissociation rates. Differential solvation of electronic states is the second mechanism by which solvent interactions can influence the intersystem crossing, by changing overall coupling matrix elements between two electronic states. These couplings can usually be cast in the form of a product of an electronic matrix element, and nuclear F-C factors. Since molecule-solvent interactions are generally weak, the electronic part is not expected to change significantly in going from the gas to the solid. However, the F-C overlap now includes the solvent coordinate  $Q$  in addition to the internal coordinate  $q$ . The heavier reduced mass, and the very different interaction potentials along  $Q$  for the different electronic states, guarantee poor F-C factors. In effect, the solvent atom blocks electronic predissociation.

The entire discussion of matrix isolated SH was carried in the framework of a triatomic SH-Rg complex. All of the considerations made here should therefore be applicable to isolated complexes prepared in molecular beams. It would be highly desirable to carry out such an experimental study, to clarify the interaction potentials and to establish the caging of predissociation by a single solvent atom.

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